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STUDIES OF THE PHYSICAL CHEMISTRY OF CLAYS

BY

KIM LOUISE KASPERSKI

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SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
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Department of Chemistry, University of Alberta
Edmonton, Alberta, CANADA T6G 2G2
Telephone: (403) 432-2762

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University of Alberta

From Loren G. Hepler
Professor of Chemistry & Chemical Engineering

Charles T. Hepler
Summer research assistant

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Loren G. Hepler

(Supervisor)

Marvin J. Dudas

B. Kratochvil

P. Kebarle

Ronald E. Verrall

(External Examiner)

Date : 10 FEBRUARY 1988

TO MY PARENTS

ABSTRACT

A critical review of the properties of and the technology for treatment of clay tailings produced during the processing of mined oil sands is presented. An evaluation of current technology in tailings treatment is provided as well as some recommendations concerning the more promising treatment methods.

The viscosities and densities of dilute aqueous suspensions of Na-kaolinite (25°C) and Na-montmorillonite (22-55°C) and of mixtures of Na-kaolinite/Na-montmorillonite (25°C) were measured. Results of the measurements on pure clay suspensions at 25°C have been analyzed in terms of the Einstein equation, which has been extended to be applicable to non-spherical clay particles and to allow for the fact that montmorillonite is a swelling clay. Viscosities of mixed clay systems are nearly consistent with a simple additivity model; the small non-additivities can be explained in terms of adsorption of relatively small montmorillonite particles on the surface of relatively large kaolinite particles. The effect of temperature on the viscosities of suspensions of montmorillonite is consistent with the idea that aggregation of clay particles diminishes with increasing temperature.

The thermodynamics of adsorption of several gaseous hydrocarbons on the surface of kaolinite was studied by gas-solid chromatography. Retention data obtained at several temperatures in the Henry's Law region were used to calculate the enthalpies (ΔH°), entropies (ΔS°), and Gibbs energies (ΔG°) of adsorption.

It has been common practice to obtain enthalpies and entropies of adsorption from the temperature dependance of the Henry's Law constant, as mentioned in the preceding paragraph. Results obtained in this research (only for the "best" systems) are accurate enough to justify a double differentiation with respect to temperature and thence an evaluation of the increment in heat capacity (ΔC_p°) associated with adsorption. A simple "molecular" picture of adsorption permits prediction of the sign of ΔC_p° in accord with present experimental results. These ΔC_p° values also permit evaluation of partial molar heat capacities of adsorbed gases.

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CHAPTER 1

Introduction

This thesis describes three kinds of investigations of the physical chemistry and technology of clay systems.

An introduction to the extensive, and often deleterious, effects that clays can have in a physical system is provided in Chapter 2. This chapter is a critical review of tailings (waste) properties and management in the oil sands mines of northern Alberta as well as other mining industries worldwide. Suspended clays in aqueous wastes from these mines have led to problems in disposal and recycle that have important economic and environmental consequences.

One of the notable properties of clays is the often significant effect that small amounts of clays have on the rheological properties of aqueous suspensions. Chapter 3 describes studies that were done to investigate the viscosities of clays and clay mixtures in aqueous suspensions.

Chapters 4 and 5 describe research on the thermodynamics of adsorption of organic vapours on clay surfaces, using gas-solid chromatography. Chapter 4 describes experimental procedures, and gives experimental results that permit calculation of the enthalpy (ΔH°), entropy (ΔS°) and Gibbs energy (ΔG°) of adsorption. Chapter 5 describes the calculation of the heat capacity change ($\Delta C_p{}^\circ$) for this adsorption process, which is information that has rarely been obtainable from gas-solid chromatography or from conventional equilibrium or calorimetric measurements.

CHAPTER 2

A Review of Properties and Treatment of Oil Sands Tailings

Introduction

Oil production from the oil (tar) sands in northern Alberta has been feasible since the development of the Clark hot water process for bitumen[1] extraction and Syncrude and Suncor have proven that it is commercially viable as well. One of the major problems that remains to be solved is the economical and environmentally acceptable treatment and ultimate disposal of tailings that result from the application of the Clark hot water separation process (1). An indication of the magnitude of the problem is provided in Table 2.1.

This present review first describes some chemical and physical properties of oil sands tailings and then summarizes methods that have been proposed or tested for oil sands tailings treatment, as well as some methods that have been used in other mining operations. There have been several earlier reviews (1-6) that have dealt with some aspects of the tailings problem. Partly because authors of these earlier reviews have focussed mostly on only selected aspects of the tailings problem and partly because none of these earlier useful reviews includes discussion of the most recent work, we have undertaken the present review.

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[1] Bitumen has been defined by the (Alberta) Energy Resources Conservation Board as "a naturally occurring viscous mixture, mainly of hydrocarbons heavier than pentane, that may contain sulphur compounds, and that in its naturally occurring viscous state is not recoverable at a commercial rate through a well" (7).

Table 2.1. Material handling in oil sands mining operations. Data taken from Strom and Dunbar (7).

	Weight of Material Handled (10^3 t/d)	
	Syncrude	Suncor
Oil sands mined	230	110
Extraction water and steam	190	80
Bitumen extracted	25	12
Tailings discharged	380	170
Tailings reclaim water	120	50
Reject discharged	12	6

There are two major points at which tailings can be treated. One such point is before they are dumped into tailings ponds, and the other is after storage for a period of time in ponds. There are also various levels of desirability in dealing with tailings problems. The least desirable is to pump all waste to tailings ponds without treatment, with the ponds being left as permanent storage. Next in order of desirability is treatment of pond tailings or tailings streams to produce maximum amounts of water for recycle and a solid, non-toxic residue that can be handled easily and used as backfill. Ideally there would be a treatment scheme whereby all tailings produced could be treated so that no permanent tailings ponds would be needed. After mine closure the site could therefore be converted to an environmentally safe area. Finally, the method chosen must be economical, especially when one considers the huge volumes that must be treated. In 1977 Suncor estimated that a cost of 1$ per 1,000 imperial gallons ($0.22/1,000 L) treated would be reasonable (3).

Presently, plant tailings from oil sands mining operations are impounded behind dikes up to 35 m high with a pond area of approximately 15 km^2 at Syncrude and corresponding dimensions of 100 m and 3 km^2 for the ponds at Suncor. This impoundment is necessary because suspended matter in the tailings ponds consolidates only to a very limited extent leaving a persistent, unrecyclable sludge. This sludge, plus sand and dirty water that make up the rest of the tailings, has a bulking factor of about 1.4 (1), which means that without treatment, there is not enough space in the mined out pit to store all the tailings. The impact of this tailings problem has been described by the Energy Resources Conservation Board in terms of the fact that tailings ponds could cover eight billion barrels of mineable, recoverable reserves (7).

Physical and Chemical Properties of Oil Sands Tailings

There are four major sources of tailings from hot water process plants. First is screen oversize, removed from the conditioning drum, that is returned to the mined out pit. Second is the bottom, mostly sand, layer from the primary separation vessel that is mixed with the third source, the scavenged middlings stream, for pumping to retention ponds. These tailings from the primary separation vessel will be referred to in this review as the primary or extraction tailings stream. Fourth is a combined stream from the froth treatment plant, called centrifuge or froth treatment tailings, that is also pumped to tailings ponds. In total, the oil sands tailings stream is a warm, aqueous suspension of mainly sand, silt, clay, and residual bitumen and naphtha at a pH between eight and nine.

Oil sands composition varies considerably, so tailings composition also varies. It should also be noted that composition changes with time, due mostly to settling, oxidation, and bacterial action (8).

Description of tailings ponds

When the effluent is discharged into the tailings pond, two layers are formed: (1) coarse sand, which is either used for building dikes or deposited as beach sand during overboarding into the pond, and (2) dilute sludge that runs off into the pond. Figure 2.1 shows a schematic cross-section of an oil sands tailings pond, illustrating the different zones that are present.

The floating bitumen mat has been recovered by skimmers (9,10) and the relatively clear water below is recycled to the processing plant. After sedimentation over a period of a few months to reach 20 wt% solids content, the sludge layer consolidates very slowly over the next couple of years to mature sludge that contains 30-40 wt% solids (12,13,179). The dynamics of settling in oil sands tailings ponds have been thoroughly investigated by Scott et al. (13,14,15,179,180).

Tailings composition

The compositions of various tailings samples are given in Table 2.2. The main components are water, sand (defined as having a particle size greater than 44 μm), silt (particles from 2 to 44 μm), clay (particles smaller than 2 μm), bitumen and naphtha (unrecovered solvent from the froth treatment plant). There are also small concentrations of dissolved organics and heavy minerals.

The composition in tailings ponds varies according to depth as shown in Table 2.3. Mineral contents as high as 55 wt% at the bottom of a Suncor tailings pond have been reported, but such high values were considered exceptions (1), with deep sludge usually reaching an equilibrium solids concentration of around 35 wt%.

Tailings mineralogy

Tailings minerals consist of sand, clays, and trace metals. The sand is 97.5-99 % SiO_2, 0.5-0.9 % Al_2O_3, and 0.1-0.9 % Fe (16). As expected, the

Figure 2.1 - Schematic cross-section of Syncrude tailings pond (adapted from Camp (1) and Dusseault et al. (11)).

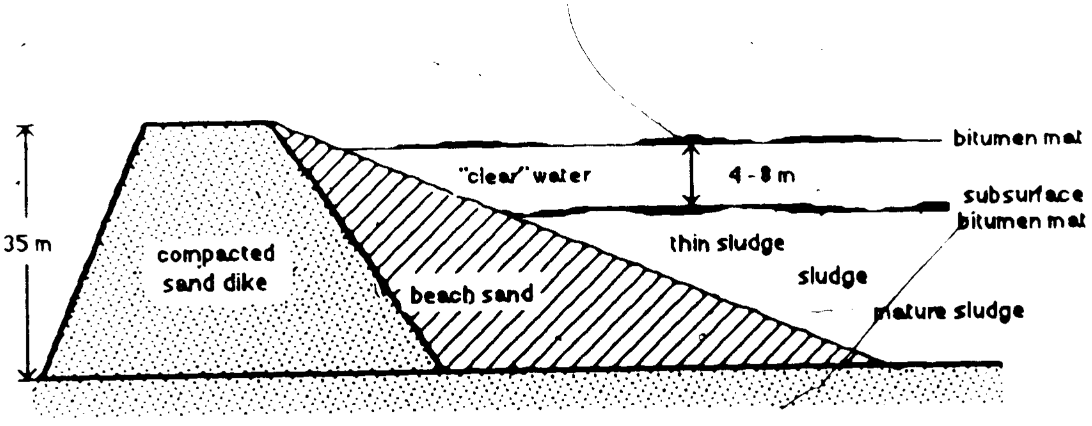

Table 2.2. Tailings composition (values are given in wt%)

Tailings Source	Water	Sand and Silt	Clay	Bitumen	pH	Reference
Primary						
	48	25-35	10	1.0		19
	25-30	------- 65-70 -------			8-8.5	20,21
		------- 42-68 -------		0.4		17
Centrifuge,						
				4.8 (+2.5 naphtha)		17
solids	6.8	------- 89.8 -------		2.3 (+1.2 naphtha)		22
Pond Sludge						
	75-95	------- 5-25 -------			8-8.5	20,21
	65	------- 29.0 -------		6		23

Table 2.3. Tailings pond composition (values are in wt%). Assay of Suncor tailings pond (data taken from Camp (1)).

	Overall Composition			Mineral Composition		
Depth	Water	Mineral	Bitumen	Sand	Silt	Clay
Dike	22.8	77.0	0.2	95.3	3.2	1.5
6 m	74.7	33.0	3.3	0.0	59.0	41.0
12 m	70.1	40.8	3.9	0.0	62.0	38.0
18 m	65.5	47.5	4.5	0.0	58.5	41.5

amounts and types of clay vary considerably, but more recent assays of tailings pond sludge show approximately 2/3 to 1/2 kaolinite and 1/3 to 1/2 illite (17,18). A more detailed profile from older assays is given in Table 2. 4.

Heavy metals detected in tailings include Ti, Zr, Fe, V, Mg, Mn, Al, Pb, Zn, Nb, and Mo (24-26). The most important are titanium and zirconium as these are valuable enough and present in large enough quantities to warrant consideration of their recovery from tailings (24,27).

Organic composition of tailings

Various types of dissolved and clay-associated organics, besides residual bitumen, are found in tailings. While nearly every class of organic compound has been detected (28,29), the majority are organic acids and polyphenolic aromatic compounds (21,29,30). For a review of water soluble substances derived from heavy oils and bitumens see Hepler et al. (31).

An analysis of tailings pond dike drainage water showed 100-120 mg/L organic carbon, of which 55% were organic acids. This study also found 4 mg/L organic sulphur compounds and 3 mg/L phenolic compounds. The concentrations of other classes of compounds such as aldehydes, ketones, quinones, amides, and amines were below 1-2 mg/L (29). Adsorbed on clay surfaces, perhaps linked via Fe^{3+}, are polyphenolic carboxylic acids or ketones derived from lignins or tannins (32-34).

Among organic acids detected are two classes of surfactant: carboxylic and sulphate/sulphonic acids (21,35,36,37). Both of these classes of surfactant

Table 2.4. Tailings mineralogy

Total Tailings				
(17)[1]	85 % quartz	9 % clay	6 % feldspar	trace heavy minerals
Fines Fraction (< 2 μ)				
(3)	22 - 76 % kaolinite	7 - 10 % illite	1 - 8 % montmorillonite	
	trace: chlorite, quartz, calcite, dolomite, siderite, feldspar, ankerite, zircon, ilmenite, leucoxene, rutile.			

---

[1] The numbers in brackets refer to the references from which the data were taken.

which are generated by the addition of sodium hydroxide to the tar sands and hot water mixture, are necessary for bitumen recovery in the hot water process (37,38,39). However, the same surfactant properties that aid bitumen recovery adversely affect settling of clays in tailings (21).

Inorganic composition of tailings

Dissolved ions that have been detected in tailings samples (including recycle water) include Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, $Fe^{2+/3+}$, NH_4^+, ions derived from SiO_2, Cl^-, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^-$, HCO_3^-, and CO_3^{2-}. Sodium is the most abundant cation at 200-300 mg/L, while carbonate/ bicarbonate is the most abundant anion at 300-700 mg/L. The concentrations of other dissolved ions range from 1 to 100 mg/L (25,40). These values were obtained from samples collected in the late 1970's and 1980/81 from Syncrude's tailings stream (40) and pond (25), and Suncor's tailings pond (40); the actual values have increased since then due to recycling of recovered water.

Physical properties of tailings

The densities of some tailings components are: 1.0-1.3 x 10^3 kg/m^3 for pond sludge (depending on the depth at which the sample was taken) (11,25), and 1.6 x 10^3 kg/m^3 for beach sand (17). Size distributions of particles in tailings have been reported (12,41,42) .

Electrophoretic studies (17,43) have shown that tailings clay particles have a zeta potential of approximately -60 mv. The electrophoretic behaviour of the sludge particles is due mostly to kaolinite and small amounts of montmorillonite in the suspension (43).

Reasons for sludge stability

It is important to know the reason(s) why oil sands tailings yield such a stable suspension as such knowledge can provide a useful guide to development of a practical tailings treatment process. In the various proposed explanations for this stability, one or more of three sources have been implicated: suspended clay particles, residual bitumen, and dissolved organics.

Various authors have written that soluble organic surfactants such as sulphonic and carboxylic acids disperse clay particles, creating a stable suspension in pond sludge (3,30,36,39). Speight and Moschopedis (20,21) have shown that asphaltic acids derived from bitumen decrease surface and interfacial tension and may therefore disperse clay particles. A stable dispersion could also be formed as a result of repulsive forces due to the high negative surface charges of the clay particles (8,41,43,44,45,46). It is also possible that bound organics on clay particle surfaces link with bitumen in tailings and thus help to create a stable suspension, thus reducing the ability of oil sands tailings to consolidate (18,32,34,47). Finally, Scott, Dusseault, and Carrier (13) suggest that residual bitumen in mature sludge acts as a deformable solid that clogs pores in the sludge, decreasing permeability and hence drastically increasing consolidation times. They argue that there is no direct problem with settling rates as adsorbed bitumen on clay surfaces actually increases settling rates by increasing agglomeration.

Oil Sands Tailings Treatment

There are various approaches to dealing with tailings problems and treatment methods have been proposed for all of them. These include designing retention ponds to store all unrecyclable tailings produced, physical methods, chemical treatments, geotechnical methods, and process modifications. It should be noted that there are also various goals with respect to dealing with tailings that could involve the use of any treatment method in the aforementioned categories, either singly or in combination. Obviously the design of a treatment method will depend on whether the aim is to (for example) decrease pond sludge accumulation, increase recycle water, produce a solid for landfill, or clarify water for return to the environment.

Storage

Temporary retention ponds have been built by Syncrude and Suncor on their lease sites to hold unrecyclable tailings while the mines are in operation. At least two major engineering studies were carried out (16,48) to design tailings disposal options using ponds. They concluded that for wet tailings disposal, it was most economical to maximize the use of in-pit ponds once space became available, which was projected to be after approximately eight years of mine operation. Hardy Associates (16) recommended pumping total tailings to in-pit ponds once they were built, and later to pump the sludge formed to an out-of-pit pond located beyond surface mineable limits, leaving behind the settled sand as backfill. The Techman and Rheinbraun group (48) proposed the reverse, with sludge being stored in-pit while sand and overburden were to be stored out-of-pit, as they thought that this would reduce the risk of pollution if the pond dikes failed.

Although it has been necessary to build temporary retention ponds, there are disadvantages to their use for permanent storage. These include the facts that ponds may cover useful oil sands, constructing and maintaining dikes is expensive, and the dikes would probably have to last hundreds of years before the sludge finally solidified. There are also environmental considerations such as the toxicity of pond drainage water and therefore tailings pond water, and the hazard to birds created by oil slicks on the pond surface (12,16,28,48,49).

As outlined in a report by Hardy Associates (50), government agencies such as the Development and Reclamation Review Commitee (DRRC) and the Alberta Oil Sands Environmental Research Program (AOSERP) that were responsible for evaluating and developing reclamation plans had the objective that land disturbed by mining operations should be returned to a level of productivity the same as or better than that prior to development. It is quite obvious that leaving huge ponds containing millions of gallons of toxic sludge would not meet this criterion.

Reclamation

Environmental studies of reclamation processes have been carried out, with emphasis on ways of stabilising and reclaiming the sand dikes by re-vegetation.

The vegetation used to reclaim tailings pond dikes has to be drought resistant because of the low water holding capacity of the fine dike sand (48,49). This vegetation should also preferably need a minimum of care in the way of irrigation and fertilization. It may be that a combination of Jack pine, which grows well on sandy soils, and lichen to maintain moisture in the soil would work (51,52), although we have not found any report of actual testing on a pond sand dike. It has been shown that under laboratory test conditions mixing overburden and peat with tailings sand provides an adequate soil for plant growth (53,54,55) and this is the current practice. Presently Suncor uses a combination of grasses and both deciduous and coniferous trees to stabilise tailings dikes. Due to dehydration stress caused by the low water holding capacity of the sand, however, many of these plants are damaged by insects (560. It is therefore questionable as to whether there is at present a stable self-perpetuating ecosystem on the dikes ,which should be the ultimate goal of these dike reclamation programs (51).

Process modification

Process modification refers to proposals that call for a change in the current operating procedures of the oil sands processing plants in order to decrease sludge production. In this section we limit our discussion to modifications of the processing of surface mined sands (also see Kessick and Jobson (2) for a review of this subject). There have been many studies of alternate ways of getting bitumen out of the ground (57) (and as such could be considered "process modifications") that potentially would lead to a smaller tailings problem, but this area is beyond the scope of this review.

People who have suggested process modifications to deal with tailings have taken the approach that the best way of coping with the problem is not to create it in the first place; or at least decrease the amount of tailings produced. However, given the size of oil sands treatment plants, it is unlikely that the companies involved would adopt any extensive, and hence expensive, changes unless some sort of remarkable benefit could be demonstrated. Camp (1) has pointed out that some if not most suggested modifications are probably counter-productive in that bitumen extraction efficiency would likely be decreased from the current levels of around 90%. It is possible however, that companies that decide to operate new mining projects might choose a different bitumen extraction procedure, especially in view of the fact that the tailings produced by the hot water process have created such a big problem. Some early patents describe bitumen extraction procedures other than the hot water extraction process that may produce a decreased amount of tailings.

In the 1960's Puddington's group at the National Research Council developed the spherical agglomeration process that could recover 96% or more of the bitumen from oil sands (58,59,60). The final product contained a maximum of 73% bitumen (versus approximately 65% for froth from the hot water process (10)) and in some cases less than a third the amount of water (12% for the spherical agglomeration process versus 42% for the hot water process). The bitumen obtained from the spherical agglomeration process could be used for direct coking because of this decreased water content. While the tailings volume from the spherical agglomeration process would be greatly increased, as it uses about two and a half times more water than the hot water process, the settling and consolidation behaviour of these tailings may be more favorable as sodium hydroxide is not essential to the process (if indeed sodium hydroxide is responsible for sludge stability).

In Fischer's process (61,62), tar sands are pulped with a hot aqueous sodium silicate solution and a light oil to extract bitumen, leaving behind a sand residue. The liquid fraction is treated in a separator after the addition of Ca^{2+} and an alkylene oxide polymer to help flocculate the clay. The clay settles out as a sludge, the bitumen is removed in the oil phase and the aqueous sodium silicate layer can be recycled. Although it was not stated explicitly, residual calcium (if any) in the recycle water did not seem to adversely affect the pulping step.

A process developed by Simpson (63) that treats stored oil sands that have become acidic upon exposure to air, is similar to Fischer's process. Oil sands, various hydrocarbon solvents (containing some aromatic compounds, to extract the asphaltene fraction of bitumen), 1 wt% water (vs weight of oil sands being processed) and enough base to raise the pH to 5 (to increase filtration rate at the next step), are mixed together and then filtered to separate sand from solvent. The solvent is then recovered from the sand residue by steam stripping, and the bitumen is recovered by an unspecified process. Tailings produced consist of moist sand that could be readily used as back fill.

The Dow-Kellogg process (64) uses organic solvents alone to get a claimed bitumen recovery of 97%, or better. Oil sand is mixed with dichloromethane (this was the best of the solvents tried) and then the bitumen/dichloromethane stream is rinsed from the sand using recycled bitumen/dichloromethane. This stream is then sent for fines removal and distillation while the sand residue is dried to remove excess solvent and then dumped in the mined-out pit. Advantages of this process as outlined by the developers include: a tailings pond is unnecessary, it is a fast process, it works well on low grade ore, and it consumes low amounts of water.

Kruyer (65) developed the Oleophilic Sieve® for recovering bitumen from oil sands or residual hydrocarbons from tailings. It consists of a steel drum containing oleophilic steel balls into which oil sand slurry (no sodium hydroxide; no details are given as to the slurry composition) or tailings are fed. The bitumen coats the balls and is eventually sloughed off through the drum screen onto an oleophilic sieve mesh belt that passes around heated steel rollers where the bitumen is released. In a two stage process this technique gave greater than 90% bitumen recovery from low grade oil sand with an original bitumen content of 8%, and 98% recovery from higher grade oil sand with an original bitumen content of 12%.

The RTR/Gulf process (66) is similar to the hot water process in that it also uses hot, alkaline water to extract bitumen, but the way the water is used in this process is different. In the conditioning step of the RTR/Gulf process, excess amounts of hot, alkaline water are used under mild mixing conditions instead of the minimum amount of water and turbulent mixing conditions of the hot water process. In this way, clay aggregates are not dispersed, which is important for subsequent water recovery steps. A liquid rich stream and a solid rich pulp are removed separately from the conditioning vessel and sent to an oil/water separator and a desander, respectively, as opposed to the total mixture being sent to a primary separation vessel in the hot water process. Froth is separated from middlings in both the oil/water separator and desander, and then sent to be washed. Final recovery of bitumen ranged between 84% and 91% in the most recent study (66). The middlings are sent to a flocculator and clarifier from which water is recovered and recycled back to the extraction step, thus conserving both heat and water. The flocculated solids are removed for disposal as are the coarse solids from the desander and the oil/water separator. The most economical method of disposing of the damp sand was found to be hydraulic pumping to a central discharge area (see Robinsky (67) and Shields (68) for descriptions of thickened discharge methods of tailings disposal). The flocculated fines can be surcharged with sand and then left to consolidate in disposal beds (69). Economic evaluations have shown that the RTR/Gulf process is potentially less expensive than the current hot water process due to savings in energy from recycling hot water and in tailings handling as tailings ponds are not needed (66,69).

An alternative to any type of extraction process is direct cracking of bitumen in oil sand as described by Taciuk (70). Oil sand is dried and then transferred to a reaction zone where it is mixed with hot sand and the bitumen is thermally cracked. Lighter hydrocarbons are collected as a vapour while coke coats the remaining sand, which is transferred to a combustion zone where it is burned to provide heat for the whole process. Waste consists of oil depleted sand that can be used to fill mined out areas. Pilot plant studies have been completed successfully and the process is currently ready for commercial development. This method seems promising as it works well on low grade ores and one cost analysis claims it is actually cheaper than the hot water process. However, hydraulic pumping is the most economical method of transporting large amounts of solids, whether the solids are initially dry or wet. Thus, the cost and difficulty of handling tailings produced by the Taciuk process may be just as great as for the hot water process.

Other proposed process modifications involve changes or additions to the currently used hot water extraction process and these will be discussed under their respective categories (i.e. whether a physical or chemical modification); but again we emphasise that the specific aims of the various processes described in this review may vary.

Physical methods

Common physical processes that could be used to aid in tailings treatment include filtration (various types), centrifugation, cycloning, evaporation or distillation to separate liquid from solid. Here we mention some processes specifically developed for oil sands tailings.

Baillie and Malmberg (71) patented a process in which they centrifuged chemically flocculated pond sludge to recover usable recycle water. Flocculation by itself did not work and centrifugation without flocculation took too long. This method removed 37-87% of total solids from a 7.1% solid suspension where the actual efficiency depended on the extent and speed of the centrifugation. Hepp and Camp (72) also combined a chemical and physical treatment in which they adjusted the pH of the suspension either above 9.5 or below 7.5 and followed with vacuum pre-coat filtration, as they also found that neither treatment worked well alone.

Maloney (73) combined spherical agglomeration with the hot water process in order to reduce the bitumen, silt and clay content of the tailings stream. Tailings of any form, but preferably pond sludge, is mixed with oil sand and then fed into an inclined tube provided with propellers, where it undergoes a kneading/agglomeration process. The recovered material consists of sand, bitumen agglomerates, and an aqueous effluent stream substantially reduced in solids that is claimed to be suitable for recycle to the hot water process (no data are given on actual compositions). There are some unanswered questions however, - How much bitumen is left on the oil sands used in this process, and do the bitumen agglomerates require extra processing because of their increased content of silt and clay?

As was previously mentioned, Kruyer's (65) Oleophilic Sieve® can be used to recover residual bitumen from tailings. In this process an average of 85% of total bitumen was recovered from a sludge feed containing 6.1 wt% bitumen, 70.7 wt% water and 23.3 wt% minerals, as a product containing 58 wt% bitumen, 15 wt% mineral and 27 wt% water.

Flintoff and Plitt (74) found that electrophoresis-assisted gravity settling of tailings solids decreased the solids content of diluted pond sludge containing 2.4% solids (diluted from 14% solids) by 68.3% as compared to just 33.3% by gravity settling alone. However, because of the high conductivity of sludge a lot of power was required and therefore the authors thought that this method was too expensive. In 1976, cost was estimated at a capital investment of $22 million with operating costs of $0.85/1,000 US gal. of 2.4% sludge processed.

Ritter (75,76,77) also worked on an electrophoretic treatment of either pond sludge or fresh tailings, although he preferred dealing with sludge alone (no sand) in order to minimise the amount of solids treated. Electrophoresis by itself produced a solid too wet for disposal, and one could not get below 5% solids in recovered water. To overcome this problem, Ritter pre-treated the sludge with 0.5-3.5 g $Ca(OH)_2$ or CaO per liter of sludge and then reduced the pH to between 9-10.5 with carbon dioxide or ammonium carbonate or bicarbonate. This sludge mixture was then passed through a container with a moving anode belt on the bottom and a cathode grid suspended above (but still submerged in the sludge). In the 10 v field the negatively charged clay particles were deposited as a rigid mass of 40 wt% solids on the anode and later removed as the belt moved along. Electroosmosis, which occurrs concurrently, helped to dry the deposited solid to 65% solids or more, which was suitable for backfill. The recovered water contained less than 3.0% solids and could be recycled to the hot water process. As shown by pilot plant tests, this technique seems to work well but it is again rather expensive, with capital cost in 1982 estimated at $123 million and an operating cost of $15.8 million a year, or about \$5.00/m^3 (\$0.80/barrel) bitumen produced .

Fear and Camp (78) treated tailings (or middlings) with sonic waves to separate and agglomerate fine minerals, bitumen, and water - all of which are recovered separately after settling. Adjusting the pH above 9.0 or below 7.5 or adding a coagulant aided the process.

Chemical methods

Chemical methods involve the use of some form of additive (either during the hot water extraction process or to the final tailings) that is intended to flocculate or otherwise speed the settling of suspended solids. Some examples of additions of chemicals to steps in the hot water process, which could be considered process modifications, are given below.

One way of decreasing the amount of tailings produced is by decreasing the amount of fresh water used in processing. Usually, enough water has to be added to the primary separation tank to maintain the clay/water ratio below 0.12 to prevent "setting up" in the separation tank, which is a condition where the mixture in the tank is too viscous for the bitumen to float to the top (79). Camp (79) proposed that a deflocculator such as sodium silicate, sodium polyphosphate, or sodium lignosulfonate be added to the primary separation tank at a rate between 0.1 to 5 lbs/ton oil sands to keep the viscosity low. However, he did not discuss the possibility that the added deflocculant would perhaps increase the difficulty of handling the reduced volume of tailings produced. Camp (80) also proposed an alternative to adding a deflocculant, which would be to remove the Ca^{2+} and Mg^{2+} ions (which act as flocculators) from the tailings that are destined for recycle using ion exchange resins. In this way a clay/water ratio larger than 0.12 could be used in the separation tank without it "setting up". In one example the fresh water requirement was reduced from 382 tons fresh water/1,000 tons oil sand treated~~, to~~ 210 tons fresh water plus 210 tons ion-exchange treated sludge/1,000 tons oil sand. An added benefit of this method is that only half the sodium hydroxide usually used is needed.

In a variation of the usual hot water process, described as an alkali recycle process by Kessick (81,82), oil sand is slurried with hot aqueous sodium hydroxide (approximately 0.1 wt% is used) in a 1:1 mix, to form an O/W emulsion. This emulsion contains about 87% of the original bitumen as a mixture containing 12.7 wt% bitumen and 16.8 wt% solids. After settling, the emulsion is separated from the sand and then aerated with carbon dioxide free air after which just enough calcium hydroxide is added to invert the emulsion (too much leads to suspended clays being trapped in the emulsion). The W/O emulsion can then be dewatered by, for example, adding an organic solvent (to speed phase separation by reducing viscosity), followed by phase separation by settling or centrifugation. The organic layer formed is sent to a bitumen processing plant while more calcium hydroxide is added to the aqueous layer to settle the clay, which is then removed by some physical means and used as backfill. The aqueous sodium hydroxide formed is recycled (Na^+ because of ion exchange of Ca^{2+} for Na^+ in clays). The apparent advantage to this method is that the amount of water used is reduced and sodium hydroxide is, recovered for recycle (81,82). Tailings from the present hot water process or pond sludge can be treated this way where they enter the process at the first addition of calcium hydroxide. This leads to recovery of residual bitumen and a usable backfill (83).

In what could be considered a chemical treatment Camp (84) took advantage of the surface active properties of solids in tailings pond water. He mixed pond water with an immiscible organic solvent (with or without pre-treatment with a flocculant or coagulant) and collected the interface zone where the solids concentrated, leaving behind recyclable water and solvent. The collected interface could then be treated further to recover water and solvent. However, this procedure needed a lot of solvent (two thirds the volume of pond water treated) and was meant for low solids concentration (about 2%) and so would have limited applicability.

Nearly all other patents and references dealing with chemical treatments have dealt with the problem of coagulating suspended clay in the final tailings or pond sludge to produce recyclable water and a solid residue. Most types of chemical treatments have to be combined with some physical process as discussed previously to separate the aggregated solid from the water. The type of chemicals used can be divided according to the following categories.

Organic flocculants

Table 2.5 gives a summary of some of the types of organic flocculants that have been tried on oil sands tailings.

Table 2.5. Organic flocculants used on oil sands tailings

Reference : Lang and Hentz (85)
Additive : acrylic acid/polyacrylamide, then cationic or nonionic polymer or inorganic salt
Comments : use of primary and secondary flocculants.

Reference : Kessick (86)
Additive : polyacrylamide
Comments : used with $Ca(OH)_2$ treatment.

Reference : Specken (87)
Additive : Aquafloc (431,464-467), Klar-aid 15, Nalcolyte (607,3670,8175), WT3000, CA2325, Cyfloc (326,345,346), Separan NP10, Hercofloc (818.2,815.3,834.1).[1]
Comments : flocculants included anionic, cationic and nonionic polymers used at 5 and 20 ppm.

Reference : Schulz and Morrison (45)
Additive : Alchem (603,607,623,8172,8863,43025,82070), Purifloc (C-31,C-41), Separan (200,MGL,711,SA-1704.2), Drewfloc (1,020,01P,03,21), Cyanamid (521C,560C,573C,575C,577C, 579C,581C, 900N-902N, 905N), Jaguar (MDD,387,402,MD-7A, MRL-22A,MRL-91), Polyhall (295,430, 540, 630, 650), Catrez 3, TFL (300,310,311,315,320, 325,330, 335, 336)[1], Dearborn (431,462-464), Mogul (9001-9004,9006-9008, 9011), carboxymethylcellulose, dodecylamine, micro-aid.

Table 2.5. continued

Comments : used at concentrations of 25-500 ppm ; the latter three were tried at 10-10^4 ppm and 0.1-10^3 ppm (Micro - aid is a Yucca plant glucoside).

Reference : Speight and Moschopedis (21)
Additive : Gendriv (162,458), Polyhall 295, Jaquar HP-1, Keltex.[1]
Comments : They are, respectively, polygalactomannan (cationic), polyacrylamide (cationic), polygalactomannan (nonionic), Na-alginate (anionic).

Reference : Hocking and Lee (36)
Additive : Purifloc C-31, Separan MG200, Separan AP273
Comments : They are, respectivley, cationic, anionic, and nonionic polyacrylamide.

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[1] Aquafloc and Klar-aid 15 are products of the Dearbom Chem.Co.; Nalcolyte is from Alchem; WT3000 and CA2325 are from Calgon; Cyfloc is from Cyanamid; Separan, from Dow, and Hercofloc, from Hercules Inc.; Jaguar, Polyhall, and Catrez are from Hallmark; TFL, from Tretolite; Gendriv comes from General Mills; Polyhall and Jaquar are from Stein & Hall; Keltex is from KELCO (21,45,87).

Lang and Hentz (85) patented a process involving acrylic compounds in which they used a combination of primary flocculant to settle suspended clay, followed by secondary flocculant to settle suspended silica, leading to clear water from sand depleted primary separation vessel tailings or pond sludge. The primary flocculant could be acrylic acid or polyacrylamide used at 1-2.5 lb/ton suspended solids and the secondary flocculant could be a cationic or nonionic polymer (used at 1-3 lb/ton suspended solids) or inorganic salt (used at 3-50 lb/ton suspended solids). The flocculants were added as a dilute suspension so there was also dilution of tailings. The resultant flocs settled rapidly and could be separated from the water by any physical process and the water reused or returned to the environment. They did not give any details on water recovery or the water content of the settled solids.

Kessick (61) also used polyacrylamide to destabilize sludge by destroying the hydrophilic nature of surfactants present. In laboratory tests he added 2-5 mg polyacrylamide per liter, then 0.5 g $Ca(OH)_2$ per liter, then 17.5 mg more polyacrylamide per liter of sludge. About half the sludge volume was recovered as a clear filtrate and the filter residue contained 75% solids. About the same amount of water was recovered after a week of settling (instead of filtration).

Specken (87) found that treating dilute suspensions of 2-7 wt% solids with 0.03-0.14 g $KMnO_4$ /L and 2-30 ppm of a medium anionic polyelectrolyte (such as Aquafloc 466) increased settling rate of solids in tests by up to 50%.

Schulz and Morrison (45) used 25-500 ppm organic flocculants to treat tailings sludge. The flocs formed created a gel instead of settling the solids and a physical process would therefore be needed to separate solids from liquid. Speight and Moschopedis (21) obtained similar results using 10-400 ppm flocculants on sludge. None of the flocculants was able to coagulate clay particles in a 22 wt% solid suspension, but they had minor success when the sludge was diluted by doubling the volume with water before flocculant was added. The best results were obtained when the diluted sludge was first neutralized with hydrochloric acid and then treated with flocculant. The solids precipitated to 75% of the original sludge volume after 12 hours.

Hocking and Lee (36) also found that flocculants worked best on dilute sludge. While they found that dilution alone with up to eight times the volume of distilled water did not affect solid settling rate, diluting one part sludge with four parts water and then adding 12.5 ppm flocculant increased the settling rate to one and a half times that of a blank. They found that Separan MG200 gave the best floc formation and settling. However, although settling rates were generally increased by flocculants, packing of the settled sludge was not improved.

Generally, organic flocculants gave at most an enhanced settling rate. When used by themselves, without dilution of the tailings, flocculants usually produced a thickened, unworkable sludge (21,45). The flocs occupy too much volume and contain too much water to be used as land fill (unless mixed with considerable sand). Flocs should be dewatered, which can be tricky, and is another expense. Thus, as has been pointed out by Schutte (88), using organic flocculants is too expensive and too inefficient to be a practical tailings treatment.

Inorganic coagulants

Various inorganic cations have been proposed as coagulants[1] in tailings treatments. These include Na^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}, used at a wide variety of concentrations. As in the case of organic flocculants, some form of physical treatment has usually been proposed to separate the coagulated clays from the liquid phase and to increase the solid content or decrease the water content of the final product so that it can be used as backfill.

According to the Schulz-Hardy rule, the value of the critical concentration of electrolyte required to flocculate solids in a dispersion is determined by the valency of the counter ion. Using the Derjaguin, Landau, Verwey, and Overbeek theory one can show that a lower concentration of a higher valence counter ion is needed to have the same effect as a given concentration of a lower valence electrolyte. However, the Schulz-Hardy rule

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[1] Lane (17,46) has differentiated between the use of the terms coagulation and flocculation as applied to clay suspensions, while most other authors seem to use the words interchangeably. Inorganic cations are said to coagulate clays as they decrease the thickness of the Gouy-Chapman double layer of the clay particles, and thus allow them to adhere to one another. Organic polymers flocculate clays without changing their (the clays) surface charge properties, by acting as bridges between the particles. This review uses the terms interchangeably.

only holds for simple, well defined systems and so would not be expected to be exactly applicable to such a complicated system as tailings. For example, Schulz and Morrison (45) found that 50 mg Al^{3+} or Fe^{3+}/L and 150 mg Ca^{2+} or Mg^{2+}/L coagulated pond sludge containing 20% solids to the same degree (although they do not give any data on the settling properties of the resultant mixture), and Hocking and Lee (36) found that 2 wt% $Al_2(SO_4)_3$ coagulated pond sludge just as effectively as 5.1 wt% $CaCO_3$ or 5.1 wt% $BaCl_2$. However, Hall and Tollefson (89) found that Ca^{2+} was about seven times as effective as Al^{3+} in coagulating tailings. Processes such as complex formation, cation exchange in clays or solubility effects are all possible contributors to tailings coagulation as well as double layer compression on which the Schulz-Hardy rule is based. Calcium in particular may be an exception to the rule as it may act as a bridging agent between clay particles and bitumen, which would lead to agglomeration (46,89).

As calcium is an effective coagulant and because lime is a relatively inexpensive chemical, many groups have studied the use of calcium to settle tailings. The amount of calcium needed depends on a variety of factors, including the composition and properties of the tailings sample being treated. The amount of carbonate dissolved in the tailings also controls calcium dosage as enough calcium has to be added to precipitate the carbonate ion as calcium carbonate before the remaining calcium ions can interact with the suspended clays (17). Some examples of calcium concentrations found to coagulate tailings are: equal to or greater than 0.1 g calcium/100 mL sludge (20,30,90), 0.6-1.0 g lime/L tailings (17), 150 ppm calcium (45), and 5.1 wt% $CaCO_3$ (36). It is obvious from this short list that there is no easy formula for deciding how much calcium to use, but one should at least use the more soluble calcium oxide or hydroxide rather than the relatively insoluble carbonate.

Krofchak (90) claimed, based on laboratory tests, that a weight bearing solid could be formed directly from pond sludge by rapidly and thoroughly dispersing 0.1 wt% calcium salt and/or mineral acid into pond sludge, and then pumping the mixture to a storage area where it would be left to solidify via the formation of large, binding silicates.

While most proposals for the use of inorganic cations have involved the treatment of the sludge fraction of oil sands tailings, a treatment of whole tailings with lime combined with vacuum belt filtration has been patented by Liu et al. (91,92) and Fuhr et al. (93) and has been investigated for several years at Syncrude. They found that flocculating whole tailings (that is, fines and sand together) greatly enhanced the filterability of the solids. In their process they control the amount of lime added either by monitoring the zeta potential of fines (enough lime has been added when the potential reaches zero), or by monitoring fines concentration in the oil sand feed. Adding between 0.2 to 1.6 g CaO /kg solid gave optimum results, with the precise value depending on the fines concentration of the suspended solids.

Lane et al. (46) also proposed adding lime to whole tailings, at 0.8-0.9

g CaO /L whole tailings, but also added 8-10 mg/L of a polymeric flocculant (to increase the permeability and density of the settled solids). This treatment gives rapid settling of suspended solids, although Lane also outlined a similar procedure using approximately 1.5 g CaO /L tailings with no added polymer.

Hall and Tollefson (44,94) diluted sand-depleted tailings with two to three volumes (relative to tailings volume) hard water and found an increased settling rate of the final suspension, although the final sludge volume was not much lower than that of untreated, settled tailings. They attributed this effect to calcium ions present in the water and proposed that the calcium ion concentration be increased by adding calcium oxide in order to decrease the volume of water needed for dilution.

Using calcium also has the potential advantage that it may interact further with the clays in the settled solids to form particle binding compounds such as calcium silicates or calcium aluminates via pozzuolanic reactions (17,46,95). However, the high content of sand and organic compounds of oil sand tailings may make it a poor candidate for this type of stabilization (17).

As many have pointed out, the problem with using Ca^{2+} for tailings treatment is that excess Ca^{2+} in the recycle water would decrease bitumen recovery. One way around this is outlined in a patent by Yan and Chung (96). They suggested adding 20-500 ppm Ca^{2+} to the total tailings stream to settle out clay, before it is sent to the tailings pond and then the Ca^{2+} is precipitated from recycle water in calcite precipitators using added carbonate. However, Lane (17) claims that excess free Ca^{2+} would not be a problem as the excess

Ca^{2+} would precipitate out naturally as calcium carbonate after reaction with dissolved HCO_3^-/CO_3^{2-}, either with or without aeration to increase the HCO_3^-/CO_3^{2-} concentration.

Speight and Moschopedis (21) tried sodium chloride on diluted (9 wt% solids) pond sludge and while some flocculation was seen, it would not seem practical as more than 2.5 wt% NaCl was needed. Hall and Tollefson (94) also unsuccessfully tried alum ($Al_2(SO_4)_3 \cdot 16H_2O$) as a coagulant for tailings. While 300 mg/L alum increased the settling of centrifuge plant tailings by about 10%, it created a gel in primary separation vessel tailings (minus sand) and was rejected as a treatment method.

Bakshi (97) proposed mixing tailings with fly ash (which consists of silica, alumina, CaO, Fe_2O_3 and MgO). In laboratory tests the suspension that formed when about 6 g fly ash were added to 50 g tailings filtered well, giving a dry cake and 60% recovery of water. This method has a practical difficulty, however, as thousands of tonnes of fly ash per day would be needed.

Schulz and Morrison (45) added Portland cement to sludge and found that at 1% cement the mixture was semi-solid, at 2% a friable solid formed, and at 5% cement the solid had some strength. The amounts used are similar to those used when treating tailings with lime, but a comparison of treatments should be made to test whether the solid produced using cement has enough of an improved quality to justify the extra expense. Schulz and Morrison (45) also unsuccessfully tried 10% Na_2SO_4 to remove water by absorption.

In order to detoxify tailings pond water *in situ* Specken (98) proposed that activated carbon be added, followed by a coagulant such as calcium sulphate, then about 20 ppm flocculant, and finally 0.3-1.0 g/L bentonite to clarify the water. Sometimes potassium permanganate had to be added to oxidize certain polymeric compounds (no more than 0.76 g/L was used). In another patent Specken (99) proposed the use of 20-200 ppm (by weight) potassium permanganate alone to clarify tailings suspensions. The process could be accelerated by adding 1-20 ppm anionic or non-ionic polymer flocculant.

Costerton (100) has also patented a method for detoxifying pond drainage water using bacteria from the Athabasca river, but he made no claims that the same could be done for the whole tailings pond.

Altering pH

Various groups have shown that decreasing the pH of plant tailings or pond sludge using various means such as adding HCl (aq), H_2SO_4 (aq), or bubbling CO_2(g), HCl(g) or SO_2(g) through the samples (or in Nedapac's case (101), just applying CO_2 to the tailings pond surface), increased the settling rates and compaction of suspended solids to a limited extent (21,25,36,71,72, 88,89,94,101).

Schutte (88) found that decreasing the pH of tailings to between 5.5 and

6.5 increased flocculation and coagulation of suspended clay as well as decreased amounts of surfactants and organic residues found in the clarified water, the net effect of which would be the reduction of sludge settling pond area needed. He noted that, if the clarified water was left standing in contact with the settled sludge for a few days, it's pH returned to neutral and the recovered water could be recycled or possibly returned to the environment.

In a subsequent study, Speight and Moschopedis (21) found that acidifying diluted sludge (approximately 9% solids) to a pH approximately equal to 6 with hydrochloric acid flocculated the clays and led to limited settling to about 85% of the original sludge volume. However, they found that acid treatment of non-diluted sludge (approximately 22% solids) made the situation worse, as a thick mud formed. Hall and Tollefson (89,94) also found that below a critical pH value in the range between 5 and 6 (obtained using sulphuric acid), solids in centrifuge plant tailings settled more rapidly as compared to untreated sludge. Acid treatment also improved the clarity of the water obtained. Hall and Tollefson suggested that since Schutte (88) showed that acidification removes dissolved organics, acidification had potential for detoxifying water that was to be returned to the environment, although they did not actually measure toxicity levels. They found that this treatment only worked on centrifuge plant tailings and not on primary tailings sludge as, similar to Speight and Moschopedis' (21) study, acidification actually decreased the settling rate. Hall and Tollefson recommended against acidification as a tailings treatment because of the expense and the fact that recovery of residual bitumen would be difficult.

In another study, MacKinnon and Retallack (25) again showed that acidification helped settle out solids as well as detoxified the recovered water whereas other treatments (e.g., adding calcium oxide or physical separations) did not detoxify recovered water.

Hepp and Camp (72) proposed that either a decrease in pH below 7.5 or an increase above 9 (using sodium hydroxide or sodium carbonate) would flocculate suspended clays, which could then be removed by vaccum pre-coat filtration. Baillie (71) also proposed a similar pH treatment but thought that centrifugation, rather than filtration, would be better for separating solid from liquid.

Oxidizing or reducing agents

Hocking and Lee (36) suggested that destroying surfactants would help settle tailings solids. They tried various oxidizing agents such as O_3, H_2O_2, and Cl_2, and reducing agents such as SO_2, H_2, and CO and found none to be effective that did not decrease the pH at the same time. Unfortunately, these experiments did not show whether the surfactants were destroyed by these treatments; this information would help establish whether surfactants play a role in sludge stability.

Geotechnical Methods

We define geotechnical methods as those methods that depend on the inherent drainage or settling properties of tailings (perhaps mixed with some inert solid), and do not use chemical modifications of the tailings or mechanical physical treatments (for example, centrifugation, vacuum filtration or electrophoresis).

Schulz and Morrison (45) tested a variety of solids for their abilty to aid the dewatering of pond sludge, although they did not give details on how the sludge was actually treated with these materials. The solids tested included 1% sand, 1% silicon dioxide, 2% iron powder, 1% fluorite, and 3% coke, all of which were ineffective, and 1-2% talc, 2% charcoal, and 1-4% graphite, all of which increased settling to a limited extent. Given the limited success of this technique, it is not recommended.

In an early patent Baillie (19,102) suggested that tailings be discharged down a gentle, unpacked sand slope into a collection pond. The fines concentration would decrease as the suspension percolated through the sand, because fines would be trapped in the spaces between sand grains. The increased surface area of the water would also increase the rate of evaporation. This would decrease the need for storage space and increase the amount of recyclable water for the hot water process or for diluting hot water process tailings for pumping. This is actually equivalent to overboarding, which is already in use. In order to reduce the requirement for fresh water in the hot water process, Baillie and Van Dyck Fear (103) later proposed that pond sludge, instead of fresh water, be used to dilute primary separation vessel tailings for pumping to the tailings pond. This would have the added advantage that again, as sand from the fresh tailings settles, clay from recycled sludge fills voids formerly occupied by water. In this way, requirement for fresh water for pumping is decreased and the tailings pond water has a decreased solids concentration so that more can be recycled to the hot water process.

A similar patent by Bain and Roberts (104) describes a process in which sludge is recovered from the tailings pond, added to the fresh tailings stream, and then pumped to a settling tank from which the upper aqueous layer is pumped back to the tailings pond and the lower aqueous sand/sludge layer is dispersed down a sand pile, thus trapping clay and fines in sand interstitial space. However, in this process the upper layer of the settling tank and the water that drains from the sand pile still have 25% total solids (although the total amount of solids in suspension has decreased) and can not be recycled to the hot water process.

Schutte (105) patented a process that uses two settling zones. Tailings are pumped to the first zone from which part of the upper layer is used to fluidize hot water process tailings for pumping to this settling zone, thus decreasing one of the major demands for water. Another part of the upper layer from the first settling zone is pumped to a second settling zone. The upper layer of this latter zone is clear enough to use as process water in the hot water process.

In Lane's reports referred to in the section on the use of inorganic coagulating agents (17,46) he has mentioned that he is developing a process whereby instead of having to use some form of physical technique to separate the coagulated clay, tailings are treated with lime and then directly deposited down a gentle slope in a manner conducive to obtaining clarified effluent and a trafficable solid sediment. In test runs they obtained a sediment of about 70-80 % solid that is quite permeable and workable, but as it still holds a lot of water it is liquifiable and therefore can not be used for strength-bearing duties immediately.

Scott and Cymerman (12) have used three component phase diagrams (for example, solid-fines-water) to predict what combination of materials would give a disposable solid. In order to be considered solid enough for reclamation, Syncrude determined that the material would have to have an undrained shear strength of 5 kPa, which would be equivalent to at least 70 wt% solid. Scott and Cymerman had a variety of materials to select from such as overburden, beach, dyke or underflow sand or various densities of pond sludge. Various combinations of materials are possible, one example being one part mature sludge and three parts sand that gives a mixture with 65% solids and a high consolidation rate. In this proposal, pond sludge is pipelined to a mixer where other materials (overburden or sand) are added and the mixture is allowed to settle. After settling, the bottom layer is pumped to its final destination where the tailings can be capped and revegetated once they consolidate sufficiently. There had been some large scale tests in progress, as well as planned, at the time of the 1984 symposium where this information was presented (12).

In another proposal Dusseault et al. (11) plan to use the swelling properties of clay shale that is present in overburden to dewater pond sludge. In this method pond sludge is diluted with middlings to 25% solids and then pumped to the overburden mine face where it is mixed with equal amounts (by volume) of clay shale. The mixture would then be pumped into the mined out pit where it would soon form a reclaimable surface. Laboratory tests showed that such a mixture developed a mean shear strength of 29.3 kPa in 24 hours with lowest strengths of about 4-7 kPa.

Scott and Dusseault (106) have developed a sand spraying technique similar to the one used in the treatment of phosphatic waste in Florida. In this long term process, clay is left to settle to 12% solids during summer and then a 40 vol% sand slurry (total tailings can be conveniently used) is sprayed on top during winter. This sand spraying is supposed to increase the clay consolidation rate by creating vertical channels through the sludge that help to release trapped water. The mixture would now be about 50-70 wt% solids, which can accomodate sand fill and allow reclamation. This technique also has the advantage that the tailings bulking factor is decreased from 1.4 to 1.2.

Yong (107) has reported an internal sand surcharging technique for tailings treatment (as opposed to Scott and Dusseault's (106) sand spraying process). According to Yong, ordinary surcharging, in which sand is layered on the sludge surface, does not work as the sand layer collapses into the sludge. In his process hot water process tailings are dosed to 25-75 ppm (by volume) hydrolyzed starch and then stored in a tailings pond for six months to two years. Sludge is then pumped out and an unspecified amount of sand and the same amount of starch as before is added to it. This mixture is then transferred to a permanent storage area where, by self-weight, a porous piston effect is achieved for compressing and dewatering the sludge. The sludge is now capable of supporting a sand or overburden layer for reclamation. The starch is vital to this process as it is the only chemical that was found to increase the permeability and shear strength characteristics of the treated sludge. Without starch, Yong found that sand surcharging did not work as the sludge was incapable of supporting the sand layer necessary for compression.

Freeze-thawing has been proposed as a method for dewatering sludge. In laboratory experiments Kessick (18) recovered 60% of the water (by filtration) after freeze-thawing pond sludge containing 0.3 wt% $Ca(OH)_2$ or 0.2 wt% $CaCl_2$. He predicted that adding lime, followed by freeze-thawing, would decrease sludge volume by two and a half times. Elliot (108) used three freeze-thaw cycles on pond sludge treated with either 0.6 g H_2SO_4/L sludge or 1.6 g alum/L sludge to obtain a product containing up to 30 wt% solids. In a process nearly identical to Elliot's, Tibbitt (109) used freeze-thaw to separate solids from liquids after the solids were flocculated using both an acid and base treatment. In Boyer's (110) freeze-thaw process, cooled tailings or pond sludge were pumped into a pressure vessel, mixed with compressed air and then blown out the end of a nozzle when the ambient temperature was below 0°C. The snow that formed was substantially reduced in clay and when it melted the clarified water could be collected.

In a minor process modification patented by Minkkinen (111), some heat and water that are lost to the tailings stream can be recovered. Tailings are exposed to air so that the air's temperature and humidity increases, and then this air is contacted with water so that the water in turn increases in temperature and its volume increases as it picks up between 2-10% of the original tailings water. This water can then be recycled to the hot water process.

Recovery of residual hydrocarbons

The most expensive parts of the current bitumen recovery process at Syncrude are removing overburden, mining and transport of oil sand; it is therefore advisable to recover as much bitumen as possible from oil sand entering the hot water process. Currently Syncrude and Suncor recover approximately 90% of the bitumen, with the largest loss (at Syncrude) being to the sand tailings of the primary separation vessel. Syncrude lost over 0.76×10^6 m^3 of bitumen in 1983 alone and this value is likely to increase as ore quality decreases, as this in turn results in decreased extraction efficiency of the hot water process (10,112).

Syncrude has already modified the basic hot water process in order to recover residual bitumen that was previously lost to tailings. They have added a tailings oil recovery vessel in which sand tailings and middlings from the primary separation vessel are mixed and aerated so that bitumen is recovered as a surface froth and sent for further processing. This is in addition to the already existing secondary flotation circuit consisting of frothers and froth settling tanks to float off residual bitumen in middlings alone. Naphtha is also recovered from froth treatment plant tailings using vacuum stripping (after testing and rejecting steam stripping) (112). A patent by Simmer (113) describes a method to recover naphtha from froth treatment plant tailings. Tailings are passed through a vacuum tower where naphtha and some water is vaporised and later condensed. The naphtha is then separated from the water in a settling tank.

There are several patents on other methods of increasing the amount of bitumen extracted at various steps in the hot water process as well as recovering residual bitumen from tailings and pond sludge. Since tailings pond sludge will have to be treated eventually in some way, it would seem advantageous to incorporate a bitumen recovery process in any method developed (94).

One of the simplest proposals for recovery of residual bitumen, as described by Bain and Roberts (114), is to dilute recovered pond sludge to between 6-18% solids, and then settle for up to 100 hours. Bitumen is recovered as a froth, the middlings fraction (less than 6-18% solids) is sent to the retention pond, and sludge (greater than 6-18% solids) can be removed for further dewatering. Bassaw (115) reported that the simplest way to treat the sludge obtained from this process was to let it dry in air to a disposable solid. This is similar to the findings of Ripmeester and Sirianni (116) who found that removing free bitumen from tailings increased the evaporation rate of water from the remaining suspension.

Various groups have proposed exploiting the oleophilic nature of coke produced at the oil sands plant by using it to adsorb bitumen from tailings. According to Hall and Tollefson (94,117), the most important consideration in using coke is the contacting method. In their process tailings and coke are mixed together and bitumen is adsorbed on the coke particle surfaces. They found that shaking for two to three hours was the best contact method, while tumbling, stirring, percolation or a bubble aerator were less efficient contact methods. In laboratory tests they recovered 60-70% of residual bitumen from primary separation vessel tailings and 70-93% residual hydrocarbon from centrifuge plant tailings using 10 g coke/100 mL tailings. The coke with adsorbed bitumen could then be recovered by filtration or differential settling and then the bitumen recovered by steam treatment. While the external surface area of the coke was one of the controlling factors for recovery efficiency, the size of the internal surface area governed the removal of water soluble organics.

In a process using coke, developed by Hudson and Seitzer (118), middlings or tailings as a liquid or vapour would be passed through a deep coke bed (although vaporising tailings would not seem feasible when one considers the energy requirements). In laboratory trials, 68% of residual bitumen was recovered when using 10 g coke/100 mL slurry. In a pilot plant trial, 500 tons of tailings were overboarded onto a 125 ton coke bed and 66% of residual bitumen was recovered. The authors proposed to burn the coke with adsorbed bitumen for fuel.

In a recovery process similar to that of Maloney's (73) process described under 'physical methods', which was developed by Sirianni and Ripmeester (119), tailings, tar sands, and enough coke to give a concentration of 0.5-5 wt% were mixed together and then agitated with shearing action. The coke adsorbed the bitumen from tailings and tar sands until eventually an organic phase was formed. This phase was separated by screening or coarse filtration and the bitumen recovered while the aqueous phase, now with a fifth to a tenth the original tailings hydrocarbon content, was discharged to the tailings pond.

Majid et al. (120,121) described a spherical agglomeration process in which tailings, coke, and extra water were mixed to form agglomerates of coke and organics that could then be recovered for further processing. They found that recovery rate was directly proportional to the BET area of the coke used. In laboratory tests when coke and pond sludge were mixed together in a blender recoveries ranged between 50%, using a mixture containing 20 wt% coke, to 80% using 40 wt% coke. Adding a total of 0.1 wt% sodium silicate or ligno-sulphonate increased this recovery by about 10%.

Ashton and Davitt (122) patented a method for recovering residual bitumen from tailings ponds *in situ*. Pond sludge is pumped into the top of a closed vessel standing in the tailings pond. Bitumen would float to the top where it could be recovered while sludge would flow out holes near the bottom of the container. Bitumen recovery is increased because of agitation of the sludge as it is pumped up to the surface. This technique would also decrease the hazard to birds as all floating bitumen would be in the sealed container.

There are several patents describing variations of aeration and/or agitation for recovering bitumen from tailings from various sources. These include techniques that are already in use in some areas. Essentially any form of turbulent shearing motion, whether from tumbling, mixing, aeration or combinations of these, is useful in dispersing bitumen and bitumen-mineral agglomerates so that the bitumen can rise to the surface as a froth (123). The recovered froth can then be sent to the regular froth treatment plant.

An example of a typical aeration/agitation process is outlined in a series of patents by Davitt (124-128). [illegible]he basic process pond sludge is simultaneously agitated and aerated and the froth layer that forms is collected and settled in a settling tank. The upper layer that forms in the settling tank is then sent for bitumen recovery. In one example using 22 wt% solids pond sludge containing 3 wt% bitumen, Davitt recovered about half of the residual bitumen. The upper layer sent for bitumen recovery contained 40 wt% bitumen, 11.7 wt% solids and 41.3 wt% water (124).

Suncor (23) has developed a bitumen recovery process from pond sludge, based on Davitt's patents (124-128), which has undergone pilot plant studies. Sludge is pumped from the tailings pond to a mixing tank where in the first stage of the process the sludge is diluted to 15% solids and then sparged with compressed air. This aeration displaces carbon dioxide from solution and hence increases the pH of the solution from 6.8 to 8.0. The dilute, aerated sludge is sent from the mixing tank through a series of rougher, scavenger, and then cleaner flotation tanks to recover the bitumen froth. The froth is sent through an Oleophilic Sieve® and the recovered bitumen is then transferred to the centrifugation circuit of the regular froth treatment process. This process recovered about 70% of bitumen in sludge. Half the water used for diluting the sludge was recovered after sixty days settling and nearly all was recovered after six months.

To recover residual bitumen from primary separation vessel sand tailings, Hall and Tollefson (123,129) designed a procedure in which the sand underflow was diluted with either pond sludge, centrifuge plant tailings, or primary separation vessel middlings, and then agitated in some way, such as by tumbling. This process recovered 66% of the residual bitumen in the froth formed, and if aeration by carbon dioxide was added the recovery increased to 91%. Carbon dioxide was used as it decreased both overfrothing and the viscosity of the mixture.

The form of agitation or aeration that is most efficient depends on the type of material being treated. Hall and Tollefson found that aeration using either a frit (129) or jet (123) gave the best results for centrifuge plant tailings. They recovered froth containing 37-48% combustible hydrocarbons and an increased (but not specified) level of solids, for a residual bitumen recovery of between 60-80%. Adding carbon dioxide increased the recovery level by up to 40%. However, they found that this treatment did not work on the sludge fraction of primary separation vessel tailings. Instead, steam or heating combined with aeration gave the best recovery of 53%. Agitation by tumbling gave the best recovery of about 50% for total primary separation vessel tailings (123,129).

Other variations that have been tried using aeration and/or agitation include: Steinmetz's (130) patent to use stirring, mixing or turbulent pumping of middlings, instead of aeration, to recover 88 wt% residual bitumen as a froth containing 5 wt% fines, as compared to 21 wt% recovery as a froth containing 7.4 wt% fines from aeration; St. Denis and Kessick's (131) method of diluting pond sludge (one volume sludge to two volumes water) followed by aeration to get 100% bitumen recovery; and Porteous et al.'s (132,133) patents on agitation and aeration of centrifuge plant tailings with nitrogen (to prevent explosive mixtures with naphtha) in a sealed vessel (in order to be able to recycle the nitrogen) for 65% hydrocarbon recovery as a froth containing 8-28 wt% hydrocarbon, 37-70 wt% water and 22-43 wt% solids.

Various pretreatments of tailings have also been proposed to increase the efficiency of aeration/froth flotation process. These include increasing the pH with base then decreasing it again with acid (134); adding sodium silicate (126,127) or 10-10,000 ppm (by weight) ammonium lignin sulphonate (135); diluting sludge between 1:10 to 2:1 (water:sludge) (136); or cycloning sand tailings and middlings to provide an enriched bitumen stream for aeration (137,138).

Lane (139) claimed that flotation methods to recover residual bitumen may be useless as the increased fines content of the froth may block final bitumen recovery in the froth treatment plant. He has suggested that it may be more economical to forget about residual recovery and instead treat whole tailings to get a stable solid. To circumvent this problem, Cymbalisty (140) suggested that tailings be diluted, preferably aerated, and then left to settle quietly (as opposed to constant aeration as is usually proposed). Froth obtained by this method had a decreased solids and water content as compared to that of other aeration methods (froth composition this method: 77 wt% bitumen, 5 wt% solids, 18 wt% water, compared to 52 wt% bitumen, 13 wt% solids, 35 wt% water from usual aeration process). Alternatively, Elanchenny and Seitzer (141) proposed that the froth produced in the first flotation process can be treated further to reduce fines content by for example dilution with water and then further aeration, or as reported by Porteous et al. (132), by dilution with naphtha followed by centrifugation to upgrade froth to 84% bitumen, 4% solids and 11% water.

Various groups used carbon dioxide instead of air for aeration as they found it gave an increased recovery rate and decreased frothing (101,123,129).

While most proposed methods involved treating material in specially constructed vessels, Nedapac (101) and Hall and Tollefson (123) suggested a process in which carbon dioxide or air is added directly in the tailings pipe as tailings are being pumped to the pond. The bitumen rich froth would then be recovered as the tailings settled.

Two groups have tried to devise a treatment that would simultaneously extract residual bitumen from pond sludge and cement the mineral solids. Joshi and Prasad (142) added a total of 0.4% of an unidentified chemical to sludge containing 27% solids in bench top experiments, and recovered up to 54% bitumen floating on top after centrifugation, as opposed to 45% bitumen recovery with no chemical treatment. At higher chemical concentrations the sludge gelled and without centrifugation bitumen could not be recovered. They found that after the bitumen was removed the centrifuged solids took only three weeks to dry. Kutasinski (143) patented a treatment of mature sludge that consisted of adding a total of 0.006 wt% sodium aluminate and/or methanamide (at a cost of 0.1¢ per gallon sludge treated in 1977) directly into the tailings pond. The bitumen would float to the top to be skimmed off and the sludge left behind would solidify.

As an option to recovering residual bitumen, Hocking (144) proposed that indigenous hydrocarbon-using microorganisms be used to clean up tailings. He found that mixing sludge with urea and aerating led to breakdown of some bitumen and an increase in the settling rate of remaining solids.

Recovery of metals

The few reports (27,145,146,147) on recovery of useful metals from tailings deal with the recovery of titanium and zirconium as these metals are valuable enough to pay for their extraction. These metals are found in oil sands tailings as the minerals zircon ($ZrSiO_4$), rutile and anatase (TiO_2), ilmenite ($TiO_2 \cdot FeO$), and leucoxene (minerals containing TiO_2 and FeO) (145,24).

Centrifuge plant tailings provide the richest source of heavy minerals (24,148) with values reported between 5-9 wt% for titanium and 2-5 wt% for zirconium (24,146). Therefore, proposed extraction schemes use this tailings stream as the starting material. In a process developed by Syncrude (27), centrifuge tailings are first treated to remove residual hydrocarbons by burnoff in a fluidized-bed reactor. The residue is then fed into a hydrocyclone system followed by gravity separators to separate a zirconium and titanium rich material. Zircon is then separated from the titanium based minerals by using high-tension separators. The titanium mineral fraction produced is relatively pure while the zircon enriched fraction requires a clean up by using magnetic separation and high tension separators.

Subsequent patents have suggested modifications of this procedure as for example, using dry sieving of the burnoff residue to separate the titanium and zirconium minerals that are then sent to the high-tension separators (146), or by inserting a preliminary air flotation step to concentrate the minerals further (up to 28-30% anatase and 10-12% zircon with 80-90% recovery) before subsequent recovery steps (147).

Based on mine capacity, Trevoy et al. (27) thought that the Syncrude mine could provide enough titanium and zirconium minerals to support commercial plants for titanium pigment and zirconium metal production.

Properties and Treatment of Clay Tailings from Other Sources

There are other mining/extraction industries worldwide besides oil sands mining in northern Alberta that have problems in dealing with slow settling clay suspensions. It is possible then that one could get some ideas on how to treat oil sands tailings by seeing what was successful in these other industries. Kessick and Jobson (2) have also reviewed this area.

Phosphate Mining

From 1932 to 1973 between $2x10^6$ and $27x10^6$ tonnes of slime solids were produced each year by the phosphate mining industry of Florida. These solids are pumped to tailings ponds for storage as a 3-5% solids suspension (149). As of 1979 there was an estimated $2x10^9$ tonnes slime solids in storage (150). The sludge ponds are usually 1.2-3.2 km^2 in area with 6-18 m high dikes. About 10 km^2 are added each year to the 325 km^2 already in use as tailings ponds (151,152,153).

Phosphatic tailings characteristics

Phosphatic slime solids contain montmorillonite, attapulgite, kaolinite, quartz, fluorapatite, dolomite (149), illite, wavelite and crandalite (150). In one sample, 72-84% of the total solids present were clays and 55-88% of these clays were attapulgite and kaolinite while the rest was montmorillonite (149). Most of the clays were Ca^{2+} clays while others were Na^+ or Mg^{2+} (150). The clay composition and concentration were highly variable in slime solids collected from different locations.

In a review Pittman et al. (152) state that the clays in phosphatic tailings solidify in four stages. The first stage is sedimentation during which the clays settle out of supernatant water; next is consolidation, the most important process, during which the clays solidify under their own weight, thus squeezing out trapped and interstitial water; third is consolidation under hydraulic gradients (which makes bottom pond drainage very important); and lastly, surface stabilization where surface water is removed leading to increased drying and the creation of a surface crust.

Phosphatic tailings treatment

There is an excellent review of processes developed for treating phosphatic waste material, published by the U.S. Bureau of Mines (152). In this review the authors covered early de-watering techniques, techniques currently being tested, and methods that are being developed.

Most of the early methods developed have been abandoned as being impractical. These included:

- electroosmosis, which was too slow and consumed too much power, or electrophoresis using moving belt anodes, which did not yield clear water;

- the use of ultrasonic energy to precipitate clays, which was still under investigation;

- centrifugation, which was impractical because of high capital costs and energy requirements;

- process modifications such as using dry extraction methods or magnetic separation, which were not considered to be feasible;

- using flocculants; but these had the problem that methods that worked in the laboratory often did not work in the field due to the high sample variability. Of all types of flocculants tested the higher molecular weight polyacrylamide polymers were the most effective, and anionic were better than either cationic or non-ionic polymers;

- using chelating agents to speed settling, but none was used on a practical scale;

- using colloidal gas aphrons, which are dispersions of micrometer-sized gas bubbles, to induce flocculation and flotation, which was still being tested;

- adding hydrated lime;

- clay aggregation using fungi; some species worked but the method was deemed impractical.

Some methods that had undergone large scale tests were:

- freeze-thaw, which was too expensive;

- crust development, using grains or grasses; Japanese millet was found to work well;

- spreading the material over a large area to speed drying; this was considered impractical;

- mixing an overburden slurry with clay wastes, but this just produced an even bigger mess, mostly due to the organics in the overburden, which led to very stable suspensions;

- using moving screens to break up gel structure in the tailings pond and therefore free interstitial water. The method worked: for example it took about four days to reach 25.2% solids from 5% solids but because the screens had to move extremely slowly, it was not practical;

- forming a sand-clay sandwich, which was based on the idea of increasing the weight on the clay to increase dewatering. The method worked but it was still rather slow and large areas and special equipment were needed;

- using a flocculant, which did work, but a lot of variables had to be controlled, such as the sand/clay/flocculant ratio, and it was thought to be too expensive;
- using sand wicks (columns of sand) in the tailings pond to increase dewatering, but the columns were very difficult to set up in existing ponds;
- using a series of settling tanks, cyclones and dewatering screens to process flocculant treated tailings; it was a very expensive process and was thought to be no better than conventional settling over a longer time period;
- mixing tailings with thickened sludge dredged from the tailings pond bottom, which did not work;
- pumping thickened sludge dredged from the tailings pond bottom into mined out pits and then covering with a sand layer to obtain a stable landfill. The method was promising but layering the sand was proving to be difficult;
- spraying sand on thickened sludge. The sand would slowly settle into the sludge, creating channels and thus releasing water. Although initially the method did not appear to work, after two years 50-70% solids were obtained.

Terichow et al. (154,155) developed a slime treatment method based on the electrophoretic properties of phosphatic slime solids. Pre-treatment with 0.01 N $Al_2(SO_4)_3$ made the suspended particles positively charged, and when the suspension was mixed with negatively charged gypsum or anthracite they found increased settling. The filterability of the settled solids was also increased, the best fitration rate occurring when there was the largest attraction between slime solids and added material (usually at 1:1 mixtures, weight slime solids : weight added gypsum or anthracite).

Of all the flocculants tested on phosphatic waste, high molecular weight polyethylene oxides (molecular weight of around 5×10^6 g mol^{-1}) are the ones that have been developed to the point of large.scale field tests. Laboratory studies showed that adding polyethylene oxide as a dilute solution (final amount added was 1-3 kg/t slime solids) to a 4-5% solids slime suspension gave a 40% solids product; the largest molecular weight polyethylene oxides worked best. The amount of polyethylene oxide needed depended on the composition of the sample being treated, and in particular it seemed to be correlated with the surface areas of the clays in suspension. A trommel was used to dewater the flocs as, once the polyethylene oxide was added, the flocs had to be dewatered immediately to prevent them from breaking up (156).

Large scale tests treating 60 gal/min of suspension using three pounds polyethylene oxide per ton of slime solids gave a 22-25% solids product which, when disposed of in shallow (4ft deep) pits, dewatered to 40% solids after 45 days (157). Larger scale field tests treating up to 200 gal/min gave similar results, although in these cases they added lime to convert the clays to the Ca^{2+} form before adding the polyethylene oxide (153,158). Stanley and Schreiner (159) studied the effect of the cation form of the clay on dewatering of phosphatic waste, and found that the floc size and structure of the settled solids depends on the cation form of the clay, with Ca^{2+}-clays forming the most compact structures.

Treating Senegal phosphatic waste (15% solids), which contains mostly apatite with some montmorillonite and kaolinite, with polyethylene oxide, led to a better solids product than the same treatment of Florida phosphatic waste. Using a total of about 0.4 lb polyethylene oxide (as a dilute (0.01%) suspension) /ton gave a 45% solids product (160).

Ways of reducing expenses by decreasing the amount of polyethylene oxide used were investigated. After testing various chemicals including inorganic cations, organic flocculants, and hydrogen bonding compounds (to mimic the action of polyethylene oxide), it was found that adding two pounds of guar per ton of slime solids worked well and was cheaper than polyethylene oxide alone (161).

A method to recover vanadium as V_2O_5 from phosphatic waste was developed but in 1[illegible]5 the process was too expensive relative to then current world prices for vanadium (162).

Sand Washing

Slow settling clay tailings are produced by sand washing operations of various Australian mines. The initial suspension is usually 1-5 wt% solids but does settle to 40 wt% solids in tailings ponds (163). At one site about 4,000 tonnes dry solids are produced each month.

The major component of suspended solids in these tailings is kaolin and there are trace amounts of quartz, mica, gibbsite and pyrite. At some sites there is also organic matter, which has been washed from the sand. The liquid limit of this material varied between 46 and 60% solids. There are various dissolved inorganic cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) at concentrations ranging between 4 ppm (K^+) to 360 ppm (Na^+), and inorganic anions (Cl^-, SO_4^{2-}, PO_4^{3-}) at concentrations ranging between 16 ppm (PO_4^{3-}) to 490 ppm (Cl^-).

Clay suspensions from sand washing operations can often take decades to settle out, even to a limited extent. Due to economic necessity Sparrow's group in Australia has worked on dewatering methods that maximize use of gravity and solar driven processes. While tailings from sand washing can be dewatered by filtration or centrifugation after flocculation, the capital and operating costs make these methods too expensive (163).

Sparrow et al. (163-167) have shown that dewatering of these clay tailings is significantly improved if the tailings are allowed to drain as the solids settle. A combination of decantation and drainage is used at the start, then evaporation and drainage once a thick sludge is obtained. They have developed an equation to predict rate of water loss based on the evaporation rate and hydraulic conductivity of the tailings pond. From field tests and calculations they found that large, shallow (maximum height of 40 cm), ponds with sand beds are needed for efficient drying. Under these conditions dewatering to 60 wt% solids took one month, starting with 20 wt% solids pumped from current settling ponds.

Ihle and Sparrow (168) tested the effect of additives on drainage behaviour of clay tailings. They found that while cationic or non-ionic polyacrylamides increased the settling rate they also increased the volume of the settled solids and were therefore not used.

Ore Processing

Libor (169) patented a process based on the use of flocculants to treat clay suspensions formed during ore processing in mining industries. Macromolecules such as proteins, polymeric amides or polysaccharides are used at concentrations of 50 mg/kg solid in suspension to flocculate the clays. The flocs that form are then further thickened by adding a polyamine, polypeptide or polyacrylic acid, and after a filter aid is added, such as calcium oxide or barium oxide, the suspension is either centrifuged or vacuum filtered to separate solid from liquid. Theoretically, the process can handle suspensions from 0.05-35% solids using 0.003-0.5% flocculant.

Smelley's group at the US Bureau of Mines has applied their method for treating phosphatic wastes by flocculation with polyethylene oxide followed by dewatering to clay suspensions from other ore processing industries (160,170).

Polyethylene oxide flocculation was used to increase the solids content of potash-clay brine and hence increase potash recovery. The original solids content was 3.8% with the major clay constituent being montmorillonite. Again, using a dilute polyethylene oxide (0.1%) suspension, Smelley's group recovered a solid fraction containing 35-40% solids using 2-5 lb polyethylene oxide /ton. In this case the amount of polyethylene oxide needed depended directly on the brine concentration (160,171).

Flocculation with polyethylene oxide also worked on uranium mill tailings (15% solids), talc (hydrated magnesium silicate) mine tailings (9.7% solids) (160,172), and to a lesser extent on TiO_2-HCl-Fe-Cl slurry (1.7% solids) from the acid leaching of ilmenite (160,170).

Vreugde and Poling (173) also reported on the use of flocculants to treat Cu-Mo flotation tailings. These tailings are a 10-30% solid, alkali suspension, in which 70% of the particles are less than 74 µm and 10% are less than 10 µm. Of the various commercial flocculants tried, anionic flocculants (used at 0.03%) increased settling rates the most and the greater the polyacrylamide content of the flocculant, the bigger the increase. This was despite the fact that the solid particles in the suspension were negatively charged. The authors thought that Ca^{2+} from lime added in the flotation process acted as a salt linkage between the particles and the anionic flocculant.

Sand bed filtration such as developed by Sparrow's group for the treatment of sand wash tailings has also been used to reduce the level of bauxite processing tailings (a red mud of around 25% solids) to one third to one half the original volume (174) and in treating alumina waste from acid extraction of alumina from non-bauxitic ores (175). In this latter process sand bed settling and decantation were tested on a 23% solid suspension in nine feet tall (ID 6.75 in) columns with a foot of sand at the bottom. In 186 days the mud level dropped from 108 to 69 inches and a sediment of about 50 wt% solids was obtained.

Coal Washing

As mentioned previously, Smelley's group has used polyethylene oxide flocculation and dewatering on other types of tailings, including those produced during coal washing (160,170). Just under half the particles in an aqueous suspension from a coal washery are smaller than 325 mesh and this fraction consists of kaolinite, mica, quartz and coal with minor amounts of chlorite and montmorillonite. Using 0.2-2 lb/ton polyethylene oxide (as a dilute solution of 0.05-0.25%), they achieved a 49-50 % solids product from an initial solids content of 3.6% (160). This method was field tested on dilute suspensions (2.7-8.1% solids) and more concentrated suspensions (18.5-24.1% solids), using a microsieve screen (instead of a trommel) to dewater the suspension. They found they had to increase the pH first with lime after which they obtained a dewatered product of up to 63% solids from the dilute suspension and 58% solids from the concentrated suspension (176).

In laboratory tests on coal washery tailings, Lockhart (177,178) showed that simple sedimentation followed by electroosmosis was cheaper than flocculation with polyelectrolytes followed by centrifugation. Using the former method the mostly clay solids (including kaolinite, montmorillonite, illite and mixed layer clays) sedimented in three hours to about 56 wt% solids from an initial 8 wt% solids suspension, and this sediment, when subjected to electroosmosis, produced a product of 73 wt% solids after 100 minutes at 50v (about 5 to 8 kWh/t). Flocculants actually decreased the compaction of solids during sedimentation.

Conclusions

There are three things that have become rather obvious in considering the wide variety of treatments of oil sands tailings that have been proposed, and which are probably self-evident to the people working in this area, but we will mention them here These are

a) One must have a clear idea as to the goal of the particular treatment method For example, is the aim to provide maximum amounts of recycle water, or to clean up the water enough so that it can be returned to the environment, is it the intention to provide a solid that can support heavy equipment or just to minimise sludge volume, and so on Of course these goals, or any others, do not have to be mutually exclusive, although some naturally would be.

b) If any method is to be generally applicable, one must know how the composition and characteristics of the material being treated affect the procedure being developed, so that the process can be monitored and controlled.

c) Proposed methods have to be scientifically, technologically and economically sound. In other words, a lot of developmental work has to be done at laboratory and pilot plant levels before a particular process can be evaluated completely.

There are really two different aspects to the tailings problem. These are reducing the amount of tailings produced, and dealing with the tailings that are produced.

Decreasing the amount of tailings produced would entail process modifications of the present hot water process to decrease the volume of process water used, or the use of a completely different bitumen extraction process. Extra steps could be added to the hot water process to extract bitumen not recovered from the primary separation vessel or middlings recycle, so that the maximum bitumen is recovered for a given amount of produced tailings. Syncrude has already done feasibility studies on the use of hydrocyclones, cycloseparators, dense media separators, rake thickeners, cone thickeners, counter-current decantation, induced air flotation and dissolved air flotation, amongst others, to increase the extraction efficiency of the hot water process, and eventually decided to use induced air flotation and a cone thickener (their tails oil recovery vessel) (10).

As regards using a process other than the hot water process, one could argue that one should not tamper with a successful method, which the hot water process undoubtedly has been despite the tailings problem; however as ore quality decreases, extraction efficiency of the hot water process also decreases and this has prompted the development of other bitumen extraction processes such as the RTR/Gulf process (69), Taciuk processor (70) and the Oleophilic Sieve® (65). Comprehensive pilot plant studies and economic analysis would be needed to determine whether these or other alternatives to the hot water process would be viable and, of course, whether they produce less sludge.

There is no problem in developing methods to treat oil sands tailings at the bench top scale, but there is a problem in designing a feasible and economical process that would be acceptable to the industry. This is why

Suncor has rejected most mechanical and physical methods such as filtration, centrifugation, freeze-thaw, evaporation/distillation, electrophoresis and bioprocessing (1,6).

Most chemical processes such as the addition of organic flocculants are uneconomical, even if they work. The use of lime as a coagulant may be more practical as it is an inexpensive chemical and does seem to be effective in precipitating suspended clay solids and producing a potentially disposable solid, especially when treating whole tailings (46).

Geotechnical methods often involve just the re-routing or handling of materials, which to the non-engineer seems inexpensive and easy to do, but transporting and pumping materials is one of the most expensive aspects of the oil sands extraction process. The idea of Scott and Dusseault (11,12,179) to produce a usable backfill by mixing appropriate materials such as sand, sludge and overburden seems quite attractive and the simplicity of the idea is appealing, but there is still some work to be done to determine its large-scale feasibility.

A combination of maximizing the extraction efficiency of the hot water process, together with a simple tailings treatment process such as lime assisted settling of whole tailings or the production of a usable backfill by the appropriate mixing of various waste materials, seems to be the best possible solution to the tailings problem. Maximizing the use of natural forces such as gravity and the settling and consolidation properties of tailings may be the best approach to an economical treatment method such that, when the oil sands mines shut down, a filled, reclaimed, mined out pit will be left behind instead of hectares of sludge.

At present there is no process that satisfies all of the following criteria: a) yields a solid that is suitable for disposal, with no subsequent environmental problems, b) yields water that is suitable for disposal in rivers or lakes or that is suitable for recycle to the bitumen extraction plant, c) that works reliably on a large scale under the range of weather conditions in the Athabasca region, d) that has acceptable capital and operating costs.

In view of the above, a more basic understanding of physical and chemical events that occur during the processing of mined oil sand would hopefully lead to technological developments that would be based on scientific understanding and reliable data.

It was the desire to extend and improve the understanding of clay-water systems, such as those encountered in enhanced production of conventional oil by water flooding, that has led to the research on viscosities that is described in Chapter 3.

It has been mentioned previously that naphtha is used in the commercial production of bitumen from mined oil sands and that some of this valuable naphtha ends up in the tailings adsorbed on clays. Efficient recovery of this naphtha requires some knowledge of the thermodynamics of adsorption of light hydrocarbons on clays, which has provided part of the motivation for the research described in Chapters 4 and 5.

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CHAPTER 3

Viscosities of Dilute Aqueous Suspensions of Clays

Introduction

Colloidal suspensions of clays in water and aqueous solutions have been investigated in many ways, including many investigations of rheological properties. Because of applications in such fields as ceramics and drilling muds, most of these investigations have been concerned with concentrated suspensions in which non-Newtonian flow is important. There have been only a few investigations of the viscosities of dilute suspensions, in spite of their general theoretical importance and also their practical importance in such areas as enhanced oil recovery and water treatment. Our particular interest has been in the flow properties of dilute suspensions of clays, including investigations of mixed-clay systems that may be important in connection with problems involving oil sands tailings as well as to problems related to permeabilities in enhanced oil recovery.

As background for our research we cite a few previous investigations of viscosities of dilute suspensions of clays (1-6) and evidence for interesting and potentially important interactions of different kinds of clays with each other in dilute suspensions (7,8).

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1. A version of this chapter has been published. K.L. Kasperski, C.T. Hepler and L.G. Hepler, Can.J.Chem. 64 (1986) 1919.

Experimental

Materials

Well characterized clay samples were obtained from the Source Clay Mineral Repository, Department of Geology, University of Missouri, Columbia, Missouri, USA. The kaolinite (KGa-1) came from Washington County, Georgia, and the montmorillonite (SWy-1) came from Crook County, Wyoming. Our preparations of Na-kaolinite and Na-montmorillonite for subsequent use followed procedures that have been described previously (9,10).

Apparatus and methods

Densities of suspensions were obtained with glass pycnometers of 25 cm^3 nominal volume, which we calibrated at each temperature with distilled water. Uncertainties in most of our densities of clay suspensions are less than ± 0.0005 g cm^{-3}.

Cannon-Fenske glass viscometers (ASTM 25 and 50) from Fisher Scientific were calibrated with distilled water and with 0.010 M NaOH at each temperature. Flow times ranged from 1 to 20 minutes, as timed with a stopwatch; total timing uncertainties (due to the stopwatch and our response times) were about ± 0.1 sec. At the low flow rates of our measurements, there were no complications due to non-Newtonian flow, hence we were unable to investigate the non-Newtonian rheology that becomes important at higher flow rates and for more concentrated suspensions (2,3,5,11).

Particular care was taken with cleaning the viscometers between measurements because of the tendency of clay particles to adhere to the walls, of the capillaries of the viscometers, which was particularly troublesome with our most concentrated suspensions

All measurements were done with pycnometers and viscometers suspended in a constant temperature water bath with temperature known to ± 0.01°C and stable to ± 0.005°C, as checked with a platinum resistance thermometer

Results and Calculations

Results of our measurements leading to densities and viscosities of suspensions of Na-kaolinite and Na-montmorillonite at 25.00°C are summarized in Tables 3.1 and 3.2, respectively, and illustrated in Figure 3.1, which is based on eq. [3.8] that is presented later.

We want to calculate the volume fractions of dry clay in our various suspensions, which requires that we know the density of our solid dry clays. Previous investigations of similar clays have led to reported densities ranging from 2.4 to 2.8 g cm^{-3} for Na-montmorillonite (4,5,12,13) and 2.58 to 2.63 g cm^{-3} for Na-kaolinite (12,14). Largely because of the substantial range in reported densities for Na-montmorillonite, we use our densities of suspensions to obtain our own values for the densities of the dry clays we have used, as follows.

We begin by assuming that the volumes of dry clay (V_C) and water (V_W) are additive so that the volumes of suspensions (V_S) are given by

Table 3.1. Densities and viscosities of suspensions of Na-kaolinite in 0.010 M NaOH at 25.00°C

Wt% clay	Density (g cm^{-3})	Viscosity (mPa s)	ϕ_d	$[(\eta-\eta_0)/\phi_d\,\eta_0]$[1]
1.18	1.005	0.909	0.00453	4.2
2.02	1.010	0.920	0.00778	4.0
2.91	1.016	0.942	0.0113	5.0
3.79	1.021	0.956	0.0148	4.9
3.86	1.022	0.968	0.0151	5.7
5.07	1.030	0.984	0.0199	5.2
6.61	1.039	1.050	0.0262	6.8
7.08	1.042	1.084	0.0282	7.6
7.44	1.045	1.070	0.0297	6.7
8.66	1.052	1.100	0.0347	6.7

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[1] The viscosity of 0.010 M NaOH is 0.892 mPa s, as compared with 0.890 mPa s for pure water. Here we use η_0 = 0.892 mPa s.

Table 3.2 Densities and viscosities of suspensions of Na-montmorillonite in water at 25.00°C

Wt% clay	Density (g cm^{-3})	Viscosity (mPa s)	$\varnothing_d$	$[(\eta-\eta_o)/\varnothing_d\eta_o]$
0.10	0.9976	0.948	3.84×10^{-4}	170
0.20	0.9983	1.007	7.68×10^{-4}	171
0.30	0.9988	1.067	1.15×10^{-3}	173
0.40	0.9997	1.156	1.54×10^{-3}	194
0.50	1.0001	1.220	1.92×10^{-3}	193
0.60	1.0007	1.280	2.31×10^{-3}	190
0.70	1.0014	1.388	2.70×10^{-3}	207
0.90	1.0026	1.630	3.47×10^{-3}	240
1.00	1.0032	1.671	3.86×10^{-3}	227
1.20	1.0045	1.980	4.64×10^{-3}	264
1.40	1.0057	2.311	5.42×10^{-3}	295
1.60	1.0070	2.556	6.20×10^{-3}	302
1.80	1.0083	3.031	6.98×10^{-3}	345
2.00	1.0095	3.622	7.77×10^{-3}	395
2.20	1.0109	4.767	8.55×10^{-3}	509

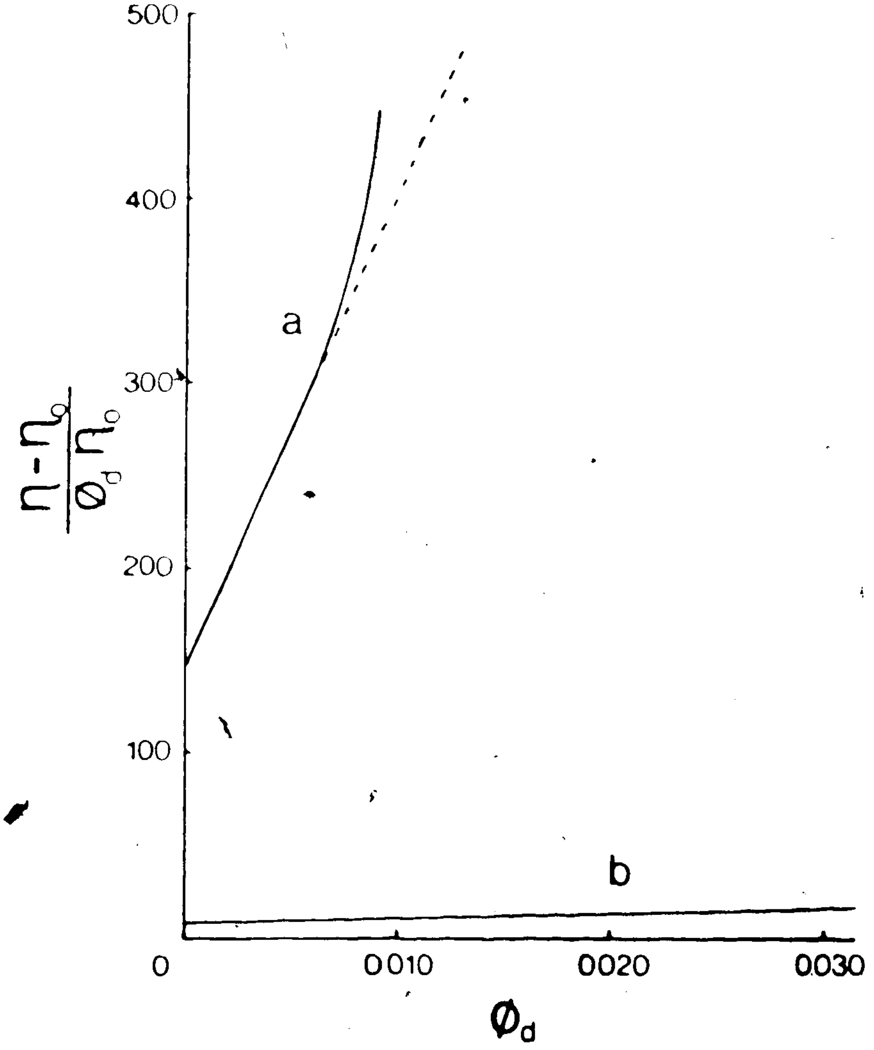

Figure 3.1. Graphs of reduced viscosity ($(\eta-\eta_0)/\phi_d\,\eta_0$) against volume fraction of dry clay (ϕ_d) for montmorillonite (a) and kaolinite (b). The dashed line for montmorillonite is an extension of the straight line corresponding to $(AS)_m =$ 148 and $(BS^2)_m = 2.6 \times 10^4$ and is drawn to show the deviation from linearity above a value of about 0.006 for ϕ_d.

[3.1] $V_S = V_C + V_W$

Very accurate results reported by Low (13) provide support for the validity of eq. [3.1] to the level of accuracy that we require here. Some algebraic manipulations with eq. [3.1] and the definition of density lead to

[3.2] $d_C = [\, d_W\, d_S P] \;/\; [100\, (d_W - d_S) + d_S P\,]$

in which the symbols have the following meanings: d_C, d_S, and d_W represent the densities of dry clay, aqueous suspension, and water, respectively, and P represents the weight percent clay in the suspension. Because of the term $(d_W - d_S)$ in eq. [3.2] and the ± 0.0005 g cm^{-3} uncertainties in our values of d_S, this equation is useful only when applied to solutions more concentrated than about one percent clay. Our calculations with eq. [3.2] applied to densities of our suspensions lead to $d_C = 2.6 \pm 0.1$ g cm^{-3} for dry Na-kaolinite and the same value for dry Na-montmorillonite, in which ± 0.1 g cm^{-3} is our estimate of the *total* uncertainty due to our experimental results and the initial assumption that volumes are additive.

There is also another way to calculate d_C from our results. Solution chemists have found it useful to define "apparent molar" properties for solutions of small molecules and "apparent specific" properties for solutions of high molecular weight polymers, with the latter being appropriate to our problem. In similar fashion we define the apparent specific volume of clay (V_ϕ) as

[3.3] $V_{\emptyset} = (V_s - V_w) / m_c$

in which V_s represents the volume of a suspension containing a specified amount of water, V_w represents the volume of that same amount of water, and m_c represents the mass of dry clay in the suspensi[illegible] Algebraic manipulations similar to those that led to eq. [3.2] lead to

[3.4] $V_{\emptyset} = [\ 100\ (d_w - d_s) / (d_s d_w P)\ ] + [\ 1/d_w\ ]$

in which the symbols have already been defined.

In eq. [3.4], just as in eq. [3.2], we have a $(d_w - d_s)$ term that limits useful calculations to suspensions containing more than about one percent clay. Calculations with data from Tables 3.1 and 3.2 in eq. [3.4] lead to $V_{\emptyset} = 0.387$ $cm^3\ g^{-1}$ for each of our clays. Since the reciprocal of $V_{\emptyset}$ is the density, we again obtain $d_c = 2.6\ g\ cm^{-3}$ for each of our clays. This value of d_c is not an independent confirmation of our identical value based on eq. [3.2] since our use of eq. [3.4] is also based on the implied validity of eq. [3.1].

Now we use the above value, $d_c = 2.6\ g\ cm^{-3}$, for dry clay as follows to obtain the volume fraction of dry clay in water ($\emptyset_d$) that will be used in subsequent calculations with the Einstein equation. Choosing to consider 100 g of suspension, we obtain

[3.5] $\emptyset_d = V_c / V_s = P d_s / 100\ d_c$

Values of $\O_d$, the volume fraction of dry clay, are listed in Tables 3.1 and 3.2 for Na-kaolinite and Na-montmorillonite.

A simple way to begin the analysis of viscosity data for suspensions is in terms of the Einstein equation, which we write as

[3.6] $(\eta - \eta_o)/\eta_o = A\O + B\O^2 + \dots$

In this equation η and η_o represent the viscosities of the suspension and of the pure solvent, $\O$ is the volume fraction of the suspended particles, and A and B are constants. It should be emphasized that $\O$ refers to the volume fraction of clay particles as they exist in suspension; that is, $\O$ may refer to the volume fraction of swollen clay particles whereas it is the volume fraction of dry clay ($\O_d$) that we know and have listed in Tables 3.1 and 3.2. All we can do now is recognize that $\O$ and $\O_d$ are related by a "swelling factor" that we denote by S so that

[3.7] $\O = S\O_d$

Substitution of eq. [3.7] into eq. [3.6] and rearrangement leads to

[3.8] $(\eta - \eta_o) / \O_d\eta_o = (AS) + (BS^2)\O_d + \dots$

As suggested by this equation, we have calculated the values of the reduced viscosities, $[(\eta - \eta_o) / \O_d\eta_o]$, that are listed in Tables 3.1 and 3.2 and have constructed graphs of these reduced viscosities against $\O_d$ as in Figure 3.1.

Least squares fits of eq. [3.8] to our experimental results lead to $(AS)_m = 148$ and $(BS^2)_m = 2.6 \times 10^4$ for Na-montmorillonite and to $(AS)_k = 3.5$ and $(BS^2)_k = 1.1 \times 10^2$ for Na-kaolinite, where the subscripts m and k refer to montmorillonite and kaolinite, respectively.

Einstein's original calculations showed that $A = 2.5$ for spherical particles. Subsequent calculations by others have shown that $A > 2.5$ for particles of non-spherical shape, such as the clays of present interest. Since it is known that montmorillonite is a swelling clay (14), we also know that $S_m > 1$. On the basis that $A_m > 2.5$ and $S_m > 1$, it is expected that $(AS)_m$ should be substantially greater than 2.5, as has indeed been found. Kaolinite, however, is not a swelling clay (15), so we expect the difference between $(AS)_k$ and 2.5 to be determined almost entirely by the non-spherical shape of the kaolinite particles.

More quantitative consideration of the magnitudes of A_m and S_m must be based on detailed considerations of the swelling of montmorillonite and on the related hydration of the clay particles in aqueous suspensions as well as on the shapes of the suspended (hydrated) particles. Although these matters are of general scientific interest and are also important in connection with many questions concerning the colloid chemistry of clays in aqueous systems, they extend beyond the realm of the present investigation and must be left as subjects for other investigations.

The B term in equation [3.6] and thence the BS^2 term in equation [3.8] is partly determined by particle-particle interactions. Even allowing for the fact that $S_m > S_k$, the conclusion from our results that $(BS^2)_m >> (BS^2)_k$ shows that particle-particle interactions are stronger in suspensions of montmorillonite (nearly neutral pH) than in suspensions of kaolinite (high pH) of similar concentrations.

Results obtained for the densities and viscosities of suspensions of Na-montmorillonite at several temperatures are given in Tables 3.3 and 3.4. Properties of distilled water used in our calculations are given in Table 3.5. The viscosities and densities decrease with increasing temperature, as expected. For dilute suspensions (0.30 weight percent) the reduced viscosity does not change significantly with temperature, as was also found by Wood, Granquist, and Krieger (1) for suspensions of attapulgite. However, for more concentrated suspensions (2.20 weight percent) the reduced viscosity increases with increasing temperature, which could be the result of a partial breakdown of relatively large nearly spherical structures to smaller less spherical structures, and which could acoount qualitatively for the observed temperature dependence.

Because many natural environments contain mixtures of clays, and earlier investigations (7,8) have shown that there are specific interactions between different clays in aqueous suspensions, we have measured viscosities of some mixed clay systems. Our densities and viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite at five different total clay

Table 3.3. Densities and viscosities of 0.30 wt% Na-montmorillonite in water at various temperatures

Temperature (°C)	Density (g cm^{-3})	Viscosity (mPa s)	$\O_d$	$[(\eta-\eta_o)/\O_d\eta_o]$
25.0	0.9988	1.067	1.15x10^{-3}	173
35.0	0.9959	0.870	1.15x10^{-3}	182
45.0	0.9917	0.721	1.14x10^{-3}	184
55.0	0.9881	0.608	1.14x10^{-3}	181

Table 3.4. Densities and viscosities of 2.20 wt% Na-montmorillonite in water at various temperatures

Temperature (°C)	Density (g cm^{-3})	Viscosity (mPa s)	$\O_d$	$[(\eta-\eta_o)/\O_d\eta_o]$
25.0	1.0109	4.767	8.55x10^{-3}	509
35.0	1.0083	4.011	8.53x10^{-3}	536
45.0	1.0044	3.457	8.50x10^{-3}	565
55.0	0.9996	3.020	8.46x10^{-3}	590

Table 3.5. Densities and viscosities of pure water at various temperatures (16)

Temperature (°C)	Density ($g\ cm^{-3}$)	Viscosity (mPa s)
25.0	0.99707	0.8904
35.0	0.99406	0.7194
45.0	0.99025	0.5960
55.0	0.98573	0.5040

concentrations (0.25, 0.50, 0.75, 1.00, and 3.00 weight percent) were measured at 25.00°C, with results given in Tables 3.6-3.10.

We investigate the possible effects of kaolinite-montmorillonite specific interactions on viscosities by comparing our measured viscosities with those that can be predicted on the basis of a simple additivity principle. This comparison can be done in two ways.

One way to express additivity of viscosity effects is by way of

$$[3.9] \quad [(\eta - \eta_o)/\eta_o]_{mixture} = [(\eta - \eta_o)/\eta_o]_k + [(\eta - \eta_o)/\eta_o]_m$$

in which $[(\eta - \eta_o)/\eta_o]_k$ and $[(\eta - \eta_o)/\eta_o]_m$ are obtained from eq. [3.8] multiplied through by $\emptyset_d$, using values of (AS), (BS^2), and $\emptyset_d$ appropriate to each component of the mixture. Comparison of results of these calculations with the measured viscosities shows that there are small (relative to uncertainties) deviations from additivity. This is illustrated in Figure 3.2 in which the values from Tables 3.6 to 3.9 of the measured specific viscosities are compared to those calculated using eq. [3.9] for different fractions of montmorillonite of the total clay in suspension.

The other (effectively equivalent) way of testing our results for additivity is to use the viscosities of mixtures having the same ratio of (kaolinite/montmorillonite) in eq. [3.8] to permit evaluation of $(AS)_{mix}$ and $(BS^2)_{mix}$ for each (k/m) ratio. To the extent that a simple additivity principle is valid, these $(AS)_{mix}$ and $(BS^2)_{mix}$ values should vary linearly with composition from the

Table 3.6. Viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite in 0.010 M NaOH at 25.00°C. Total clay concentration = 0.250 wt%. Densities of all suspensions = 0.9991 ±0.0005 g cm^{-3}.

Mass ratio (k/m)	Viscosity (mPa s)	$[(\eta-\eta_o)/Ø_d\eta_o]$	$[(\eta-\eta_o)/\eta_o]_{exp}$	$[(\eta-\eta_o)/\eta_o]_{calc}$ [1]
pure m[2]	1.040	171	0.164	0.165
0.050	1.024	152	0.146	0.156
0.100	1.031	160	0.154	0.148
0.125	1.015	142	0.136	0.144
0.167	1.024	152	0.146	0.139
0.250	1.021	149	0.143	0.129
0.500	1.007	132	0.127	0.106
1.00	0.972	91	0.088	0.078
2.00	0.952	68	0.065	0.052
4.00	0.942	57	0.054	0.032
6.00	0.922	33	0.032	0.024
8.00	0.928	40	0.038	0.019
10.0	0.930	43	0.041	0.016
20.0	0.914	24	0.023	0.010
pure k[2]	0.899	6	0.006	0.003

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[1] See footnote, Table 3.1.

[2] Samples of clays used for the series of measurements summarized here were prepared at a different time than those used for the measurements in Tables 3.1and 3.2 - hence there are small differences between viscosities reported here and in Tables 3.1 and 3.2.

Table 3.7. Viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite in 0.010 M NaOH at 25.00°C. Total clay concentration = 0.500 wt%. Densities of all suspensions = 1.0006 ±0.0005 g cm^{-3}.

Mass ratio (k/m)	Viscosity (mPa s)	$[(\eta-\eta_o)/\O_d\eta_o]$	$[(\eta-\eta_o)/\eta_o]_{exp}$	$[(\eta-\eta_o)/\eta_o]_{calc}$ [1]
pure m[2]	1.351	267	0.513	0.375
0.050	1.197	177	0.340	0.354
0.100	1.178	166	0.320	0.334
0.125	1.200	179	0.344	0.325
0.167	1.229	196	0.376	0.312
0.250	1.219	190	0.365	0.287
0.500	1.541	378	0.726	0.232
1.00	1.167	160	0.307	0.168
2.00	1.090	115	0.222	0.109
4.00	1.045	89	0.170	0.066
6.00	0.977	49	0.094	0.048
8.00	0.953	35	0.067	0.039
10.0	0.944	30	0.058	0.033
20.0	0.925	18	0.036	0.020
pure k[2]	0.894	1	0.002	0.007

[1] See footnote, Table 3.1.

[2] See footnote, Table 3.6.

Table 3.8. Viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite in 0.010 M NaOH at 25.00°C. Total clay concentration = 0.750 wt%. Densities of all suspensions = 1.0022 ± 0.0005 g cm^{-3}.

Mass ratio (k/m)	Viscosity (mPa s)	$[(\eta-\eta_0)/\varnothing_d\eta_0]$	$[(\eta-\eta_0)/\eta_0]_{exp}$	$[(\eta-\eta_0)/\eta_0]_{calc}$ [1]
pure m[2]	1.364	182	0.526	0.633
0.050	1.381	189	0.546	0.594
0.100	1.347	176	0.508	0.559
0.125	1.336	171	0.495	0.543
0.167	1.325	167	0.483	0.518
0.250	1.339	172	0.499	0.475
0.500	1.313	162	0.470	0.379
1.00	1.229	130	0.376	0.270
2.00	1.234	132	0.382	0.172
4.00	1.082	73	0.211	0.102
6.00	1.028	52	0.150	0.074
8.00	0.991	41	0.118	0.060
10.0	0.962	26	0.077	0.050
20.0	0.941	18	0.053	0.031
pure k[2]	0.916	9	0.025	0.011

---

[1] See footnote, Table 3.1.

[2] See footnote, Table 3.6.

Table 3.9. Viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite in 0.010 M NaOH at 25.00°C. Total clay concentration = 1.00 wt%. Densities of all suspensions = 1.0037 ±0.0005 g cm^{-3}.

Mass ratio (k/m)	Viscosity (mPa s)	$[(\eta-\eta_0)/\phi_d\eta_0]$	$[(\eta-\eta_0)/\eta_0]_{exp}$	$[(\eta-\eta_0)/\eta_0]_{calc}$ [1]
pure m[2]	1.782	258	0.996	0.937
0.050	1.742	246	0.951	0.876
0.100	1.856	279	1.078	0.822
0.125	1.844	276	1.065	0.797
0.167	1.706	236	0.910	0.759
0.250	2.04	333	1.28	0.692
0.500	2.40	437	1.69	0.546
1.00	2.260	396	1.530	0.383
2.00	1.340	130	0.501	0.240
4.00	no measured	viscosity		
6.00	no measured	viscosity		
8.00	0.971	23	0.087	0.081
10.0	0.950	17	0.064	0.068
20.0	0.910	12	0.045	0.042
pure k[2]	0.910	5	0.019	0.015

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[1] See footnote, Table 3.1.

[2] See footnote, Table 3.6.

Table 3.10. Viscosities of suspensions of mixtures of Na-kaolinite and Na-montmorillonite in water at 25.00°C. Total clay concentration = 3.00 wt%. Densities of all suspensions = 1.0157 ±0.0005 g cm^{-3}.

Mass ratio (k/m)	Viscosity (mPa s)	$[(\eta-\eta_0)/\eta_0]_{exp}$	$[(\eta-\eta_0)/\eta_0]_{calc}$
9.00	1.54	0.73	0.252
5.67	1.70	0.91	0.375
3.00	2.4	1.7	0.672
2.33	2.8	2.1	0.845
1.86	3.7	3.2	1.036

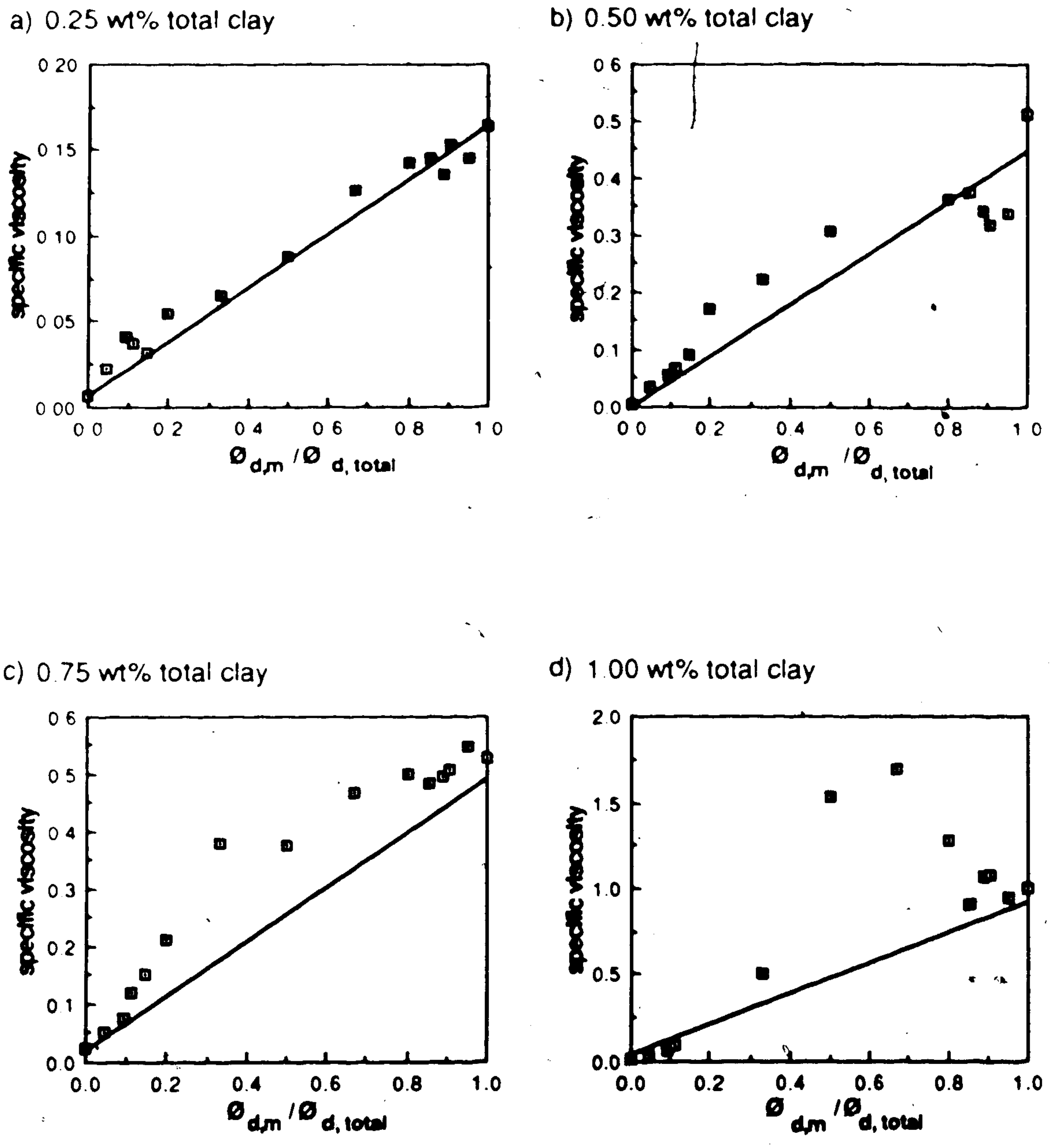

Figure 3.2. Graphs of specific viscosities against fractions of Na-montmorillonite ($\emptyset_{d,m}/\emptyset_{d,total}$) in mixtures of Na-montmorillonite and Na-kaolinite for total clay concentrations of 0.250, 0.500, 0.750, and 1.00 wt%. Experimental values (⊡) are compared to the values calculated for the additivity model using eq. [3.9] (solid line).

in this way that there are small (relative to uncertainties) deviations from additivity. The deviations (just barely statistically significant) of viscosities of dilute suspensions of mixed clays from simple additivity justify a brief summary as follows. First, viscosities of dilute suspensions with (k/m) ratios larger than about 0.25 are slightly larger than predicted on the basis of additivity, while viscosities of suspensions with smaller (k/m) ratios are close to those predicted on the basis of additivity. These observations are consistent with the idea (7,8) that relatively small montmorillonite particles are adsorbed on and coat the surface of relatively large kaolinite particles, but it should be recognized that the effects of such adsorption on viscosities of dilute suspensions are less than the effects on electrophoretic mobilities (8) and related zeta potentials.

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CHAPTER 4

Thermodynamics of Adsorption of Hydrocarbons on Kaolinite Determined Using Gas-Solid Chromatography

Introduction

Interactions that an insoluble solid (such as kaolinite) will have, whether with liquid or gaseous substances, will be mediated by adsorption at its surface: therefore, a knowledge of surface properties of the solid is important in understanding the behaviour of these multiphase systems. Adsorption thermodynamics provides basic information concerning the interaction between adsorbate and adsorbant as well as the state of the adsorbed phase. Study of the thermodynamics of adsorption of a multitude of systems has flourished since the first publications discussing the thermodynamics of adsorbed phases (1-5). Reviews of the many areas of investigation in gas-solid adsorption are given by Sing (6) and Parkyns and Sing (7).

Gas-solid adsorption thermodynamics can be studied by calorimetry, by equilibrium techniques involving the determination of adsorption isotherms at several temperatures, or by gas-solid chromatography (for a discussion of these techniques see Holmes (8) and Ponec et al. (9)). Of particular interest are the values of thermodynamic properties extrapolated to zero surface coverage (analagous to the infinite dilution state for solutions), as this state is generally considered to be best for comparison of different gas-solid systems (10). However, calorimetric studies are usually done at appreciable surface coverage of the adsorbent due to sensitivity limits, particularly in the case of physical adsorption for which the heats involved are quite small (11-13). While adsorption isotherms have been measured to very low pressures (and hence very low surface coverage) (14), there remain doubts as to the accuracy of the data obtained due to problems with measuring the low pressures and uncertainty as to whether a true equilibrium has been reached (10). By using gas-chromatography, one can obtain thermodynamic properties at nearly zero surface coverage as this is inherent in the experimental procedure and derivation of the equations that lead to thermodynamic values obtained from gas-solid chromatographic data (see Theory and Calculation Methods section).

The adsorption properties of kaolinite are of interest because of its wide use in industrial processes as well as its presence in soils and certain geological formations, such as the oil sands, that are important mineral resources.

Kaolinite is an example of a 1:1 layer clay, that is, it consists of multiple layers held together by van der Waals forces. Each layer is made up of one tetrahedral and one octahedral sheet. The tetrahedral sheet is a two dimensional array of tetrahedral silicon bonded to oxygen while the octahedral sheet is a two dimensional array of six-coordinate aluminum bonded to oxygen and hydroxyl groups. There is some very minor substitution of aluminum for silicon in the tetrahedral sheet and iron or titanium for aluminum in the octahedral sheet. These substitutions of lower valent cations, as well as broken bonds on the edges of the clay particles, lead to a net negative charge which is neutralised by adsorbed cations. Kaolinite has a cation exchange capacity usually in the range of 3-15 milliequivalents /100 g (15). Thus, the adsorption surface is a complex mix of cations, oxygen, and hydroxyl groups.

There is considerable interest in the study of adsorption of substances such as amines (16,17) and sulphates (18) from solution onto kaolinite, because of their importance in soil chemistry. Isotherms for the adsorption of asphaltenes from solution onto kaolinite and montmorillonite were also obtained due to the importance of these clays in oil reservoirs, although the authors were unable to obtain any thermodynamic data (19). The gas phase adsorption of water vapor on clays was also extensively studied in order to determine the state of the adsorbed water (20): the entropy of adsorption was evaluated from adsorption isotherms obtained at various temperatures and from these results it was concluded that water adsorbed on the clay surface had greater randomness than water molecules in bulk liquid water (though less than in water vapour) (21).

Of interest in the technology of enhanced oil recovery is how the adsorptive properties of clays such as kaolinite may interfere with oil recovery (12). As mentioned in Chapter 2, adsorption of naphtha on clays in oil sands tailings is also an important problem. As an approach to these problems, the thermodynamics of adsorption of organic vapors on kaolinite was studied as described in this thesis. There has been a report in the literature of a study of the enthalpy of adsorption of butane and butene on kaolinite in order to probe the type of adsorption sites available, using gas-solid chromatography (22).

This report will be discussed further in the Conclusions section.

Experimental

Preparation of kaolinite for gas chromatograph column

The sodium and calcium forms of well-crystallized kaolinite were prepared as described in Chapter 3, with the exception that 1 M $CaCl_2$ was used instead of NaCl to prepare Ca-kaolinite.

The wet clay obtained from the above procedure was dried for two to three days in an oven set at 70 °C. The dry clay pellet was gently broken up with a spatula and then sieved to obtain the 50/70 mesh fraction (particle diameters between 212-300 µm). Any fine particles remaining in the 50/70 mesh fraction were removed by repeated differential settling: the clay was gently suspended in about five times its volume of cyclohexane and then left to settle for approximately thirty seconds. The cyclohexane, containing fine clay particles, was decanted and the process repeated until there were no particles visible in the decanted solvent (usually about five times). The de-fined clay was dried at room temperature overnight and then stored in a vacuum desiccator.

Preparation of packed gas chromatograph column

Columns were prepared using 0.635 cm I.D. stainless steel tubing with lengths of either 0.5 or 1.0 m. The tubing was first cleaned and passivated by sequentially washing with acetone, distilled water, concentrated nitric acid, distilled water, concentrated ammonium hydroxide, distilled water, and acetone. Once dry, one end of the column was plugged with silanized glass wool and then attached to a water aspirator. The 50/70 mesh clay was poured into the other end while the column was gently tapped. Vigorous tapping or rough handling of the kaolinite was avoided as the particles were quite fragile. Packing densities ranged from 0.438 to 0.491 g cm^{-3}. The top end of the column was then sealed with silanized glass wool, stainless steel fittings were attached, and the column installed in the gas chromatograph.

The column was conditioned by heating first at 0.2 °C min^{-1} to 82 °C and then at 0.1 °C min^{-1} to a final temperature of 120 °C, while helium was passed through the column at 50 cm^3 min^{-1}. Total conditioning time was 650 minutes.

Determination of retention times

An HP 5890A gas chromatograph with an HP 3392A integrator from Hewlett-Packard were used to obtain retention times and relative peak areas. Peaks were detected with a thermal conductivity detector. 99.995% pure helium, passed sequentially through a moisture trap and an oxygen trap, was used as the carrier gas.

Organic compounds used for adsorption measurements were purified by distillation, except for 1,3-cyclohexadiene that was used as received from Aldrich Chemical Co., and heptane (HPLC grade solvent) that was used as received from Terrochem Laboratories.

The following procedure was used to obtain data needed to determine retention volumes at very low surface coverage of the adsorbed sample. The liquid sample was drawn up into a 10 µL Hamilton syringe and then expelled, thus wetting the interior walls of the syringe. 2 μL of neon were then drawn into the syringe and injected into the column. Therefore, the actual sample that was injected was some mixture of organic vapor and neon. Neon was used as a non-adsorbed substance to determine the unretained retention time, t_M. The injections of 2 μL of neon were repeated without drawing up fresh liquid, so that with each subsequent injection the percentage of organic vapor relative to neon decreased until the organic substance was undetectible. The retention times of neon (t_M) and the sample (t_R), as well as their peak areas expressed as a percentage of total peak area, were obtained from the integrator for each injection. Retention times were measured in minutes as the times at which the apexes of the peaks appeared on the gas chromatogram, with zero time corresponding to the time of injection.

Column gas flow rates were measured with a soap bubble flow meter and a stop watch. These flow rates ranged between 15 and 40 cm^3 min^{-1} with an estimated uncertainty of ±0.1 cm^3 min^{-1}, based on the standard deviation of at least five replicate flow measurements.

A platinum resistance thermometer was used to calibrate the oven of the gas chromatograph and to measure room temperature. Estimated uncertainity of the oven temperature is ±0.1 °C, based on three measurements each made four months apart.

Inlet column pressure was measured with a pressure gauge situated at the head of the column and atmospheric (i.e. outlet) pressure was measured with a mercury barometer.

Determination of clay surface areas

The surface areas of the 50/70 mesh fractions of kaolinite were determined using an Omnisorb 360 Analyzer from Omicron Technology Corporation. Approximately 1 g samples of the clays were pretreated by heating to 70 °C for 48 h, under vacuum (23). No weight loss was detected. The surface areas were calculated with the BET equation and the isotherm for the adsorption of nitrogen.

Theory and Calculation Methods

Calculation of Retention Volumes

The net retention volume (V_N, in cm^3) for an adsorbed sample was calculated from its retention time and the retention time for non-adsorbed neon according to (24,25)

$$[4.1] \qquad V_N = (t_R - t_M)\, j\, F \left(1 - \frac{P_w}{P_o}\right) \left(\frac{T_C}{T_R}\right)$$

The column pressure-gradient correction factor, j, was calculated from (24,25)

$$[4.2] \qquad j = \left(\frac{3}{2}\right) \left[\frac{(P_i - P_o)^2 - 1}{(P_i - P_o)^3 - 1}\right]$$

in which P_i is the column inlet pressure and P_o is the column outlet pressure. In eq [4 1]. F is the outlet gas flow rate in cm^3 min^{-1}, t_R is the retention time of the sample and t_M is the retention time of an unretained compound (neon in these experiments) in minutes The terms $(1-P_w/P_o)$ and (T_C/T_R) correct the measured flow rate for the effects of the vapor pressure of the soap solution in the bubble flow meter and for the temperature difference between the column and flow meter, respectively P_w is the vapor pressure of water at the room temperature, P_o is the atmospheric pressure, T_C is the column temperature and T_R is the room temperature in Kelvin

The specific retention volume, V_g^T, is given by

$$[4\ 3] \qquad V_g^T = \frac{V_N}{W_S}$$

in which W_S is the weight of solid in the column, in grams The commonly reported specific retention volume appropriate to a flow rate measured at 273 15 K, V_g^{273}, is given by

$$[4\ 4] \qquad V_g^{273} = V_g^T \left(\frac{273.15}{T_C}\right)$$

Relation of distribution coefficient (k) for an adsorption process to gas chromatographic data

The following derivation is compiled from the approaches of various authors (24-27).

Figure 4.1 shows an adsorption isotherm for the process

[4.5] $$\text{molecule}_{(gas)} \rightarrow \text{molecule}_{(adsorbed)}$$

In the isotherm, the surface concentration of the adsorbed molecules (Γ, moles adsorbed per unit surface area) is plotted against the partial pressure of adsorbate in the gas phase (P). The region of the adsorption isotherm at very low gas phase pressures of adsorbate (i.e. at very low surface area coverage) is known as the Henry's Law region, and can be expressed as

[4.6] $$k = \lim_{P \to 0} \left(\frac{\partial \Gamma}{\partial P} \right)_{A_S,T}$$

where k is the Henry's Law constant defined for adsorption. At infinitely low partial pressures of gas phase adsorbant eq. [4.6] reduces to

[4.7] $$k = \frac{\Gamma}{P}$$

Thus, at low gas phase pressures, k is the distribution coefficient of adsorbate partitioned between the gas phase and adsorbed phase. In the specific case of adsorption in a gas chromatographic column, the distribution coefficient, k, can be expressed in terms of the ratio of number of molecules on the stationary phase to those in the mobile phase.

One way to relate the adsorption property, k, to a gas chromatographic property is to use the retention ratio R' (the prime is used to distinguish between retention ratio and the gas constant, R). In gas chromatography, the retention ratio is defined as the fraction of time spent (on average) by the adsorbate in the mobile phase. The retention ratio can also be defined as the fraction of total

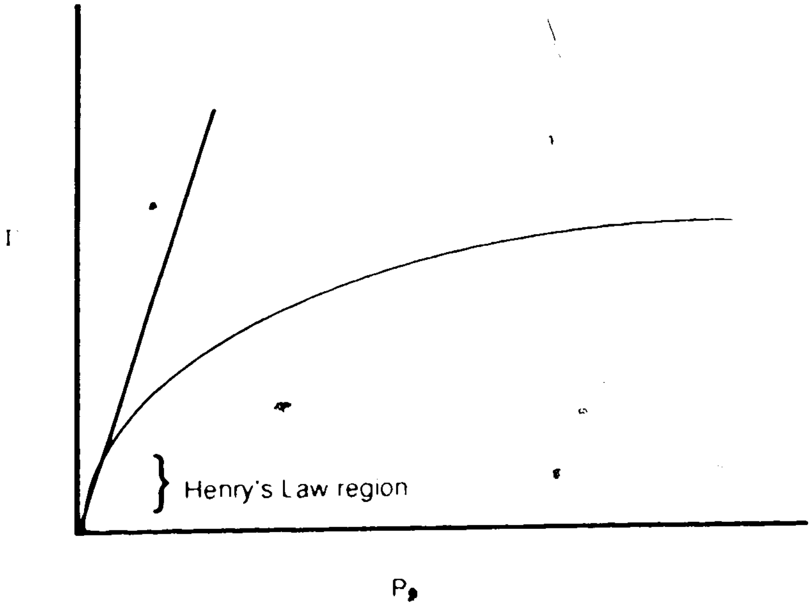

Figure 4.1. An adsorption isotherm (curved line) showing the Henry's Law region (straight line). Γ is the surface phase concentration of adsorbate in moles per unit area and P is the gas phase partial pressure of adsorbate. (adapted from reference 26).

molecules that are in the mobile phase at equilibrium. That is,

$$R' = \frac{cV_M}{cV_M + \Gamma A_s} \qquad [4.8]$$

where c is the gas phase concentration of adsorbate (mol cm^{-3}), V_M is the compressibility-corrected mobile phase hold-up (i.e. the void volume, cm^3), calculated from t_M, and A_S is the total surface area of the solid (cm^2). Combining eq. [4.7] and the ideal gas law with eq. [4.8] gives

$$R' = \frac{V_M}{V_M + k A_s R T_C} \qquad [4.9]$$

The retention ratio, as mentioned previously, can also be defined as the time that a sample molecule spends in the mobile phase relative to the total time it spends in both phases. This can be expressed as

$$R' = \frac{V_M}{V_R} \qquad [4.10]$$

where V_R is the pressure-gradient corrected elution volume for the sample, calculated from t_R. Comparing eq. [4.9] and eq. [4.10] one can see that

$$V_R = V_M + k A_s R T_C \qquad [4.11]$$

The definition of specific surface area (S, cm^2 g^{-1}) is given by

$$S = \frac{A_s}{W_s} \qquad [4.12]$$

Using eq. [4.12] and the definition of specific retention volume, which can be expressed as $V_g^T = (V_R - V_M) / W_S$, eq. [4.11] becomes

[4.13] $$k = \frac{V_g^T}{S R T_c}$$

Calculation of standard enthalpy (ΔH°), entropy (ΔS°), and Gibbs energy (ΔG°) of adsorption

From the thermodynamic relationships for an isothermal process

[4.14] $$\Delta G^\circ = - RT \ln K_{eq}$$

and

[4.15] $$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

one obtains, upon equating the above two equations and rearranging,

[4.16] $$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

For adsorption, K_{eq} refers to the process represented by eq. [4.5] and is defined as

[4.17] $$K_{eq} = \frac{(\Gamma / \Gamma^\circ)}{(P / P^\circ)}$$

where Γ° and P° represent standard states for the adsorbed phase and gas phase, respectively. Substituting this definition of K_{eq} in eq. [4.16] leads to

[4.18] $$\ln \left(\frac{\Gamma}{P}\right) = -\frac{\Delta H^\circ}{RT} + \left[\frac{\Delta \bar{S}^\circ}{R} + \ln \left(\frac{\Gamma^\circ}{P^\circ}\right) \right]$$

The term on the left hand side of eq. [4.18] is the natural logarithm of the distribution coefficient, k; therefore substituting for k from eq. [4.13] and rearranging gives

$$\text{[4.19]} \quad \ln\left(\frac{V_g^T}{T_C}\right) = -\frac{\Delta H^\circ}{R T_C} + \left[\frac{\Delta \bar{S}^\circ}{R} + \ln\left(\frac{\Gamma^\circ S R}{P^\circ}\right)\right]$$

or, using eq. [4.4]

$$\text{[4.20]} \quad \ln V_g^{273} = -\frac{\Delta H^\circ}{R T_C} + \left[\frac{\Delta \bar{S}^\circ}{R} + \ln\left(\frac{\Gamma^\circ S R\, 273.15}{P^\circ}\right)\right]$$

The specific retention volume for an adsorbed sample at "zero" surface coverage is determined at a series of temperatures and then the enthalpy of adsorption is calculated from the slope, and entropy from the intercept, of the line in a graph of ln (V_g^T / T_C) or ln V_g^{273} against $1/T_C$. The value of R used in the round brackets of eqs. [4.19] and [4.20] is 83.14 cm^3 bar K^{-1} mol^{-1} and areas are in cm^2 to agree with units of cm^3 used for retention volumes and bar for pressure. ΔG° is calculated using eq. [4.15].

The enthalpy calculated here is based on the assumption that it is independent of temperature, which means that the heat capacity of adsorption (ΔC_p°) is taken to be zero. As will be shown in Chapter 5, this is not the case for some examples.

The enthalpy of adsorption calculated using eq. [4.19] or [4.20] is a differential enthalpy, sometime called the isosteric enthalpy or heat of adsorption (q_{st})[1]. Thus, $\Delta \bar{S}^\circ$ calculated from the intercept of the above line is

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[1] q_{st} in eq. [4.19] and eq. [4.20] was obtained in reference to a standard state that is defined in terms of a fixed surface concentration (Γ°). This heat of adsorption is analagous to the value obtained from the Clausius-Clapeyron equation describing the adsorption process

also a differential quantity[1]. To investigate models of adsorption one can compare experimental entropy values with those predicted from statistical mechanical calculations; however, the experimental entropy value that is equivalent to that of the usual statistical mechanical calculation is the total or integral entropy ($\Delta S°$) because it is the total entropy that is related to the total number of possible quantum states (1). Therefore $\Delta S°$ is calculated from $\Delta\bar{S}°$ using the relationship (3)

$$[4.22] \qquad \Delta S° = \Delta\bar{S}° + R$$

Standard states for adsorption

The enthalpy of adsorption does not depend on the choice of standard states for the adsorbate, but the entropy and Gibbs energy of adsorption do depend on this choice. The choice of a standard state is generally predicated on what is the most meaningful with respect to some theory or the most convenient for calculation. For the gas phase the usual choice has been that of the ideal gas at one bar and the temperature of interest, and this is what has been used in this study. However, the selection of the most meaningful or

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[1] continued from p.123

$$[4.21] \qquad \left(\frac{\partial \ln P}{\partial T}\right)_{T,\Gamma} = -\frac{q_{st}}{RT^2}$$

in which the surface concentration is kept constant (27,28).

[1] $\Delta\bar{S}° = \bar{S}^s - S^{o,g}$ where $\bar{S}^s$, the partial molar surface phase entropy, is defined as $(\partial S^s / \partial n^s)_{T,A}$, and $S^{o,g}$ is the gas phase entropy (31).

useful standard state for the two dimensional adsorbed phase is not so straightforward. Three of the more commonly used standard states are those of DeBoer and Kruyer (29), Kendall and Rideal (30), and that of half surface coverage (4).

DeBoer and Kruyer (29) chose a standard surface state in which the average distance between adsorbed molecules is the same as that between molecules in the gas phase at 1 bar (originally 1 atm) and 273.15 K. This distance is 3.3535 $\times10^{-7}$ cm or, on the surface, the area per molecule is 1.1246 $\times10^{-13}$ cm^2. The equation of state for a two dimensional surface phase equivalent to the ideal gas law is given by

[4.23] $\Pi A = n R T$

where Π is the two dimensional pressure with units of force per unit length and A is the area per mole covered by the adsorbed phase (31). From this equation the area per mole is directly proportional to temperature so the standard surface area per mole of adsorbed sample (A°) at any given temperature, is

[4.24] $A^\circ = A\,(T/273.15)$

where $A = N \times 1.1246 \times10^{-13}$. As $\Gamma = 1/A$, the DeBoer/Kruyer standard surface phase concentration (Γ°) equals $4.0333 \times10^{-9}\ T^{-1}$ mol K cm^{-2}.

Kemball and Rideal (30) defined a surface thickness for the adsorbed phase and thus converted a two dimensional pressure to a three dimensional pressure and took the standard state as 1 bar (originally 1 atm). From the ideal gas law, the volume per molecule is 3.721×10^{-20} cm^3 at 273.15 K and 1 bar, or, at any temperature T, 1.363×10^{-22} T cm^3 K^{-1}. Kemball and Rideal arbitrarilly chose a thickness for the adsorbed layer of 0.6 nm. Using this value, the area per molecule is 2.271×10^{-15} T cm^2 K^{-1} and thus the Kemball/Rideal standard surface phase concentration (Γ°) equals 7.216×10^{-10} T^{-1} mol K cm^{-2}.

For some calculations it is convenient to define the standard surface state as that of one half surface coverage, that is, $\theta^\circ = 1/2$ where θ is the fraction surface coverage (10,32). This can be expressed as

$$[4.25] \qquad \theta^\circ = n^\circ/n_m = 1/2$$

where n° is the standard state number of moles adsorbed and n_m is the number of moles that form a monolayer of area A_m. Thus

$$[4.26] \qquad \Gamma^\circ = n^\circ/A_m$$

A_m is calculated from

$$[4.27] \qquad A_m = \sigma_m \, n_m \, N$$

where σ_m is the area occupied by one molecule and is given by (33,34)

$$[4.28] \qquad \sigma_m = 1.091 \left(\frac{M}{N\rho}\right)^{2/3}$$

in which M is the molar mass and ρ the density of the adsorbed substance in the liquid state at the temperature of the adsorption measurement. Thus

$$[4.29] \qquad \Gamma^\circ = 1/(2\,\sigma_m N) \quad \text{mol cm}^{-2}.$$

for the half surface coverage standard state.

In summary, the value of $\Gamma°$ used in equations [4.19] and [4.20] to calculate the entropy of adsorption (and thus the Gibbs energy of adsorption) was selected from one of:

(1) $\Gamma° = 4.033 \times 10^{-9}\ T^{-1}$ mol K cm^{-2} (deBoer and Kruyer)

where T is the average temperature of the study;

(2) $\Gamma° = 7.216 \times 10^{-10}\ T^{-1}$ mol K cm^{-2} (Kemball and Rideal)

where T is the average temperature of the study;

(3) $\Gamma° = 1/(2\ \sigma_m N)$ mol cm^{-2} (1/2 surface coverage)

Results and Discussion

Determination of specific retention volumes at zero surface coverage

Examples of gas chromatograms for a compound with a short retention time (pentane) and a compound with a long retention time (benzene), obtained in this study, are given in Figure 4.2. The retention times obtained from these chromatograms were used to calculate specific retention volumes by way of equations [4.3] and [4.4] as outlined in the Calculation Methods section.

Retention data were obtained for the adsorption of pentane, hexane, heptane, octane, cyclohexane, cyclohexene, 1,3-cyclohexadiene, and benzene on a Na-kaolinite column at a series of temperatures, and, in some cases, a series of carrier gas flow rates.

The data in Table 4.1 are provided to illustrate how the retention

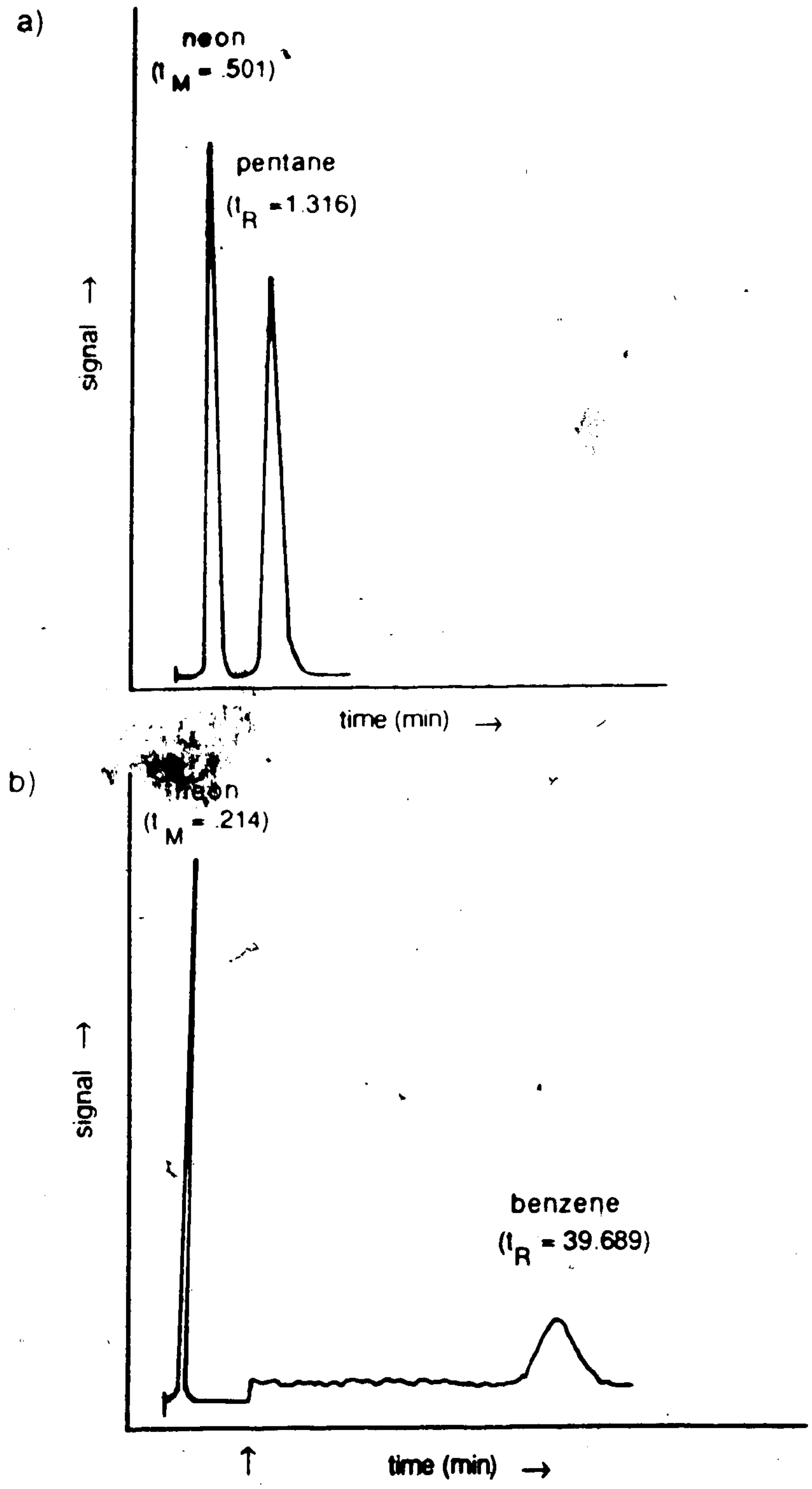

Figure 4.2. Chromatograms showing elution peaks following the injection of 2 µL of a neon/sample mix on a Na-kaolinite column at 70 °C. **a)** Pentane elution: column gas flow rate = 12.8 cm^3 min^{-1}; chart speed = 1.0 cm min^{-1}. **b)** Benzene elution: column gas flow rate = 31.6 cm^3 min^{-1}; chart speeds = 1.0 cm min^{-1} up to arrow, 0.10 cm min^{-1} after arrow. Signal magnified x32 after arrow.

Table 4.1. Values of percent pentane and corresponding retention volumes (V_g^{273}) for the adsorption of pentane on Na-kaolinite at 70 °C

Percent Pentane	Retention Volume ($cm^3 g^{-1}$)
99.31	0.740
98.79	0.862
98.18	0.917
91.37	0.975
72.78	0.991
50.79	0.998
44.02	1.001
42.42	1.000
41.19	0.998
20.88	1.000
14.34	1.003
13.69	1.001
5.00	1.005
4.45	1.003
2.89	1.003
2.05	1.003
1.85	1.042
1.68	1.005
1.31	1.014
0.81	1.005
0.70	1.001
0.19	0.991

volumes at (nearly) zero surface coverage were obtained. In this example the specific retention volumes, V_g^{273}, of pentane eluting from a Na-kaolinite column at 70°C are given[1]. The percent pentane reported in the table is the fraction of the pentane peak relative to the sum of the areas of the neon peak and the pentane peak, as determined by the integrator. These data were then graphed in order to extrapolate to zero percent pentane, as shown in Figure 4.3. A straight line was drawn through the points in the linear portion of the graph and extrapolated to zero percent pentane to obtain the value of the retention volume (V_g^{273}) that was used in the calculation of thermodynamic values (Figures 4.3 and 4.4).

The above procedure was used to obtain the zero percent retention volumes for hexane (Figure 4.5). Due to the limited linear portion of the data, a second degree polynomial was fitted to the data for heptane (except for data obtained at 80-100 °C, for which a third order polynomial least squares analysis gave the best fit), octane, and cyclohexane, and extrapolated to zero percent sample to obtain the desired retention volumes (Figures 4.6-4.8). For cyclohexene, a straight line was drawn through data points at low percentage cyclohexene and extrapolated to zero percent (Figure 4.9). A second or third order polynomial was fitted to the data at low percent sample concentration of

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[1] The temperatures that are given in the text, tables, and figures, are, for simplicity, those of the set values of the gas chromatograph. The actual values, as measured with a platinum resistance thermometer, that were used in all calculations, are given in Table 4.2.

Table 4.2. Calibration of gas chromatgraph oven

Set Temperature (°C)	Actual Temperature (°C)
30.00	29.69
35.00	34.76
40.00	39.76
45.00	44.79
50.00	49.81
5[illegible].00	54.81
60.00	59.83
65.00	64.90
70.00	69.91
75.00	74.89
80.00	79.89
85.00	84.90
90.00	89.91
95.00	94.95
100.00	99.97
105.00	104.98

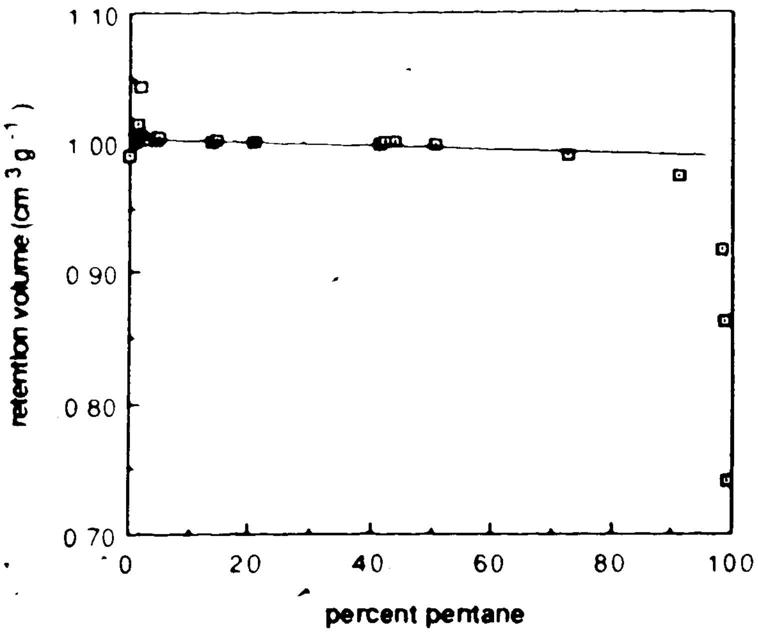
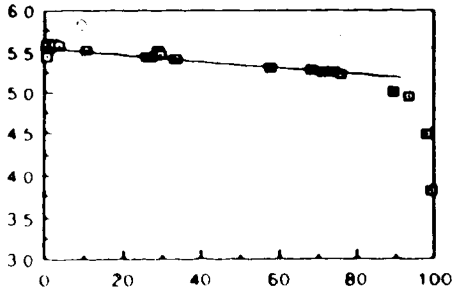
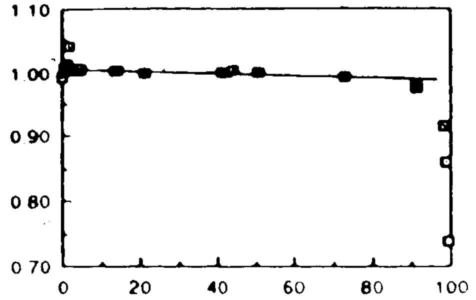


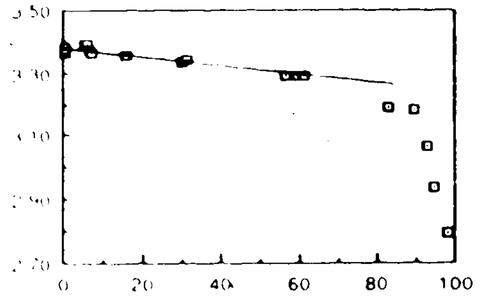
Figure 4.3. Graph of retention volume (V_g^{273}) against percent pentane showing the extrapolation to zero percent pentane, for the elution of pentane from a Na-kaolinite column at 70 °C.



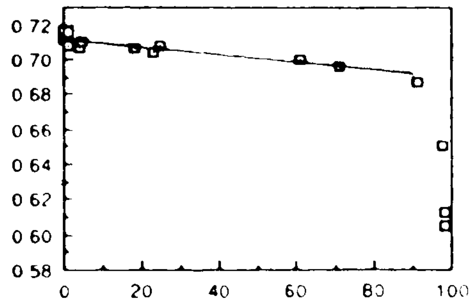
a) column temperature = 30 °C



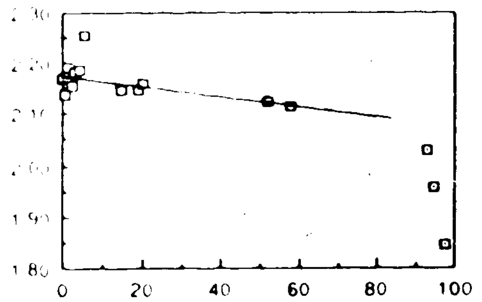
e) column temperature = 70 °C



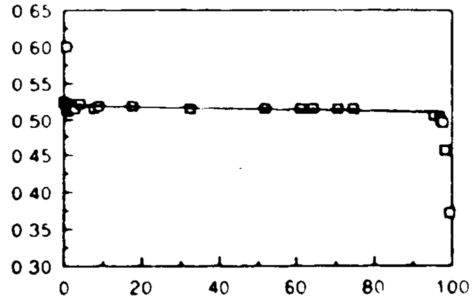
b) column temperature = 40 °C



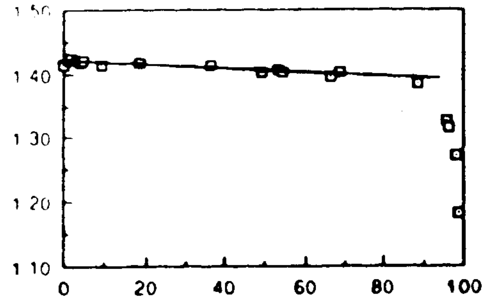
f) column temperature = 80 °C



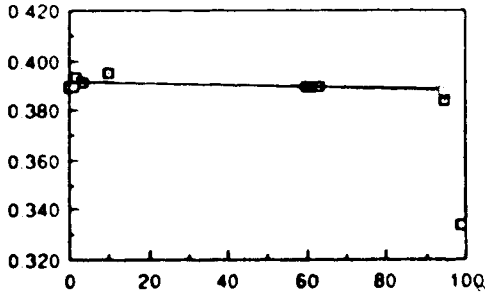
c) column temperature = 50 °C



g) column temperature = 90 °C

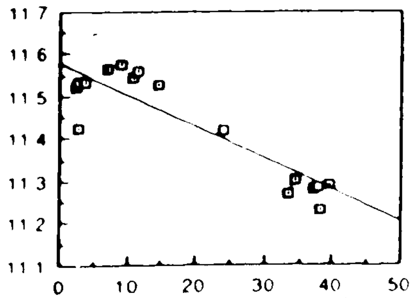


d) column temperature = 60 °C

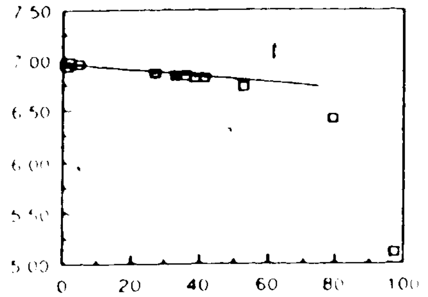


h) column temperature = 100 °C

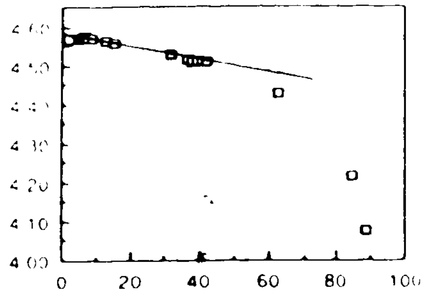
Figure 4.4. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent pentane (x-axes) showing the extrapolation to zero percent for column temperatures from 30-100 °C, for the elution of pentane from a Na- kaolinite column.



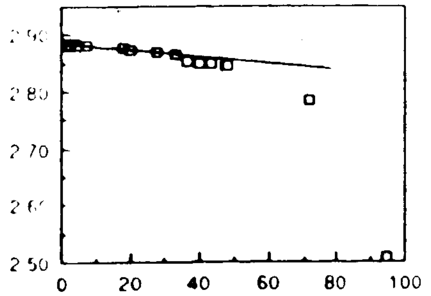
a) column temperature = 40 °C



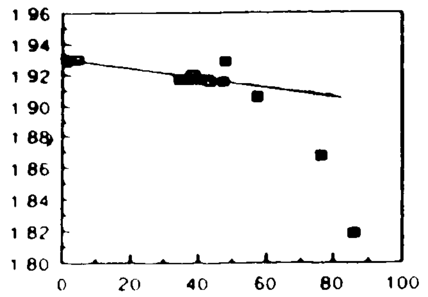
b) column temperature - 50 °C



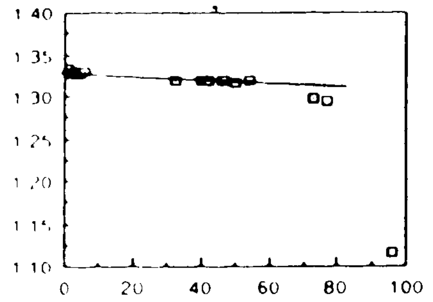
[illegible]) column temperature = 60 °C



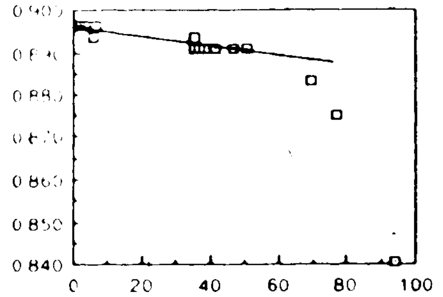
d) column temperature = 70 °C



e) column temperature = 80 °C

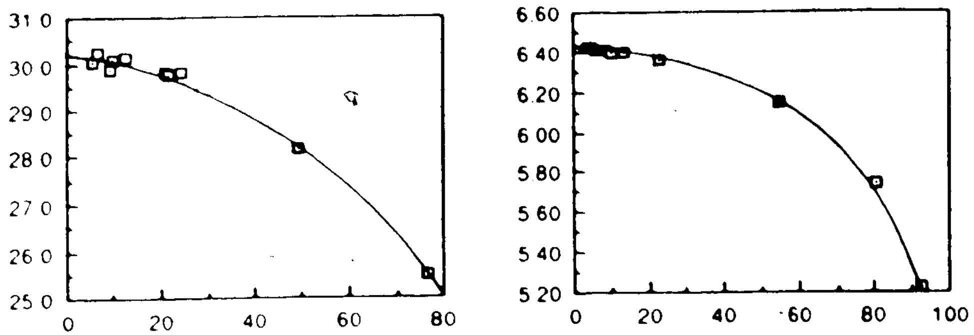


f) column temperature = 90 °C



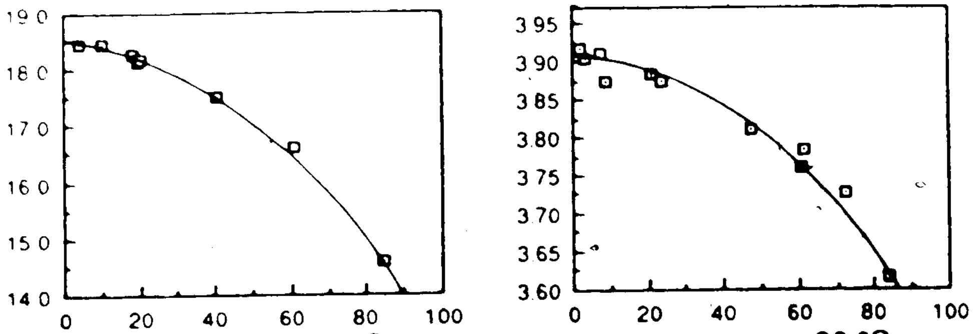
g) column temperature = 100 °C

Figure 4.5. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent hexane (x-axes) showing the extrapolation to zero percent for column temperatures from 40-100 °C, for the elution of hexane from a Na-kaolinite column.



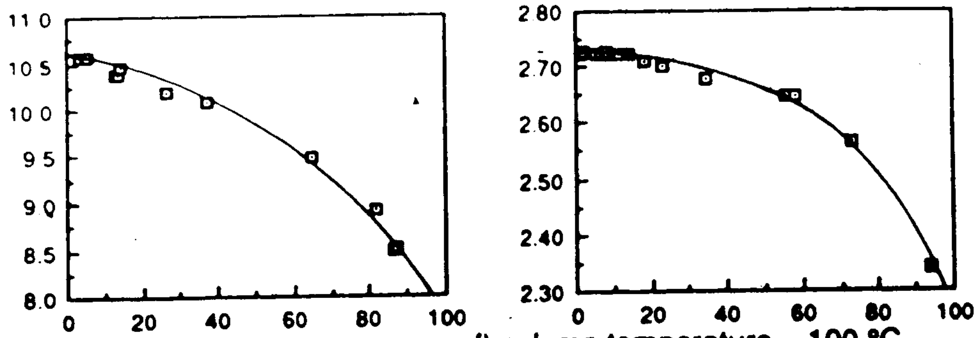
a) column temperature = 50 °C

d) column temperature = 80 °C



b) column temperature = 60 °C

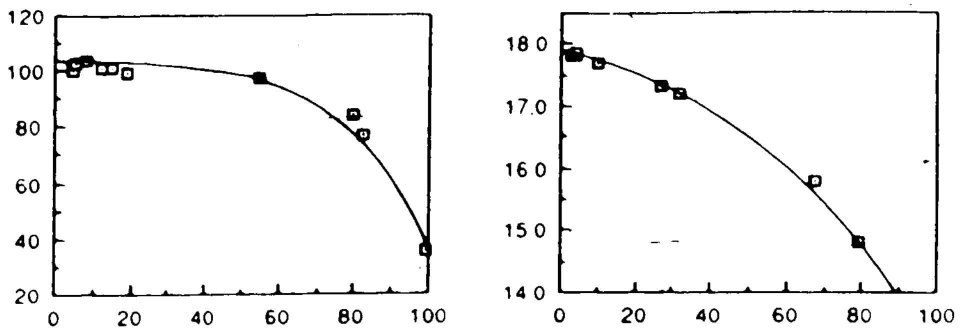
e) column temperature = 90 °C



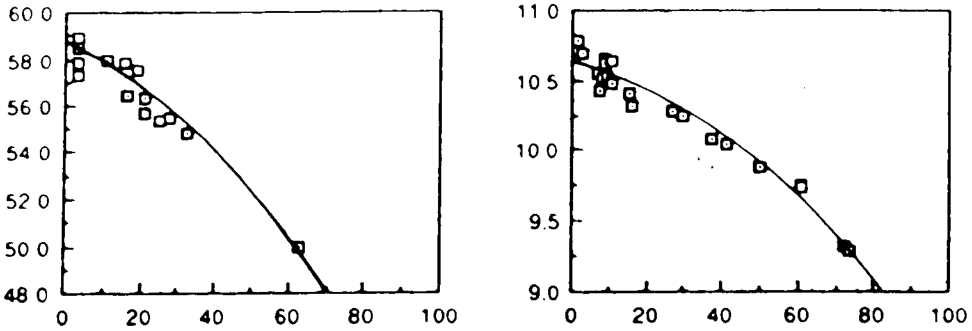
c) column temperature = 70 °C

f) column temperature = 100 °C

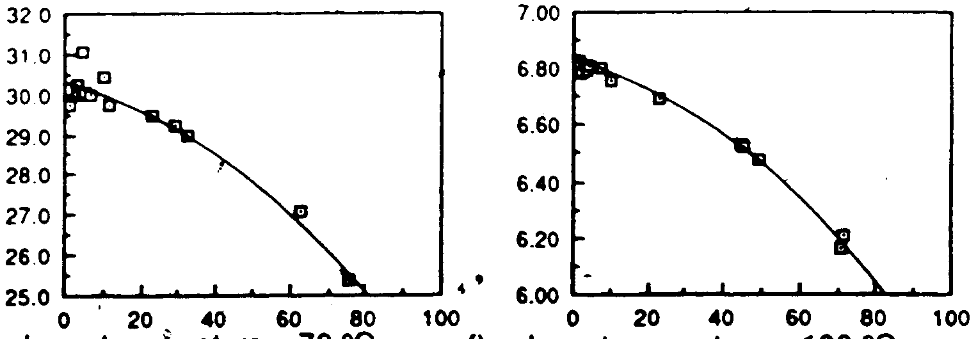
Figure 4.6. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent heptane (x-axes) showing the extrapolation to zero percent for column temperatures from 50-100 °C, for the elution of heptane from a Na-kaolinite column.



a) column temperature = 50 °C d) column temperature = 80 °C

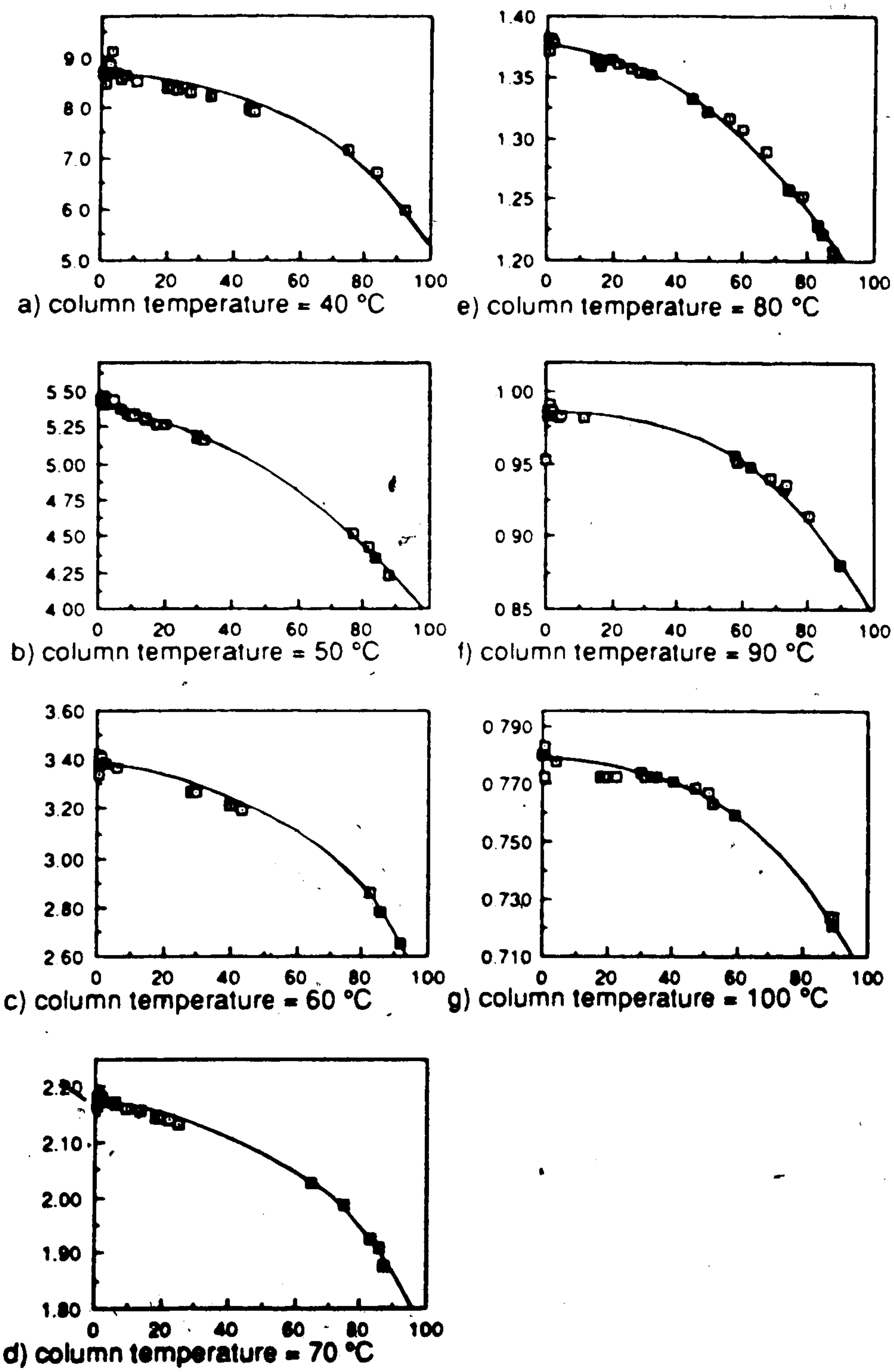


b) column temperature = 60 °C e) column temperature = 90 °C



c) column temperature = 70 °C f) column temperature = 100 °C

Figure 4.7. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent octane (x-axes) showing the extrapolation to zero percent for column temperatures from 50-100 °C, for the elution of octane from a Na-kaolinite column.



a) column temperature = 40 °C

e) column temperature = 80 °C

b) column temperature = 50 °C

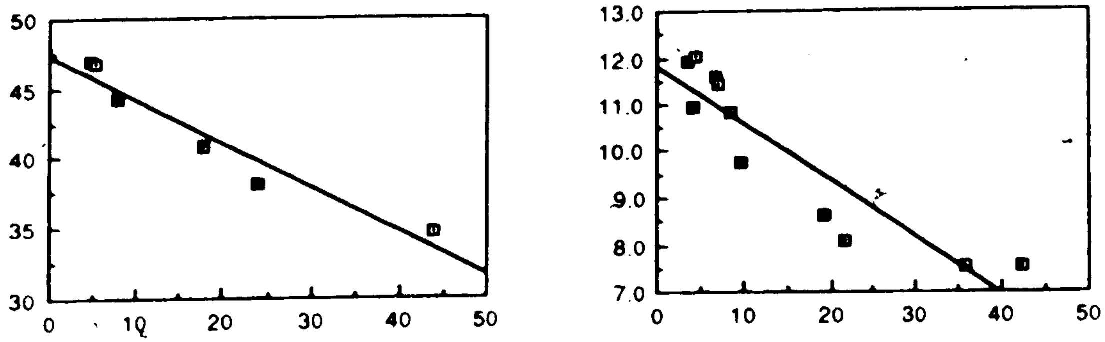
f) column temperature = 90 °C

c) column temperature = 60 °C

g) column temperature = 100 °C

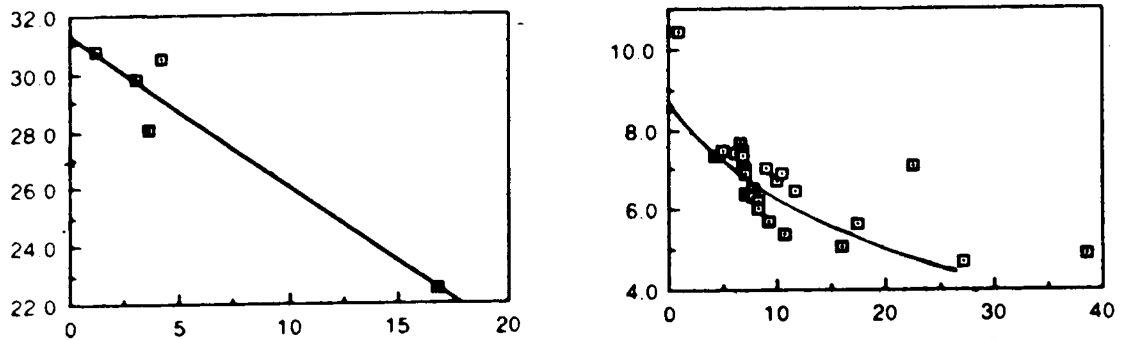
d) column temperature = 70 °C

Figure 4.8. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent cyclohexane (x-axes) showing the extrapolation to zero percent for column temperatures from 40-100 °C, for the elution of cyclohexane from a Na-kaolinite column.



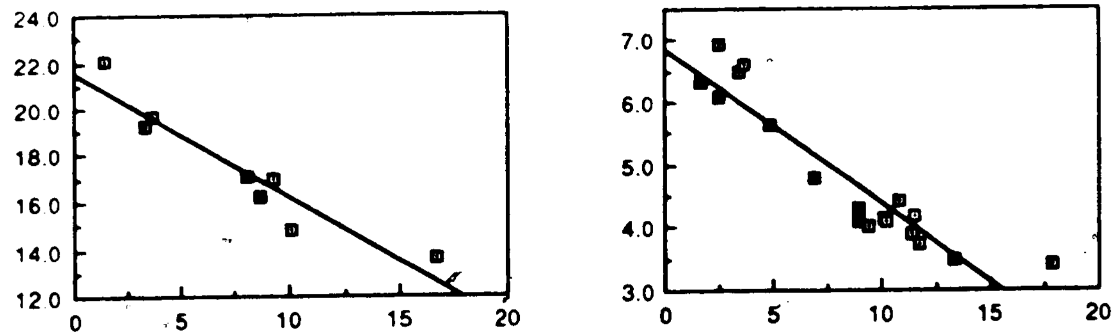
a) column temperature = 50 °C

d) column temperature = 80 °C



b) column temperature = 50 °C

e) column temperature = 90 °C



c) column temperature = 70 °C

f) column temperature = 100 °C

Figure 4.9. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent cyclohexene (x-axes) showing the extrapolation to zero percent for column temperatures from 50-100 °C, for the elution of cyclohexene from a Na-kaolinite column.

1,3-cyclohexadiene and benzene where it was justified by the availability of data, as shown in Figures 4.10 and 4.11; otherwise, a straight line was drawn through the data and extrapolated to zero percent to obtain the retention volumes.

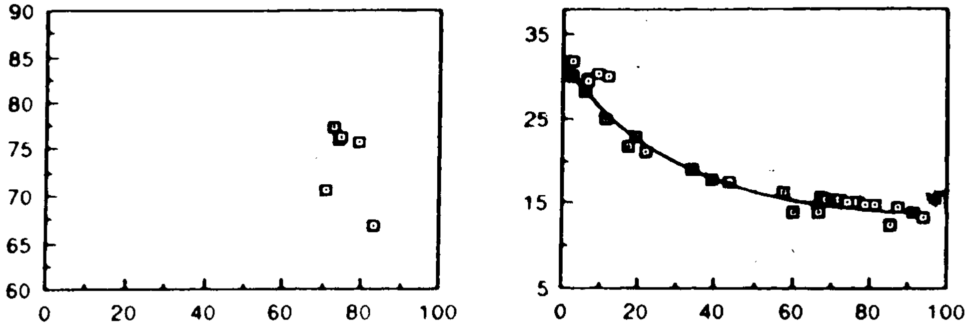
The values of zero percent specific retention volumes as a function of temperature and, for selected compounds, carrier gas flow rate, are given in Tables 4.3-4.10.

It is shown in Figures 4.4-4.11 that it was most difficult to obtain retention data at low sample concentrations when the temperature was low, for compounds with long retention times, such as cyclohexene, 1,3-cyclohexadiene, and benzene. This was due to greater band spreading with the longer retention times of these compounds, and hence a decrease in signal intensity from the TCD. Therefore, there is a greater uncertainty in the retention volumes extrapolated to zero percent and hence in the calculated thermodynamic properties for these compounds.

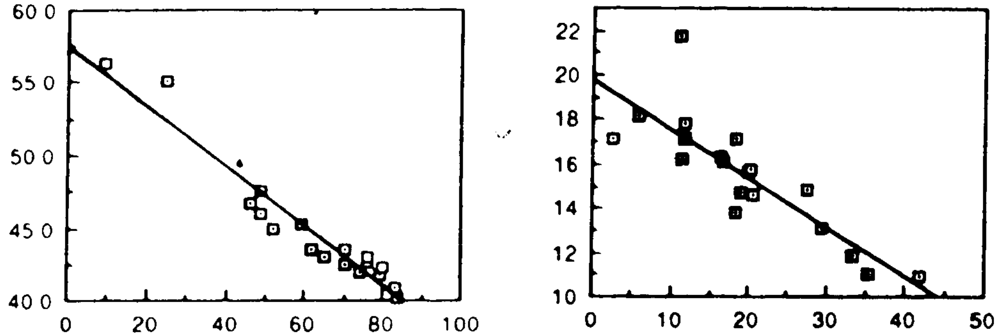
Calculation of thermodynamic properties

There are two criteria that must be met for the validity of thermodynamic calculations for adsorption at very low surface coverage: the measurements must be carried out in the Henry's Law region of the adsorption isotherm (35,36) and the adsorption/desorption process occurring in the column must be at equilibrium (36,37).

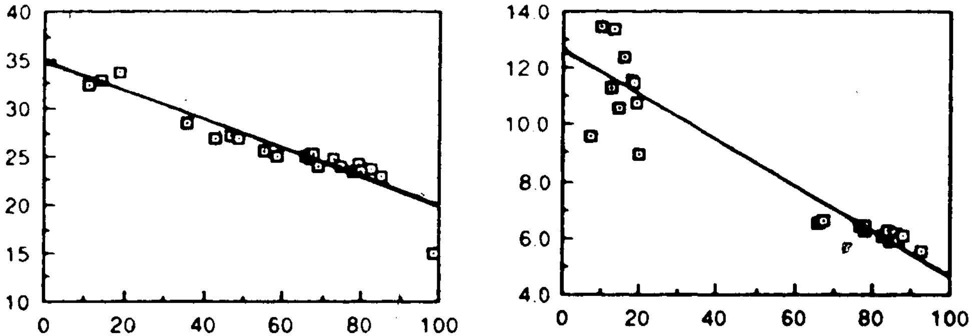
Criteria used for establishing if one is in the Henry's law region are (i) the peaks should be symmetrical (36) (or only slightly asymmetrical (26)) and



a) column temperature = 50 °C d) column temperature = 80 °C

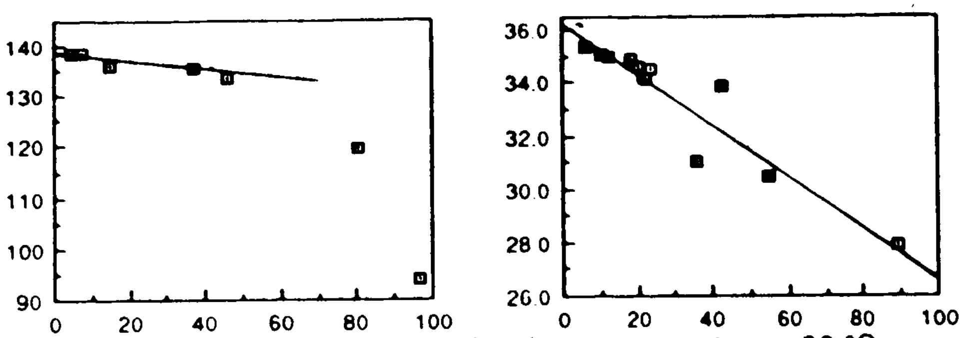


b) column temperature = 60 °C e) column temperature = 90 °C

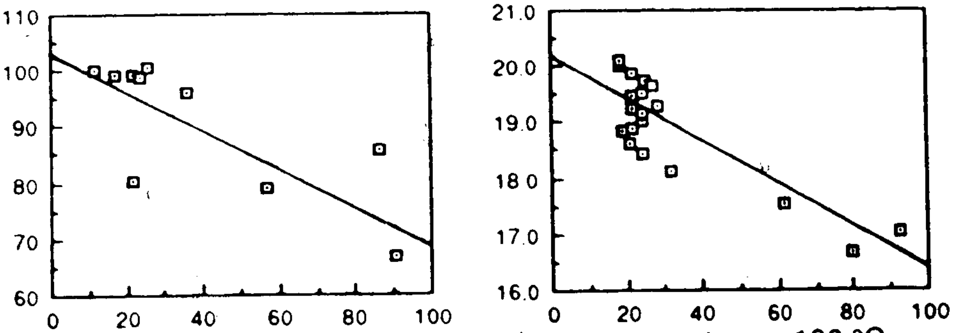


c) column temperature = 70 °C f) column temperature = 100 °C

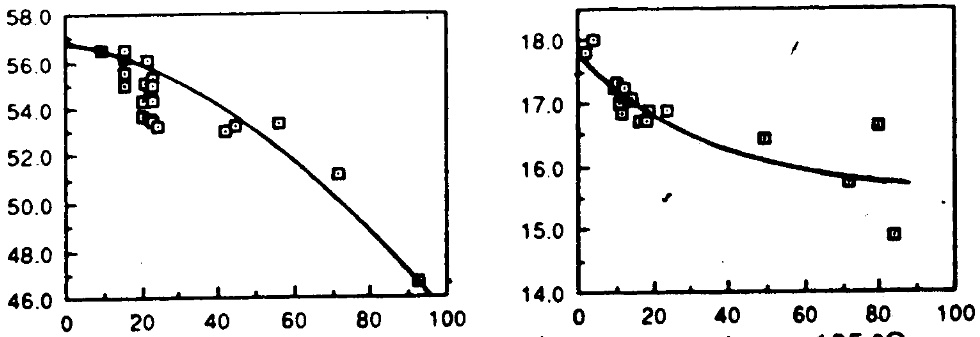
Figure 4.10. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent 1,3-cyclohexadiene (x-axes) showing the extrapolation to zero percent for column temperatures from 50-100 °C, for the elution of 1,3- cyclohexadiene from a Na-kaolinite column.



a) column temperature = 65 °C d) column temperature = 90 °C



b) column temperature = 70 °C d) column temperature = 100 °C



c) column temperature = 80 °C f) column temperature = 105 °C

Figure 4.11. Graphs of retention volume (V_g^{273} (cm^3 g^{-1}), y-axes) against percent benzene (x-axes) showing the extrapolation to zero percent for column temperatures from 65-105 °C, for the elution of benzene from a Na-kaolinite column.

Table 4.3. Zero surface coverage specific retention volumes (V_g^{273}) for pentane on Na-kaolinite as a function of temperature and carrier gas flow rate

Temperature (°C)	Flow Rate ($cm^3\ min^{-1}$)	Retention Volume[1] ($cm^3\ g^{-1}$)
30.0	16.3	5.70
	21.0	5.52
	22.7	6.65
40.0	17.5	4.11
	20.9	3.37
	22.6	3.84
50.0	17.6	2.58
	20.9	2.17
	22.6	2.41
60.0	12.8	1.54
	20.9	1.42
	22.7	1.58
70.0	12.8	1.06
	18.5	1.01
	22.9	1.08
80.0	12.8	0.76
	20.9	0.71
	22.6	0.75
90.0	15.0	0.57
	18.5	0.52
	22.7	0.55
100.0	20.9	0.39
	22.4	0.41

---

[1] Estimated uncertainties are ± 0.03 $cm^3\ g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.4. Zero surface coverage specific retention volumes (V_g^{273}) for hexane on Na-kaolinite as a function of temperature and carrier gas flow rate

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
40.0	26.7	12.85
	30.2	11.98
	33.5	11.58
50.0	24.1	7.74
	25.5	7.49
	29.9	7.46
60.0	24.8	4.56
	29.2	4.66
	30.3	4.59
70.0	24.3	2.88
	25.8	2.93
	29.2	2.94
80.0	24.4	1.95
	26.5	1.93
	29.3	1.90
90.0	25.9	1.33
	26.9	1.36
	29.5	1.32
100.0	19.0	1.04
	24.1	0.97
	34.1	0.90

---

[1] Estimated uncertainties are ± 0.07 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.5. Zero surface coverage specific retention volumes (V_g^{273}) for heptane on Na-kaolinite as a function of temperature and carrier gas flow rate

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
50.0	22.0	30.1
	30.5	29.5
60.0	20.5	18.4
	26.7	16.3
70.0	25.1	10.53
	29.1	9.40
80.0	25.1	6.41
	29.7	5.75
90.0	22.0	3.90
	27.5	3.74
100.0	25.1	2.72
	26.5	2.47

---

[1] Estimated uncertainties are ± 0.3 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.6. Zero surface coverage specific retention volumes (V_g^{273}) for octane on Na-kaolinite as a function of temperature

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
50.0	33.1	101.2
60.0	31.7	58.5
70.0	33.1	37.9
80.0	31.7	17.8
90.0	30.5	10.7
100.0	30.5	6.8

[1] Estimated uncertainties are ± 0.5 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.7 Zero surface coverage specific retention volumes (V_g^{273}) for cyclohexane on Na-kaolinite as a function of temperature and carrier gas flow rate

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
40.0	26.1	8.71
	28.9	8.45
50.0	[illegible]	5.44
	30.0	5.02
60.0	23.8	3.39
	29.0	3.09
70.0	22.5	2.18
	28.8	2.03
80.0	29.3	1.36
	31.3	1.38
90.0	25.9	0.98
	29.3	0.95
100.0	20.2	0.79
	29.5	0.70

---

[1] Estimated uncertainties are ± 0.04 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.8. Zero surface coverage specific retention volumes (V_g^{273}) for cyclohexene on Na-kaolinite as a function of temperature

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
50.0	36.9	47.3
60.0	33.9	31.3
70.0	37.2	21.5
80.0	37.2	11.8
90.0	37.3	8.9
100.0	37.6	6.9

[1] Estimated uncertainties are ± 1.2 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

Table 4.9. Zero surface coverage specific retention volumes (V_g^{273}) for 1,3-cyclohexadiene on Na-kaolinite as a function of temperature

Temperature (°C)	Flow Rate ($cm^3 min^{-1}$)	Retention Volume[1] ($cm^3 g^{-1}$)
50.0	35.8	--------[2]
60.0	35.1	57.6
70.0	34.3	34.9
80.0	33.9	31.6
90.0	36.6	19.9
100.0	30.5	12.4

[1] Estimated uncertainties are ±1.0 $cm^3 g^{-1}$ at higher temperatures, but are much larger at low temperatures.

[2] Insufficient data for extrapolation.

Table 4.10. Zero surface coverage specific retention volumes (V_g^{273}) for benzene on Na-kaolinite as a function of temperature

Temperature (°C)	Flow Rate ($cm^3\ min^{-1}$)	Retention Volume[1] ($cm^3\ g^{-1}$)
65.0	26.3	138
70.0	32.2	103
80.0	29.8	55.8
90.0	32.5	35.6
100.0	31.4	20.1
105.0	31.7	17.4

[1] Estimated uncertainties are ± 2 $cm^3\ g^{-1}$ at higher temperatures, but are much larger at low temperatures.

(ii) the retention times should reach a constant value that is independent of sample size (38). Most peaks obtained were symmetrical, as shown in Figure 4.2, although minor tailing was observed for compounds with long retention times, such as 1,3-cyclohexadiene and benzene. Figures 4.3-4.11 show that, most retention volumes (and hence retention times) reached a constant value. An exception is the adsorption of cyclohexene (Figure 4.9) which showed evidence that the Henry's Law region had not been reached.

If the adsorption process is at equilibrium the calculated retention volume should be constant with respect to changes in carrier gas flow rate (36,37). If the system is not at equilibrium, the retention volume will increase with a decrease in flow rate. This was studied for pentane, hexane, heptane, and cyclohexane. The data in Tables 4.3 and 4.4 show that, within the estimated uncertainties of the retention volumes, pentane and hexane were at equilibrium. However, for heptane and cyclohexane, retention volumes did increase with decreasing flow rate at the lower temperatures, so it is likely that retention volumes were underestimated at these temperatures. By extension, this may be true for the other compounds with large retention volumes.

In order to obtain adsorption data in the Henry's Law region it was necessary to use high carrier gas flow rates for compounds with long retention times in order to limit band spreading, so that the peaks from injections of low concentrations of sample would not fall below the detection limits of the TCD. As it was, octane, 1,3-cyclohexadiene, and benzene were marginally in the Henry's Law region while cyclohexene was not. However, as has been seen, at these necessarily high carrier gas velocities, the equilibration of the adsorption process for compounds other than pentane and hexane was limited by the kinetics of adsorption. Therefore, in cases where the adsorption process was not at equilibrium, the differences in the experimental, extrapolated retention volumes, and those that would be expected at equilibrium, shift the slope of the linear fit of eq. [4.20] from the expected value to a smaller value, and hence calculated enthalpies would be less negative than they should be.

Calculation of the standard enthalpy of adsorption (ΔH°)

Equation [4.20] was fitted to data from Tables 4.4-4.10, as well as other data not shown, and the slopes and the intercepts determined by a linear least squares analysis. Examples of graphs showing this fit are given in Figure 4.12. Enthalpies calculated from the slopes of these graphs are given in Table 4.11.

The enthalpies of adsorption are all consistent with physical adsorption: there are no values more exothermic than -60 kJ mol^{-1}, whereas chemical adsorption processes usually have enthalpies of adsorption more negative than -80 kJ mol^{-1} (31).

The enthalpies of adsorption of the alkanes show an approximate linear relation with carbon number (graph not shown) as is seen, for example, in the gas-liquid chromatography of organic compounds in which the log retention time changes linearly with carbon number for an homologous series (38,39).

In the series of six carbon cyclic compounds, increasing the number of double bonds has only a small effect on the value of the enthalpy of adsorption except for benzene for which the enthalpy of adsorption is significantly more

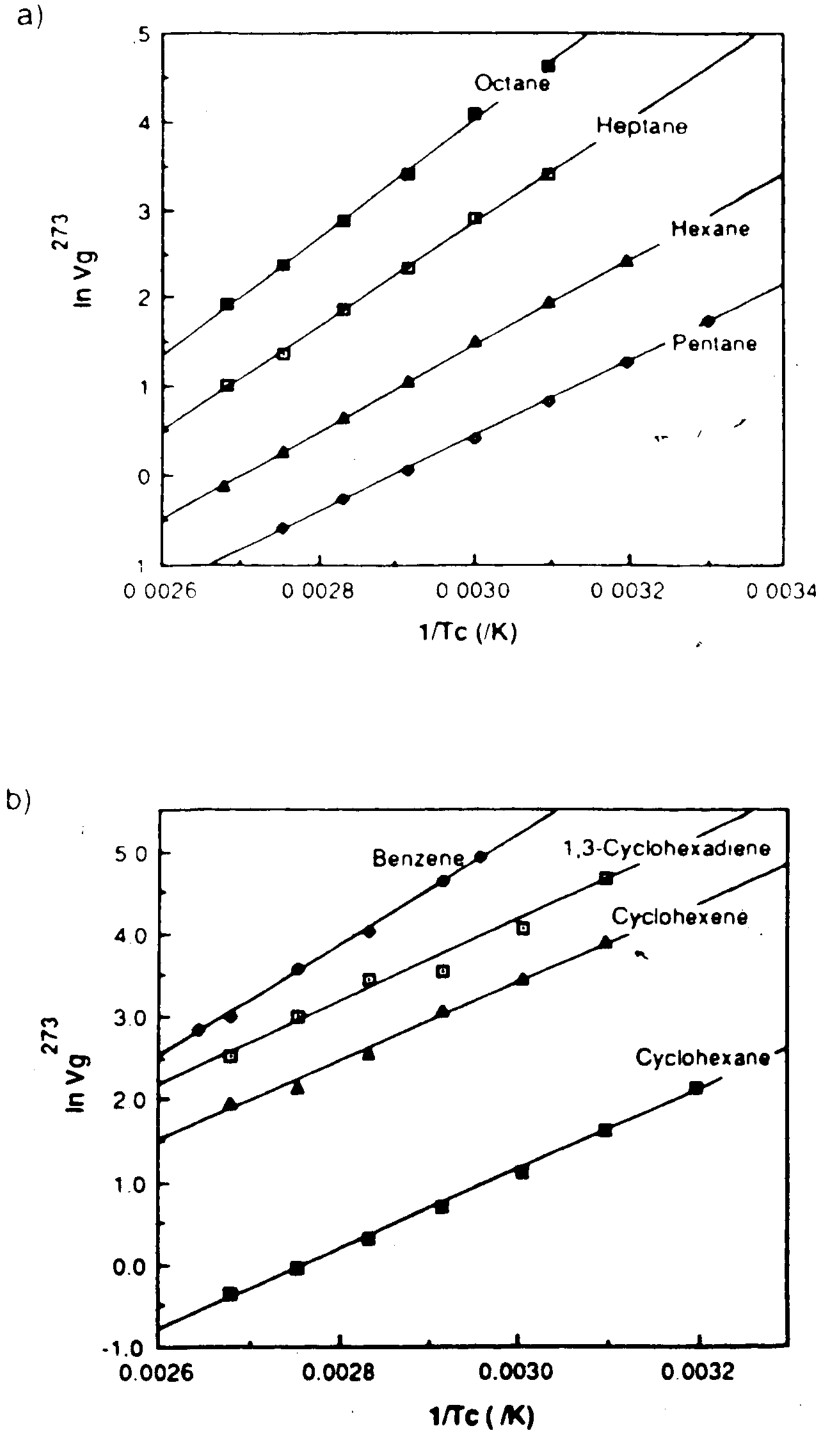


Figure 4.12. Graphs of ln V_g^{273} against $1/T_c$ (K^{-1}) for the adsorption of organic vapours on Na-kaolinite, showing the straight lines obtained from a least squares fit of eq. [4.20]. a) alkanes; b) cyclic compounds.

Table 4.11. Enthalpies (ΔH°) of adsorption of organic vapours on Na-kaolinite

Compound	Temperature Range (°C)	- ΔH° [1] (kJ mol^{-1})
pentane (5)	30 -100	36.3 ± 0.8
hexane (4)	40 - 100	41.5 ± 0.5
heptane (2)	50 - 100	49.3 ± 0.4
octane	50 - 100	54.6 ± 0.8
cyclohexane (3)	40 - 105	38.9 ± 1.0
cyclohexene	50 - 100	40.1 ± 1.7
1,3 - cyclohexadiene	50 - 100	40.2 ± 3.1
benzene (2)	65 - 105	53.4 ± 3.1

[1] The reported values are the mean ± standard deviations for replicate studies (the numbers in brackets indicates the number of replicates). Where there is no figure in brackets, only one study was done and the ± error is based on the standard error of the slope of the graph from which the enthalpy was calculated.

exothermic than for the non-aromatic cyclic compounds.

Calculation of the standard entropy of adsorption (ΔS°)

The differential entropies of adsorption were calculated from the intercepts of a least squares fit of retention data using eq. [4.20], and the integral entropies of adsorption were calculated using eq [4.21]. The specific surface area (S) used in this calculation was $6.2_6 \times 10^4$ cm^2 g^{-1}. The values of the integral entropies of adsorption for the Kemball-Rideal (K-R) and the deBoer and Kruyer (D-K) standard states are given in Table 4.12.

Comparison of experimental entropy values with the values obtained from statistical mechanical calculations can provide information about the mobilities of the adsorbed molecules on the clay surface. There may be non-localized (or mobile) adsorption in which the adsorbate molecules are completely free to move around on the surface, or there may be localized adsorption in which the adsorbed molecules are constrained to adsorption sites on the surface.

In mobile adsorption the entropy change upon adsorption is equivalent to the loss of one degree of translational freedom, perpendicular to the clay surface (4). This value can be calculated from the Sackur-Tetrode equation

$$[4.30] \qquad {}_3S^{o}_{trans} = R \ln \left(M^{3/2} T^{5/2} \right) - 9.669 \qquad \text{J K}^{-1} \text{ mol}^{-1}$$

(in which M is the molar mass and T the average temperature of the study), and the equation for the translational entropy of a two-dimensional gas as derived by Kemball (40).

Table 4.12. Experimental and theoretical entropies (ΔS°) of adsorption of organic compounds on Na-kaolinite referred to two different standard states, Kemball-Rideal (K-R) and deBoer-Kruyer (D-K). Mobile adsorption model.

Compound	- ΔS° (J K^{-1} mol^{-1})			
	Experimental[1]		Theoretical	
	K-R	D-K	K-R	D-K
pentane (5)	48.8 ± 2.1	63.1 ± 2.1	37.23	51.54
hexane (4)	55.3 ± 1.2	69.7 ± 1.2	38.03	52.34
heptane (2)	67.8 ± 1.6	82.2 ± 1.6	38.73	53.03
octane	74.0 ± 2.1	88.3 ± 2.0	39.27	53.57
cyclohexane (3)	50.6 ± 6.0	65.0 ± 6.0	37.94	52.25
cyclohexene	36.4 ± 5.0	50.8 ± 5.0	37.90	52.21
1,3-cyclohexadiene	29.7 ± 12.0	44.1 ± 12.0	37.80	52.10
benzene (2)	60.8 ± 8.0	75.2 ± 8.0	37.81	52.11

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[1] The reported values are the mean ± standard deviations for replicate studies (the numbers in brackets indicates the number of replicates). Where there is no figure in brackets, only one study was done and the ±error is based on the standard error of the intercept of the graph from which the entropy was calculated.

[4.31] $\quad {}_{2}S^{o}_{trans} = R \ln (M T A^{o}) + 275.31 \qquad \mathrm{J\,K^{-1}\,mol^{-1}}$

in which A° is the area available to the molecule according to the particular standard state, that is, $1/\Gamma^{o}$. Therefore, the theoretical entropy of adsorption based on statistical mechanical calculations is given by

[4.32] $\quad \Delta S^{o} = {}_{2}S^{o}_{trans} - {}_{3}S^{o}_{trans} \qquad \mathrm{J\,K^{-1}\,mol^{-1}}$

Table 4.12 gives the results of this calculation of the theoretical entropy change for mobile adsorption. In this calculation it does not matter whether the Kemball-Rideal or deBoer-Kruyer standard state is used, as long as the theoretical ΔS° is compared to the experimental ΔS° calculated using the same standard state: the difference between the theoretical and experimental values will be the same (see Table 4.12). There is, however, a subtle difference between the aforementioned standard states and that of θ = 1/2. In the first two, the standard state is considered to be an ideal two-dimensional gas while the latter standard state refers to a condensed phase, that of a half complete monolayer. In the derivation of eq. [4.31] the adsorbed phase was considered to be an ideal two-dimensional gas (40) and so a comparison has been made only between experimental and theoretical values calculated using the Kemball-Rideal or deBoer-Kruyer standard states to evaluate the non-localized adsorption model.

In comparison to the theoretical entropies of adsorption in Table 4.12, all of the experimental values show a greater loss of entropy than is predicted from the loss of one translational degree of freedom, which is common in the case of physical adsorption (4). This extra loss of entropy could be due to loss of rotational freedom as suggested by Kemball (40) in his study of the adsorption of organic molecules on mercury. For example, for benzene adsorption the decrease in entropy due to the change from a free rotator in the gas phase, to an adsorbed molecule that is constrained to rotate only in the plane of the ring and about only one of the axes in the plane, was calculated to be about 38.5 J K^{-1} mol^{-1}. Kemball (40) also estimated that for heptane a loss of freedom of rotation about one bond for the adsorbed molecule relative to the gas phase molecule would lead to a decrease in entropy of about 21.3 J K^{-1} mol^{-1}. These values are of the same order of magnitude as observed in this study. Therefore it is possible that organic molecules adsorbed on the clay surface are free to move about on the surface, but have some restriction in rotational freedom.

In the above discussion, contribution to entropy change due to vibrational changes has been neglected as the vibrational contribution to entropy at room temperature is small relative to rotational and translational contributions.

As previously mentioned, another model for adsorption is localized adsorption. In this case the entropy of the surface phase will be the sum of the configurational entropy (i.e. that due to the number of ways of arranging molecules amongst adsorption sites), and thermal entropy from the molecular motion about the adsorption site (3,10). As shown by Everett (3) the differential configurational entropy is given by

[4.33] $$\overline{S}_{config} = -R \ln \frac{\theta}{1-\theta}$$

where θ is the fractional surface coverage. Therefore the theoretical differential entropy of adsorption for localized adsorption can be calculated from (3)

[4.34] $$\Delta\overline{S} = \Delta\overline{S}^{*} - R \ln \frac{\theta}{1-\theta}$$

where $\Delta\overline{S}^{*}$ is the decrease in entropy from the loss of translational and rotational freedom, that, as a first approximation, is simplified to the loss of three degrees of translational freedom for the adsorption process, which gives

[4.35] $$\Delta\overline{S} = -\,{}_{3}S_{trans} - R \ln \frac{\theta}{1-\theta}$$

When a standard state of θ = 1/2 is used, the above equation simplifies to (3,41)

[4.36] $$\Delta\overline{S} = -\,{}_{3}S_{trans}$$

Experimental differential entropies of adsorption, calculated using a standard state of θ = 1/2, and theoretical entropies of adsorption for the localized model of adsorption, calculated from eq. [4.36], are given in Table 4.13. The experimental values are less negative than predicted, with the difference between experimental and theoretical entropies ranging between 50-90 J K^{-1} mol^{-1}. However, if the gas phase translational entropy has not just been lost, but has been converted to vibrational entropy, this could account for the difference (3). For example, a vibrational frequency of 6.25×10^{11} sec^{-1} at 300 K would contribute a total of 82 J K^{-1} mol^{-1} (for a total of three degrees of vibrational freedom) (4). This is in the range (10^{11}-10^{12} sec^{-1}) of frequencies

Table 4.13. Experimental and theoretical entropies ($\Delta S°$) of adsorption of organic compounds on Na-kaolinite referred to $\theta = 1/2$ standard state. Localized adsorption model.

Compound	$-\Delta S°$ ($J\ K^{-1}\ mol^{-1}$)	
	Experimental[1]	Theoretical
pentane (5)	95.9 ± 2.1	164.74
hexane (4)	101.9 ± 1.2	167.26
heptane (2)	113.9 ± 1.6	169.45
octane	119.5 ± 2.1	171.08
cyclohexane (3)	98.3 ± 6.0	166.97
cyclohexene	84.5 ± 5.0	166.97
1,3-cyclohexadiene	78.2 ± 12.0	166.66
benzene (2)	109.9 ± 8.0	166.93

[1] See footnote Table 4.12.

suggested by Hill (42) for adsorbed molecules oscillating around an adsorption site. Therefore, as Everett (3) concluded, it is quite difficult to determine whether the adsorbed molecules are mobile or localized. The entropies of the adsorbed phase molecules are given in Table 4.14. These values were calculated from the difference between the integral entropies of adsorption (Kemball-Rideal standard state) and the gas phase entropies at the average temperature of the studies, with the gas phase entropies obtained from Stull et al. (43). The adsorbed phase entropies follow the same trends as gas phase entropies: there is a gradual increase with increasing chain length of the alkanes as one would expect for an increase in rotational entropy; adsorbed benzene shows a similar drop in entropy as gas phase benzene as compared to cyclohexane, cyclohexene and 1,3- cyclohexadiene.

Calculation of the standard Gibbs energy of adsorption (ΔG°)

The Gibbs energies of adsorption were calculated with eq. [4.15]. In this instance, the differential and integral Gibbs energies of adsorption are equivalent (44). These values are given in Table 4.15 for both the deBoer-Kruyer and Kemball-Rideal standard states.

Comparison of different kaolinite preparations

It was found that thermodynamic values were reproducible when using the same column or different columns made from the same preparation of kaolinite. **This was not the case, however, when columns were used that were made from different preparations of kaolinite.**

Columns made using each of two preparations of Na-kaolinite

Table 4.14 Gas phase entropies and adsorbed phase entropies of organic compounds on Na-kaolinite

Compound	Temperature (K)	S° (J K^{-1} mol^{-1}) [1] Gas Phase	S° (J K^{-1} mol^{-1}) [1] Adsorbed Phase
pentane (5)	338	364.5	316 ± 2
hexane (4)	343	409.2	354 ± 1
heptane (2)	348	454.7	387 ± 2
octane	348	497.2	423 ± 2.1
cyclohexane (3)	343	314.9	264 ± 6.0
cyclohexene	348	328.7	292 ± 5.0
1,3-cyclohexadiene	348	----- [2]	----- [2]
benzene (2)	358	284.9	224 ± 8.0

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[1] See footnote Table 4.12.

[2] Data unavailable.

Table 4.15. Gibbs energies ($\Delta G°$) of adsorption of organic compounds on Na-kaolinite referred to the Kemball-Rideal (K-R) and deBoer-Kruyer (D-K) standard states

Compound	Temperature Range (°C)	$-\Delta G°$ (kJ mol^{-1})[1] K-R	D-K
pentane (5)	30 - 100	17.1 ± 0.1	12.3 ± 0.2
hexane (4)	40 - 100	19.7 ± 0.1	14.7 ± 0.1
heptane (2)	50 - 100	22.8 ± 0.2	17.8 ± 0.2
octane	50 - 100	26.0 ± 1.0	21.0 ± 1.0
cyclohexane (3)	40 - 105	18.6 ± 0.3	13.7 ± 0.3
cyclohexene	50 - 100	27.5 ± 3.0	22.4 ± 3.0
1,3-cyclohexadiene	50 - 100	26.9 ± 5.0	21.9 ± 5.0
benzene (2)	65 - 105	28.4 ± 0.2	23.3 ± 0.4

[1] The reported values are the mean ± standard deviations for replicate studies (the numbers in brackets indicates the number of replicates). Where there is no figure in brackets, only one study was done and the ± error is based on the combined error of the enthalpy and entropy values.

(Na-kaolinite #1 and Na-kaolinite #2; note that the body of results presented here and in Chapter 5 were obtained using Na-kaolinite #1) and one of Ca-kaolinite were used to obtain the adsorption properties of selected organic compounds. Values obtained for ΔH°, ΔS° and ΔG° of adsorption are given in Table 4.16 (Kemball-Rideal standard state). The trends are still the same in comparing the results for different organic compounds on the same column so one would obtain the same conclusions when comparing the properties of different adsorbants on a column. However, there is a significant difference in the values of the enthalpy and entropy of adsorption for Na-kaolinite #1 and the other two clay preparations, while there is no difference between Na-kaolinite #2 and Ca-kaolinite. The differences between the two Na-kaolinites cancel in the ΔG° values which indicates that ΔH° and ΔS° value are more sensitive to changes in system characteristics.

The reason for the difference between the thermodynamic properties of two preparations of Na-kaolinite, prepared by the same method, is unclear. Adsorption on Na-kaolinite #2 (and Ca-kaolinite) relative to Na-kaolinite #1 is stronger, as indicated by the increased negativity of both the enthalpy and entropy of adsorption. The slight differences in surface areas could not account for the observed differences. Therefore, there is either a greater concentration of binding sites, or there are sites of different (stronger) binding energies on the surface of the former two clays. The former is possible if these two clays have a greater cation exchange capacity than Na-kaolinite #1 and hence a greater concentration of surface cations, as the cations have been implicated by some

Table 4.16 Comparison of thermodynamic properties of the adsorption of organic compounds on different preparations of kaolinite (Kemball-Rideal standard state)

Clay	Adsorbate	- ΔH° [1] (kJ mol^{-1})	- ΔS° [2] (J K^{-1} mol^{-1})	- ΔG° [3] (kJ mol^{-1})
Na-kaolinite #1	pentane (5)	36.3 ± 0.8	48.8 ± 2.1	17.1 ± 0.1
	hexane (4)	41.5 ± 0.5	55.3 ± 1.2	19.7 ± 0.1
	cyclohexane (3)	38.9 ± 2.2	50.6 ± 6.0	18.6 ± 0.2
Na-kaolinite #2	pentane	42.5 ± 1.1	69.8 ± 3.5	18.9 ± 1.5
	hexane	48.7 ± 1.4	75.9 ± 4.0	22.3 ± 1.7
	cyclohexane	44.8 ± 1.0	70.2 ± 3.0	20.7 ± 1.5
Ca-kaolinite	pentane	41.4 ± 1.0	66.2 ± 3.0	19.0 ± 1.4
	cyclohexane	45.1 ± 1.0	70.2 ± 3.0	21.0 ± 1.4

[1] See footnote Table 4.11.

[2] See footnote Table 4.12.

[3] See footnote Table 4.15.

in the binding of adsorbed organics (45). It is also known that kaolinite has a heterogeneous surface with respect to adsorption (46), but whether the nature of the adsorption sites can be so easily changed is doubtful. Whatever the case, the effect is larger than the effect of changing the cation type on the clay surface from Na$^+$ to Ca^{2+}.

Conclusions

The results of the calculation of the enthalpy of adsorption of selected hydrocarbons on the surface of kaolinite have shown that the process is physical adsorption (physisorption). Physical adsorption is a result of van der Waals attractive forces and not, as is the case of chemisorption, due to the formation of bonds.

Kaolinite has a heterogeneous adsorption surface with two and sometimes three different heats of adsorption being found with increasing surface coverage (46). This is consistent with the complexity of its surface structure as described in the introduction. As this present study was carried out (for the most part) in the Henry's Law region of the adsorption isotherm, the calculated enthalpies reported here will be those of the most active adsorption sites. Cooper and Hayes (22) studied the energy distribution of adsorption sites on kaolinite for the adsorption of butene and butane, using gas chromatography. They found two maxima in the energy distribution curves corresponding to two main adsorption sites, one which they identified as an oxygen adsorption site with an energy of 19.7 kJ mol^{-1} and the other as an hydroxyl adsorption site with an energy of 22.2 kJ mol^{-1}. Their data did show however, a very low frequency of occupation of energy levels up to a maximum of about 31.4 kJ mol^{-1}, which value is consistent with results presented here.

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CHAPTER 5

Heat Capacity of Adsorption of Hydrocarbons on Kaolinite Determined Using Gas-Solid Chromatography

Introduction

Knowledge of the change or increment in the heat capacity for adsorption ($\Delta C_p°$) allows one to calculate the temperature dependence of the enthalpy and entropy of adsorption. In addition to this useful application of classical thermodynamics, $\Delta C_p°$ values have proven useful in other fields (such as solution chemistry) in contributing to the basic scientific understanding of molecular interactions. Because (for reasons given below) there are very few $\Delta C_p°$ values for adsorption of gases on solids, there have so far been very few of the classical thermodynamic calculations and also few contributions to microscopic understanding of adsorption using $\Delta C_p°$ values.

In principle one can obtain $\Delta C_p°$ of adsorption from knowledge of the heat capacity of the solid (no gas adsorbed) and the heat capacity of the solid with adsorbed gas, in combination with knowledge of the amount of adsorbed gas. The desired $\Delta C_p°$ can be obtained by extrapolating ΔC_p values obtained from

$$\Delta C_p = \frac{C_{p\,(\text{solid + ads gas})} - C_{p\,(\text{"bare" solid})}}{n_a} \qquad [5.1]$$

to zero n_a (number of moles of gas adsorbed per gram of solid adsorbent).

Unfortunately, the difference between the two heat-capacities in the numerator of this equation is typically very small for small n_a, which means that this direct method is rarely practical.

A few of these direct calorimetric determinations of ΔC_p values have been carried out, using specially constructed calorimeters (1-3). Such determinations have been limited to specially selected systems (low temperatures, specific solids having very small heat capacities and very large surface areas) (1).

Because calorimetric measurements leading to desired ΔC_p values (especially for low coverage) are limited to special cases that do not include systems of contemporary interest, it is highly desirable to have some other method that might be more generally applicable. To illustrate the possibilities and difficulties associated with a more general approach, it is now appropriate to consider briefly one application of thermodynamics to chemical equilibria, using acid-base equilibria as an example.

In the study of acid-base equilibria it has been common practice to obtain (or at least try to obtain) heat capacity data from equilibrium constants in the following manner. The temperature dependence of enthalpy is given by

$$[5.2] \qquad \frac{d\,\Delta H^\circ}{dT} = \Delta C_p^\circ$$

Assuming ΔC_p° is independent of temperature, integration gives

$$[5.3] \qquad \Delta H_T^\circ = \Delta H_I + \Delta C_p^\circ T$$

where ΔH_I is a constant of integration. The temperature dependence of the equilibrium constant is given by

[5.4] $$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H°}{RT^2}$$

Substituting the value for $\Delta H_T°$ into eq. [5.4] and integrating gives

[5.5] $$\ln K_{eq} = -\frac{\Delta H_I}{RT} + \frac{\Delta C_p^o}{R} \ln T + I$$

where I is a constant of integration. Thus $\Delta C_p°$ can be obtained from a double differentiation of the equilibrium constant with respect to temperature.

The derivation given above can be applied to the particular case of equilibrium constants for adsorption obtained by gas-solid chromatography. If one substitutes for K_{eq} in eq. [5.5] using eq. [4.17] one obtains

[5.6] $$\ln \left(\frac{\Gamma}{P}\right) = -\frac{\Delta H_I}{RT} + \frac{\Delta C_p^o}{R} \ln T + I'$$

where I' contains the expression for the standard states. Following a procedure similar to the one used to obtain eq. [4.20], one obtains

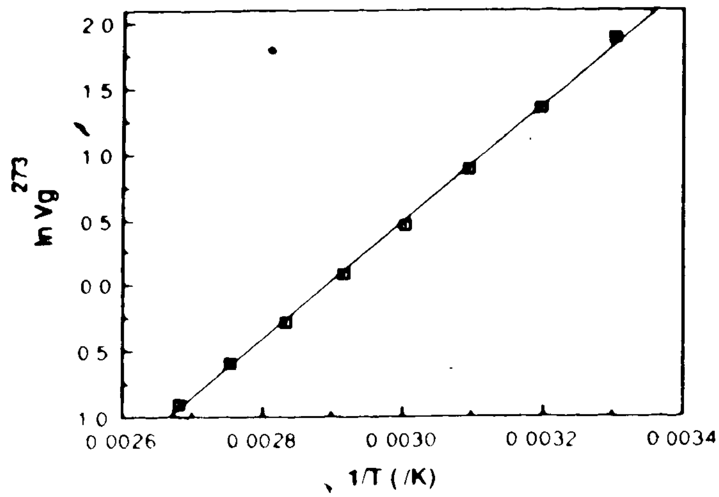
[5.7] $$\ln V_g^{273} = -\frac{\Delta H_I}{RT} + \frac{\Delta C_p^o}{R} \ln T + I''$$

where I'' is a collection of constants. Therefore, if the enthalpy of adsorption calculated using eq. [4.20] exhibited any dependence on temperature, one could calculate $\Delta C_p°$.

The uncertainty in the $\Delta C_p°$ obtained from a double differentiation will naturally be quite substantial. In a propagation of error analysis for a similar calculation to obtain $\Delta C_p°$ from pK_a data, King (4) found that for a random error of ±0.02 in the pK_a values, the standard deviation in the $\Delta C_p°$ value for a 50 °C range in temperature, with values at 10 °C intervals, is ± 117 J K^{-1} mol^{-1}. As King (4) points out, his treatment neglected systematic errors so one should probably double the "statistical" uncertainties to obtain "real" uncertainties of about 230 J K^{-1} mol^{-1}. It is therefore necessary to have very good equilibrium results over a wide temperature range to obtain $\Delta C_p°$ values that will be useful, but still will likely retain a moderately large uncertainty. But even moderately accurate $\Delta C_p°$ values will be of some usefulness and represent a start to getting better values in the future.

Results and Discussion

As was mentioned in Chapter 4, the calculation of the enthalpy of adsorption was based on the approximation that $\Delta C_p° = 0$. Least squares fits of eq. [4.20] to the retention data for the experiments reported in Chapter 4 were very good, with correlation coefficients larger than 0.95 in all cases (0.995 for some). However, an examination of residual plots showed that for some systems the enthalpy of adsorption did show a dependence on temperature, as illustrated in Figure 5.1. Figure 5.1a shows the graph for a linear least squares fit of eq. [4.20] to the data for the adsorption of pentane on Na-kaolinite, while figure 5.1b shows the plot of the residuals. The definite curve in the residuals shows that the enthalpy was dependent on temperature. An example a



b

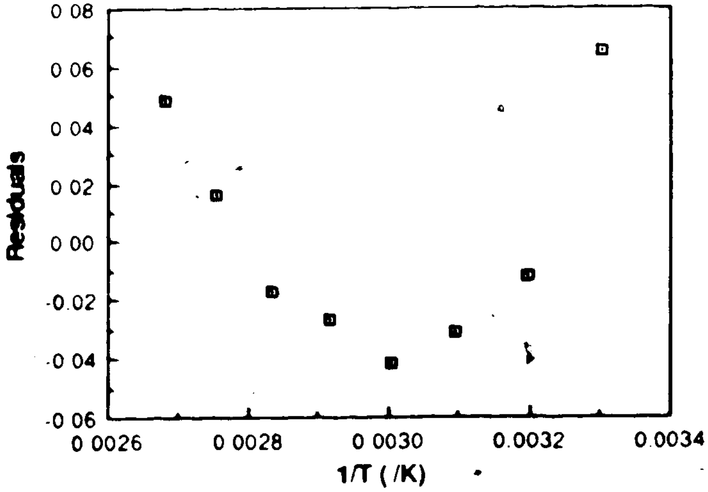


Figure 5.1. a. Graph showing the curve obtained for a least squares fit of eq. [4.20] to the specific retention volumes (V_g^{273}) obtained for the adsorption of pentane on Na-kaolinite at a series of temperatures. b. Plot of the residuals obtained from the fit in a.

of a less favorable system that does not show this curve in the residuals is given in Figure 5.2 for the adsorption of benzene on Na-kaolinite.

Equation [5.7] was fitted to data which showed a systematic temperature-dependent enthalpy. This included data for the adsorption of pentane, hexane, octane and cyclohexane on Na-kaolinite. Fits of eq. [5.7] were done using a linear least squares regression analysis. The values for $\Delta C_p°$ obtained from this fit are presented in Table 5.1. An example of the least squares fit is given in Figure 5.3a for the adsorption of pentane. The plot of the residuals after these second fits that include $\Delta C_p°$ show random scatter (Figure 5.3b) indicating that there is no justification for considering the possible temperature dependance of $\Delta C_p°$ as in

[5.8] $\Delta C_p° = a + bT + ...$

Consideration of eq. [5.8] would be equivalent to differentiating the experimental results three times or more. This inability to make use of eq. [5.8] is not surprising as even excellent data cannot stand multiple differentiation.

Conclusions

Although Sing (5) maintains that $\Delta C_p°$ of adsorption values obtained from gas-solid chromatography are of "doubtful value", there have been a few reports in the literature on these measurements. Bertush et al. (6) obtained the $\Delta C_p°$ (±50%) of adsorption of hexane and heptane on a macro-porous aerosilogel by gas-solid chromatography. Goedert and Guiochon (7) also

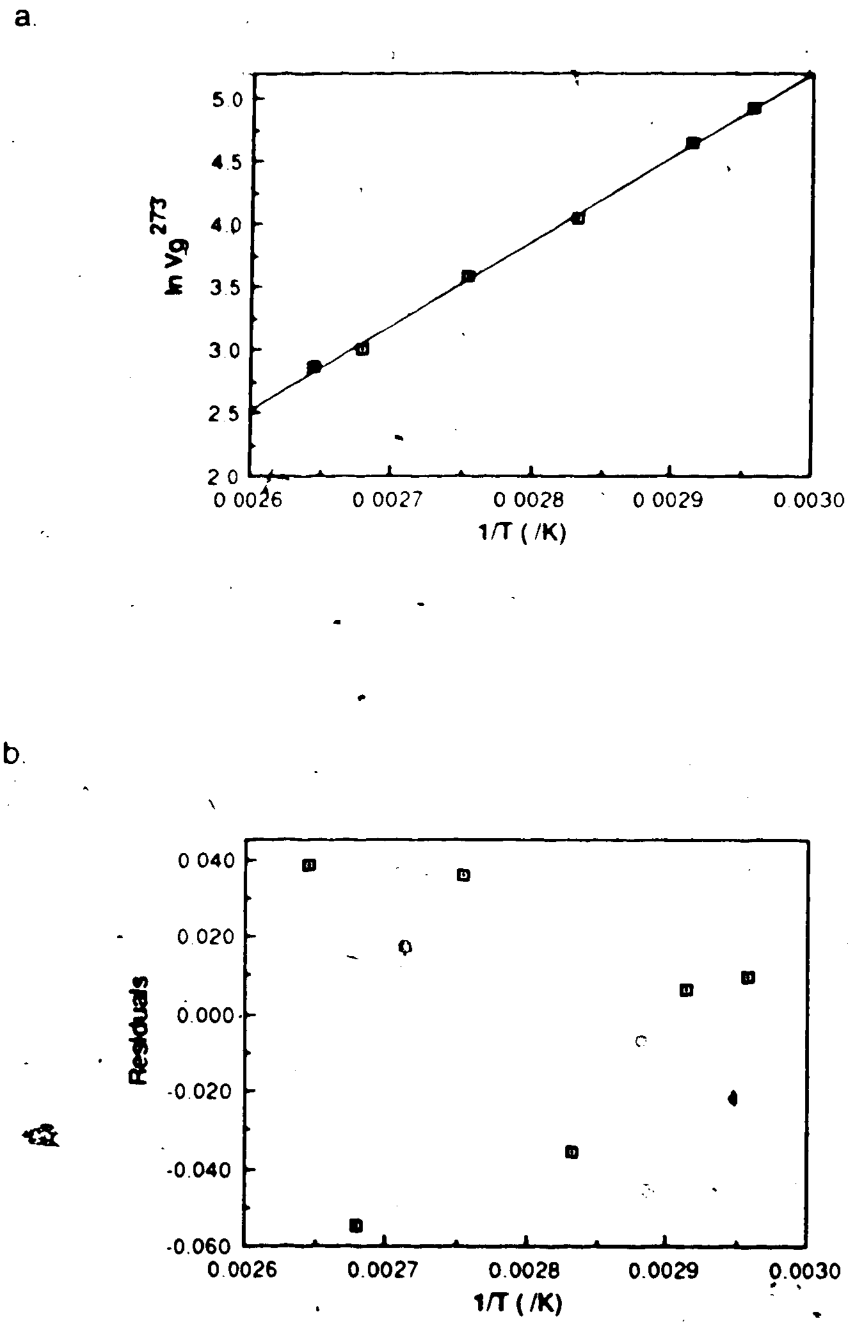


Figure 5.2. a. Graph showing the curve obtained for a least squares fit of eq. [4.20] to the specific retention volumes (V_g^{273}) obtained for the adsorption of benzene on Na-kaolinite at a series of temperatures. b. Plot of the residuals obtained from the fit in a.

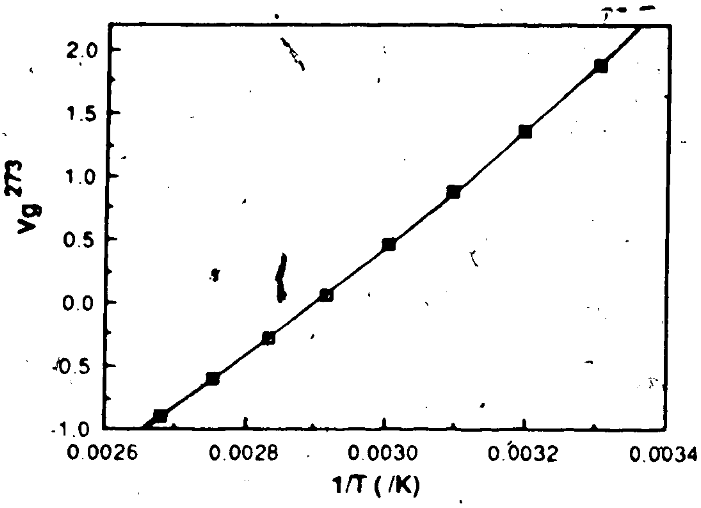
Table 5.1. Heat capacities of adsorption ($\Delta C_p°$) of organic vapors on Na-kaolinite

Compound	$\Delta C_p°$[1] (J K^{-1} mol^{-1})	$C_p°$(gas)[2] (J K^{-1} mol^{-1})	$C_p°$(ads) (J K^{-1} mol^{-1})
pentane (4)	145 ± 53	133.1	278 ± 53
hexane (3)	180 ± 122	159.9	340 ±122
heptane (2)	141 ± 44	187.6	329 ± 44
octane (1)	208 ± 76	214.0	422 ± 76
cyclohexane (3)	140 ± 46	125.5	265 ± 46

[1] The values given are the mean ± standard deviation of replicate experiments with the number of replicates given in brackets. For octane the ± value is based on the standard error of the fit obtained by least squares analysis.

[2] Data from Stull et al. (9). Uncertainties in $C_p°$(gas) are negligible compared to uncertainties in $\Delta C_p°$.

a.



b.

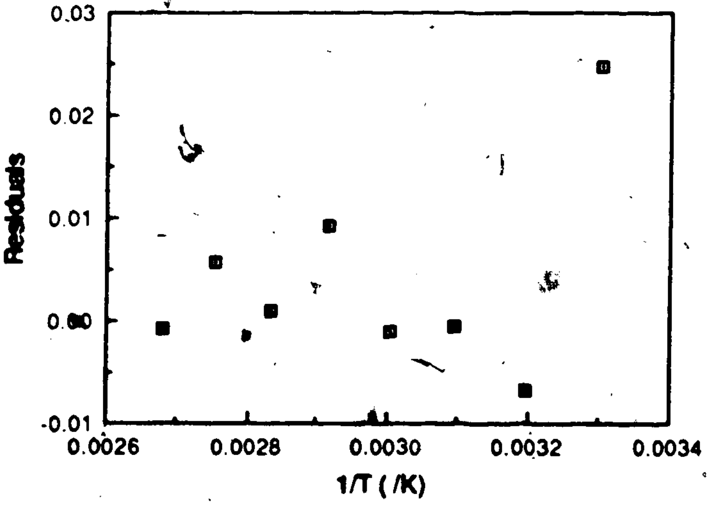


Figure 5.3. a. Graph showing the curve obtained for a least squares fit of eq. [5.6] to the specific retention volumes (V_g^{273}) obtained for the adsorption of pentane on Na-kaolinite at a series of temperatures. b. Plot of the residuals obtained from the fit in a.

noticed a curve in a ln K against 1/T plot in a study of adsorption of methane on graphitized carbon black (selected for its homogeneous surface), and wrote that it may be possible to get information about $\Delta C_p°$ of adsorption. In a later report this group (8) used gas-solid chromatography to obtain $\Delta C_p°$ for the adsorption of pentane on graphitized carbon black.

As mentioned in the introduction, values for $\Delta C_p°$ can be used in classical thermodynamic calculations of the temperature dependence of enthalpy as given by eq. [5.2], and that of entropy as given by

$$[5.8] \qquad \frac{d\,\Delta S°}{d\,T} = \frac{\Delta C_p°}{T}$$

To evaluate the significance of the $\Delta C_p°$ values obtained in terms of a molecular model one can first consider the sign. $\Delta C_p°$ can be expressed as

$$[5.9] \qquad \Delta C_p° = C_p° \text{ (ads gas)} - C_p° \text{ (gas)}$$

If the adsorbed phase can be modelled semi-realistically as a two-dimensional liquid, it would follow that $C_p°$ (2D liq) > $C_p°$ (real gas), which is in accord with our positive $\Delta C_p°$ values. One might also picture the adsorbed phase (especially for localized adsorption) as a two-dimensional solid, again leading to positive $\Delta C_p°$ as found in this research.

In conclusion, $\Delta C_p°$ values for the adsorption of several hydrocarbons on Na-kaolinite have been obtained. The positive values are consistent with a model for the adsorbed phase as a two-dimensional liquid or solid.

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CHAPTER 6

Concluding Summary

Research in the area of physical chemistry can lead to a basic understanding and provide useful data of chemical and physical processes. The investigations that have been described in this thesis are intended to contribute to such scientific understanding of the properties of liquid-solid and gas-solid systems containing clays and to provide data that will be useful in certain fields.

The importance of such information is illustrated in Chapter 2, which is an extensive review of the properties and technology for treatment of aqueous clay waste (tailings) produced during the processing of oil sands mined in northern Alberta. The information in this review is necessary background information for anyone who intends to work toward a practical solution of this economically and environmentally important problem. In addition, this review led to the identification of several specific kinds of new research that are needed, and this identification has contributed to the selection of problems for the research that is described in this thesis.

Partly because of the obvious connection between clay-water properties and the tailings problem, investigations of the viscosities of aqueous clay suspensions were undertaken as described in Chapter 3. These studies involved the measurements of viscosities and densities of aqueous suspensions of known compositions. Results of the measurements of densities of aqueous suspensions have led to evaluation of the density of dry clays. Analysis of the viscosities was carried out in terms of a modified version of the well known Einstein equation; these modifications allowed for the non-spherical shape of clay particles as well as the water-induced swelling of clay (especially montmorillonite) in aqueous suspensions. Measurements of the viscosities of suspensions of mixed clays led to results that have been analyzed in terms of the modified Einstein equation and a simple additivity model.

Chapters 4 and 5 describe another aspect of the physical chemistry of clays; that is, the thermodynamics of adsorption of gaseous molecules on the surface of clay based on gas-solid chromatographic measurements in the Henry's Law (very low surface coverage) region. Results of these measurements have led to calculation of the enthalpies, entropies and Gibbs energies of adsorption (Chapter 4) . The resulting enthalpies of adsorption confirm the expectation that we are dealing with physical adsorption rather than chemisorption. The entropies of adsorption (specified standard states) have been considered in relation to models of mobile versus localized adsorption.

The thermodynamic analysis described ~~in~~ Chapter 4 is based on the common situation in which the accuracy and range of the experimental data does not permit one to obtain any information about the possible dependence of the enthalpy and entropy of adsorption on temperature, which is equivalent to setting $\Delta C_P°$ for adsorption equal to zero. Examination of the residuals of the least squares fits described in Chapter 4 has shown that some of the present data are sufficiently accurate and have been obtained over a sufficiently wide range of temperature to justify more elaborate thermodynamic analysis in which $\Delta C_P°$ is not equal to zero. This kind of analysis led to values for $\Delta C_P°$ for adsorption of several vapors on kaolinite. Because this calculation is equivalent to a double differentiation of the equilibrium constant with respect to temperature and each such differentiation magnifies experimental uncertainties and errors, the derived $\Delta C_P°$ have large uncertainties. In spite of these uncertainties it is clearly established that the $\Delta C_P°$ values are all positive and it is also shown that such positive $\Delta C_P°$ value are consistent with the idea that the adsorbed phase may be pictured as a two-dimensional liquid.