Modeling of Kerogen Swelling by Solvents with Flory-Rehner and Regular Solution Model

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ABSTRACT

Oil and gas production from shale reservoirs has become an indispensable component of the world energy supply. However, the oil recovery rate from shale reservoirs is still relatively low. To achieve efficient exploitation of shale reservoirs, one of the prerequisites is to have a precise capture of the phase behavior of reservoir fluids in shale reservoirs. Compared with conventional oil reservoirs, shale reservoirs contain organic matters within the rock matrix. These organic matters are mainly composed of kerogen, which is in equilibrium with generated hydrocarbons during the expulsion process. Swelling of kerogen by different solvents is a well-known technique to characterize the thermodynamic properties of kerogen and to describe the phase equilibria between different solvents and kerogen.

In this thesis, experimental data of kerogen swelling tests from the literature are first collected to validate the efficacy of the Flory-Rehner and regular solution (FRRS) model in describing oil-kerogen two-phase equilibria. The FRRS algorithm can be tuned to well match the measured kerogen swelling test results. The swelling ratios of different types of kerogen are then predicted as a function of solubility parameters and molar volumes of different solvents. The effects of sulfur content and thermal maturity of kerogen on kerogen's swelling ratio are also studied. Our calculation results show that the swelling ratio of kerogen follows a bell-shaped trend with the change of solubility parameter and molar volume of solvents. Kerogen tends to absorb more aromatics and heavy hydrocarbons than light and saturated hydrocarbons. Compared with normal alkanes, naphthenes induce higher swelling ratios of kerogen. The capacity of kerogen to retain hydrocarbons decreases with an increasing thermal maturity or sulfur content of kerogen.

DEDICATION

This dissertation is dedicated to my dearest parents: Mrs. Zhenhua Zhao and Mr. Lingquan Chen.

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CHAPTER 1 INTRODUCTION

1.1.Research Background

The abundant reserves and extensive distribution of shale reservoirs makes shale oil a possible solution to solve the world's energy shortage. According to the results reported by United States Energy Information Agency (EIA)[1], the global oil resource reserves in shale reservoirs are at least 438.5 billion tons, which can be an important supplement to conventional oil resources. However, the recovery rate is still relatively low (around 10%)[1]. To achieve efficient exploitation of shale reservoirs, it is a prerequisite to well understand the complex phase behavior of shale oil. Compared with the conventional reservoirs, the unusual phase behavior in shale reservoirs is mainly caused by the extensive presence of organic matters (mainly composed of kerogen) in shale rocks. Kerogen is a complex organic matter with cross-linked network, which originates from the decomposition of biopolymers[2]. During the expulsion of hydrocarbons from kerogen, thermodynamic equilibria exist between kerogen and expelled hydrocarbons[2]. To precisely capture the hydrocarbon expulsion process, the multicomponent equilibria need to be properly considered in modeling.

Swelling kerogen with different solvents is widely used to determine the thermodynamic properties of kerogen network. In recent years, a few studies have touched on the swelling behavior of kerogen. In 1966, Sanata and Honda[3] used different solvents to swell coal samples to characterize the kerogen network structure. The swelling behavior of coals was then studied by other researchers[4-9]. In 1994, Larsen and Li[10] swelled Green River kerogen with 28 different solvents and concluded that the volumetric swelling of kerogen follows the prediction of regular solution theory[11]. In 2006, Ertas *et al.*[2] combined the Flory-Rehner theory[12] with regular solution theory[11] (FRRS) to describe the swelling behavior of Draupne type II kerogen. This paper provides mathematical formulations for calculating the chemical potential changes of the liquid-kerogen system, which can be used to calculate the swelling ratio of different kerogens. In 2020, Huang *et al.*[13] studied the swelling of Kimmeridge kerogen in different classes of solvents and concluded that the swelling of kerogen in normal alkanes is larger than that in naphthenes. They also reported that aromatics normally induce a larger swelling ratio.

1.2. Problem Statement

Although many efforts are invested to investigate the kerogen swelling behavior, there are still some questions that remain to be addressed. Firstly, the effect of type II kerogen maturity on swelling behavior remains elusive. Secondly, kerogen with a high sulfur content is widely distributed, but there is still lack of study on the swelling of high-sulfur-content kerogens. Thirdly, the swelling trends of different types of kerogen in different classes of solvents (normal alkanes, naphthenes and aromatics) need to be addressed.

1.3. Research Objectives

The objectives of this research include the following:

- To study the effect of thermal maturity of type II kerogen on its swelling;
- To study the effect of sulfur content in kerogen on its swelling;
- To study the effect of solvent solubility parameters and molar volumes on the swelling behavior of kerogen; and
- To investigate the swelling behavior of different kerogens in different classes of solvents.

1.4. Thesis Structure

This thesis is organized as follows:

In Chapter 2, the extended FRRS^2 is presented in detail.

In Chapter 3, the extended FRRS model is applied to calculate the swelling ratios of different kerogens in different solvents. The effects of several influencing factors are explored.

Chapter 4 gives the conclusions achieved in the thesis research, together with recommendations for future work.

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CHAPTER 2 METHODOLOGY

2.1. Overview

The swelling of kerogen is predicted by the extended FRRS model[1] in this study. In this model, the regular solution theory[2] is coupled with the Flory-Rehner theory[3] to determine the swelling behavior of polymer network. This theory can be used in calculating the swelling ratio of kerogen based on the following assumptions[1]: (1) Kerogen matrix is in thermodynamic equilibrium with solvents; (2) Kerogen has cross-linked network; and (3) Regular solution theory is applicable.

2.2. Mathematical Formulations

In this section, we will introduce the main mathematical formulae used in kerogen swelling calculations. In the two-phase oil-kerogen equilibrium calculation, equation (1)[1] must be satisfied:

$$\Delta\mu_i^{(a)} = \Delta\mu_i^{(l)} \quad (1)$$

The extended FRRS model[1] is used to calculate the changes of chemical potentials in the two-phase oil-kerogen equilibrium calculation. According to Flory (1953)[4], the changes of chemical potentials for polymer networks are contributed by the changes of conformational entropy and enthalpy. There are two main sources of conformational entropy[4]: (1) the entropy of the cross-linked network structure and (2) the entropy of mixing. As is proposed by Flory[4], the elastic free energy stored in the network could be computed as:

$$\Delta S_{el} = -k_B\left(\frac{N_e}{2}\right)\left[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - 2\ln\left(\alpha_x\alpha_y\alpha_z\right)\right] \quad (2)$$

where ΔS_{el} represents the conformational entropy change of a cross-linked network, k_B is Boltzmann constant, α_i is the elongation in different direction, N_e is the effective number of chain elements in the kerogen network, and subscripts *x*, *y*, *z* represent three principle directions. If we assume the elongations are uniform in each direction and equal to α_s, Equation (2) will become[1]:

$$\Delta S_{el} = -k_B(\frac{N_e}{2})(3\alpha_s^2 - 3 - 2ln\alpha_s^3) \quad (3)$$

Moreover, the entropy of mixing can be expressed as[4]:

$$\Delta S_M = -k_B \sum_i n_i ln v_i \quad (4)$$

where ΔS_M is the change of the entropy of mixing, n_i is the total mole number of solvent *i* and v_i is the volume fraction of solvent *i*. Mixing of solvents and kerogen will cause solvent dissolution in the kerogen network, causing enthalpy change. The enthalpy change during this process can be expressed as[3]:

$$\Delta H_M = k_B T(\sum_i \chi_{i0} n_i v_0 + \sum_{i \neq j} \chi_{ij} n_i v_j) \quad (5)$$

where ΔH_M is the enthalpy change during the mixing process, χ_{ij} is Flory–Huggins interaction parameter between component *i* and component *j*, and χ_{i0} is the parameter between component *i* and kerogen. Based on Equations (3), (4) and (5), Ertas *et al.*[1] gave the following formula of the change in chemical potential for species *i* in contact with other solvents and the polymer network with respect to a pure liquid of *i* in absorbed (kerogen) phase:

$$\frac{\Delta \mu_i}{k_B T} = \frac{1}{k_B T} \frac{\partial}{\partial n_i} [\Delta H_M - T(\Delta S_M + \Delta S_{el})]$$

$$= lnv_i + \sum_j v_j \left(\frac{V_j - V_i}{V_j}\right) + V_i\left(\sum_{j\neq i} b_{ij} v_j - \sum_{j<k} b_{jk} v_j v_k\right) + v_0 + V_i[b_{i0} v_0^2 + v_0 \sum_j v_j \left(b_{i0} - b_{j0}\right) + \frac{N_e}{V_0}(v_0^{1/3} v_{eq}^{2/3} - v_0)] \quad (6)$$

where b_{ij} is the interaction density parameter and V_i is the molecular volume of solvent i. The subscript 0 represents the kerogen phase. The value for b_{ij} can be obtained by[3]:

$$k_B T b_{ij} = (\delta_i - \delta_j)^2 \quad (7)$$

where δ_i is the Hildebrand solubility parameter value for solvent i. Note that the changes of chemical potentials of each component in the oleic phase (which does not have a polymer network) can be calculated by using the first three terms in Equation (6). Therefore, based on Equation (6), the constraint shown in Equation (1) can be satisfied by updating v_i.

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CHAPTER 3 RESULTS AND DISCUSSION

3.1. Validation of Extended FRRS Model

To validate the extended FRRS model we have programed in this study[1], it is first applied to calculate the swelling ratios of kerogen by absorbing different solvents. The calculated swelling ratios are then compared with the experimental data. The swelling ratios of kerogen can be calculated by the following equation:

$$Q_v = \frac{V_{swelled}}{V_0} \quad (31)$$

where Q_v represents the swelling ratio, $V_{swelled}$ and V_0 are the swelled and initial volumes of kerogen, respectively.

The calculated swelling ratios are to be compared with those measured by Ertas *et al.*[1] and Kelemen *et al.*[2]. In their experiments, eleven organic solvents were brought into contact with different types of kerogens 30ºC and 100 kPa, and then the corresponding swelling ratios were measured. Table 3-1 lists the thermodynamic properties of the Draupne type II kerogen, average type II kerogen and average type IIIC kerogen. Table 3-2 summarizes the solubility parameters and molar volumes of these solvents provided by the references[1, 2].

Table 3-1 Thermodynamic parameters of the Draupne type II kerogen[1], average type II kerogen[2] and average type IIIC kerogen[2].

Property	**Solubility Parameters (δ_0) (J/cm^3)**	**Cross-link Density (N_e/v_0) (mol/cm^3)**	**Native Swelling Fraction (v_{eq})**
Draupne Type II Kerogen	24.3	0.285	0.75
Average Type II Kerogen	22.5	0.16	0.76
Average Type IIIC Kerogen	23.3	0.25	0.85

Table 3-2 Solubility parameters and molar volumes of different solvents at 25ºC[3, 4]

Solvent Name	**Solubility Parameter (J/cm^3)**	**Molar Volume (cm^3/mol)**
n-decane	15.8	195.9
n-hexadecane	16.3	294.1
cyclohexane	16.8	108.7
decalin	17.7	154.2
toluene	18.2	106.9
tetralin	19.4	136.3
1-methylnaphthalene	20.2	139.4
2,5 dimethylpyrrole	20.3	101.7
pyridine	21.9	80.6
benzofuran	21.1	108.3
benzothiophene	21.8	124.7

Table 3-3, Table 3-4 and Table 3-5 compare the swelling ratios of Draupne type II kerogen, average type II kerogen and average type IIIC kerogen by absorbing different solvents calculated by the extended FRRS model and those measured by Ertas *et al.*[1] and by Kelemen *et al.*[2] The absolute relative error (*ARE*) between the calculated swelling ratio and the measured one are calculated as follows:

$$ARE = \frac{|Q_{vexp} - Q_{vcal}|}{Q_{vexp}} \quad (30)$$

where Q_{vexp} represents the kerogen's swelling ratio measured by experiments, and Q_{vcal} represents the calculated kerogen's swelling ratio. As shown in Table 3-3, Table 3-4 and Table 3-5, the *AREs* are small enough to consider that the extended FRRS model can give an accurate prediction of kerogen absorption behavior.

Table 3-3 Comparison of the swelling ratios of Draupne type II kerogen by absorbing different solvents calculated by the extended FRRS model and those measured by Ertas *et al.*[1]

Solvent Name	**Mean Swelling Ratio***	**Mean Swelling Ratio Calculated by the Extended FRRS Model**	**Absolute Relative Error**
n-decane	1.228	1.207	1.710%
n-hexadecane	1.212	1.213	0.083%
cyclohexane	1.287	1.272	1.166%
decalin	1.245	1.281	2.892%
toluene	1.338	1.312	1.943%
tetralin	1.328	1.327	0.075%
1-methylnaphthalene	1.400	1.340	4.286%
2,5 dimethylpyrrole	1.320	1.356	2.727%
pyridine	1.415	1.389	1.837%
benzofuran	1.360	1.364	0.294%
benzothiophene	1.362	1.366	0.294%
Average Error		1.573%	

***Note:** these values are retrieved from the paper by Ertas *et al.*[1]

Table 3-4 Comparison of the swelling ratios of Average Type II Kerogen by absorbing different solvents calculated by the extended FRRS model and those measured by Kelemen *et al.*[2]

Solvent Name	**Mean Swelling Ratio***	**Mean Swelling Ratio Calculated by the Extended FRRS Model**	**Absolute Relative Error**
n-decane	1.216	1.205	0.905%
n-hexadecane	1.204	1.207	0.249%
cyclohexane	1.278	1.296	1.409%
decalin	1.250	1.301	4.080%
toluene	1.358	1.344	1.031%
tetralin	1.318	1.355	2.807%
1-methylnaphthalene	1.400	1.368	2.286%
2,5 dimethylpyrrole	1.439	1.392	3.266%
pyridine	1.416	1.427	0.777%
benzofuran	1.375	1.396	1.527%
benzothiophene	1.371	1.391	1.459%
Average Error		1.800%	

***Note:** these values are retrieved from the paper by Kelemen *et al.*[2]

Table 3-5 Comparison of the swelling ratios of Average Type IIIC Kerogen by absorbing different solvents calculated by the extended FRRS model and those measured by Kelemen *et al.*[2]

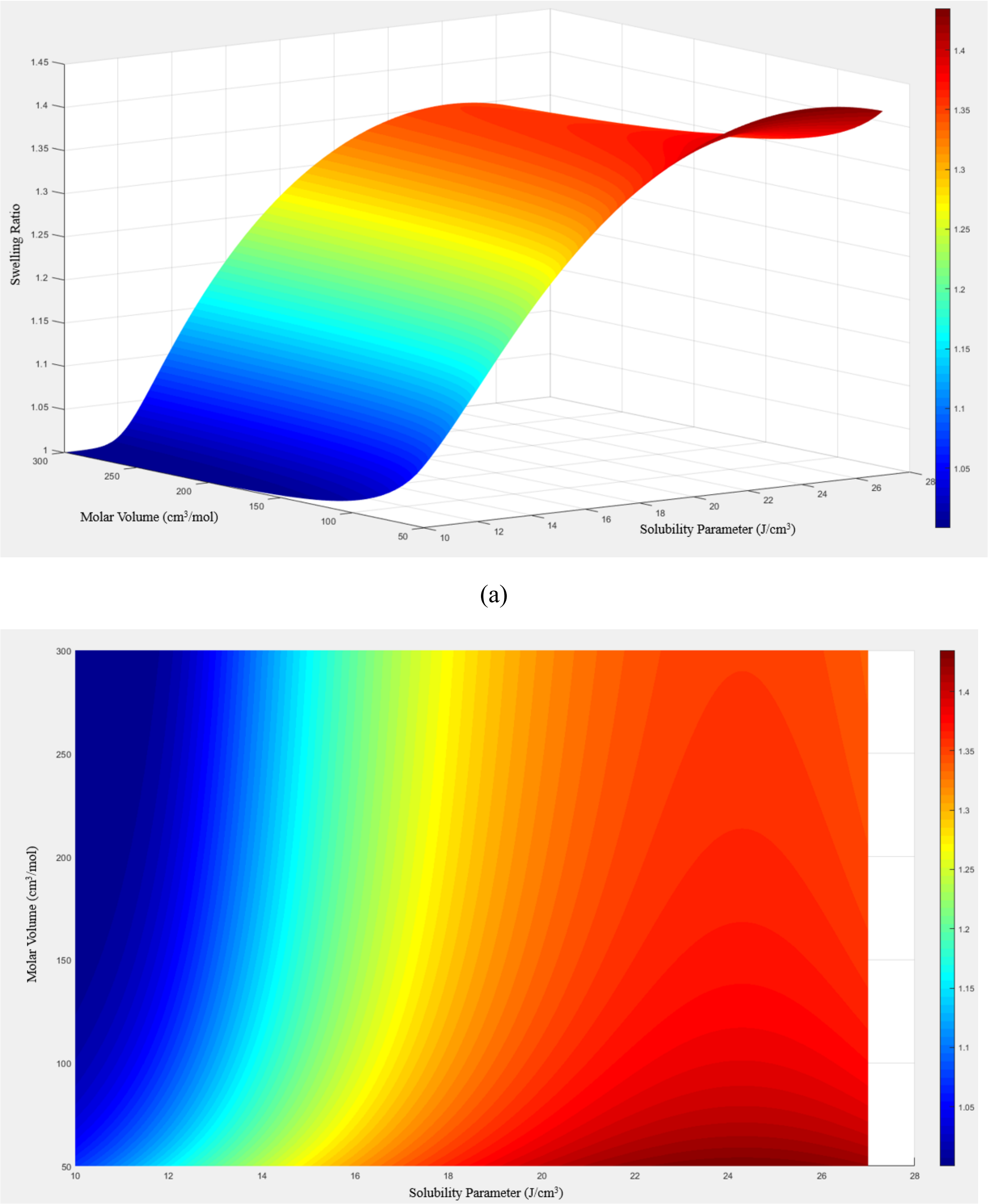
Solvent Name	Mean Swelling Ratio*	Mean Swelling Ratio Calculated by the Extended FRRS Model	Absolute Relative Error
n-decane	1.081	1.093	1.110%
n-hexadecane	1.105	1.091	1.267%
cyclohexane	1.174	1.158	1.363%
decalin	1.131	1.160	2.564%
toluene	1.175	1.192	1.447%
tetralin	1.173	1.200	2.302%
1-methylnaphthalene	1.222	1.211	0.900%
2,5 dimethylpyrrole	1.261	1.230	2.458%
benzofuran	1.213	1.234	1.731%
benzothiophene	1.226	1.232	0.489%
Average Error		1.563 %	

***Note:** these values are retrieved from the paper by Kelemen *et al.*[2]

3.2. Prediction of Kerogen Swelling Ratio

3.2.1. Effect of Solvent Molar Volume and Solubility Parameter on Kerogen Swelling Ratio

In this part, the swelling ratios of three different kerogen are predicted as a function of solubility parameters and molar volumes. The three model parameters for each type of kerogen are listed in Table 3-1. In the swelling ratio calculation process, the solubility parameters of different solvents take an initial value between [10 J/cm^3, 27 J/cm^3], while the molar volumes take an initial value between [50 cm^3/mol, 300 cm^3/mol]. Figure 3-1, Figure 3-2 and Figure 3-3 show the predicted swelling ratio of Draupne type II kerogen, average type II kerogen and average Type IIIC kerogen, respectively. Figure 3-1 (a) shows the three-dimensional (3-D) distribution of the swelling ratios of Draupne type II kerogen, while Figure 3-1 (b) shows a contour distribution of the swelling ratios of the Draupne type II kerogen. Figure 3-2 and Figure 3-3 show the same results obtained for average type II kerogen and average Type IIIC kerogen, respectively. A bell-shaped trend can be observed in the calculated swelling ratio vs solvent solubility parameter or molar volume, which is in qualitative agreement with the experimental data[5] and the prediction results from Huang *et al.*[6]. It can be observed from the prediction results that the swelling ratios of kerogen first increase with an increasing solubility parameters, reach a maximum when the solubility parameter of solvent is close or equal to the solubility parameter of kerogen, and then decrease with the further increase in the solubility parameters. On the other hand, the swelling ratio of kerogen decreases with an increasing molar volume of solvents. This can be attributed to the fact that fewer solvent molecules can be absorbed into the kerogen matrix as the molar volume of solvent increases[6]. Compared with the average type II kerogen, the average type IIIC kerogen shows a smaller swelling ratio. It indicates that with an increasing maturity of kerogen, the swelling of kerogen generally decreases. It confirms that lighter products are produced during the maturation process of kerogen matrix, which increases the cross-link density of kerogen[1].



(a)

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Figure 3-1 Predicted swelling ratio of Draupne type II kerogen as a function of solubility parameters and molar volumes: (a) 3-D distribution; (b) contour distribution.

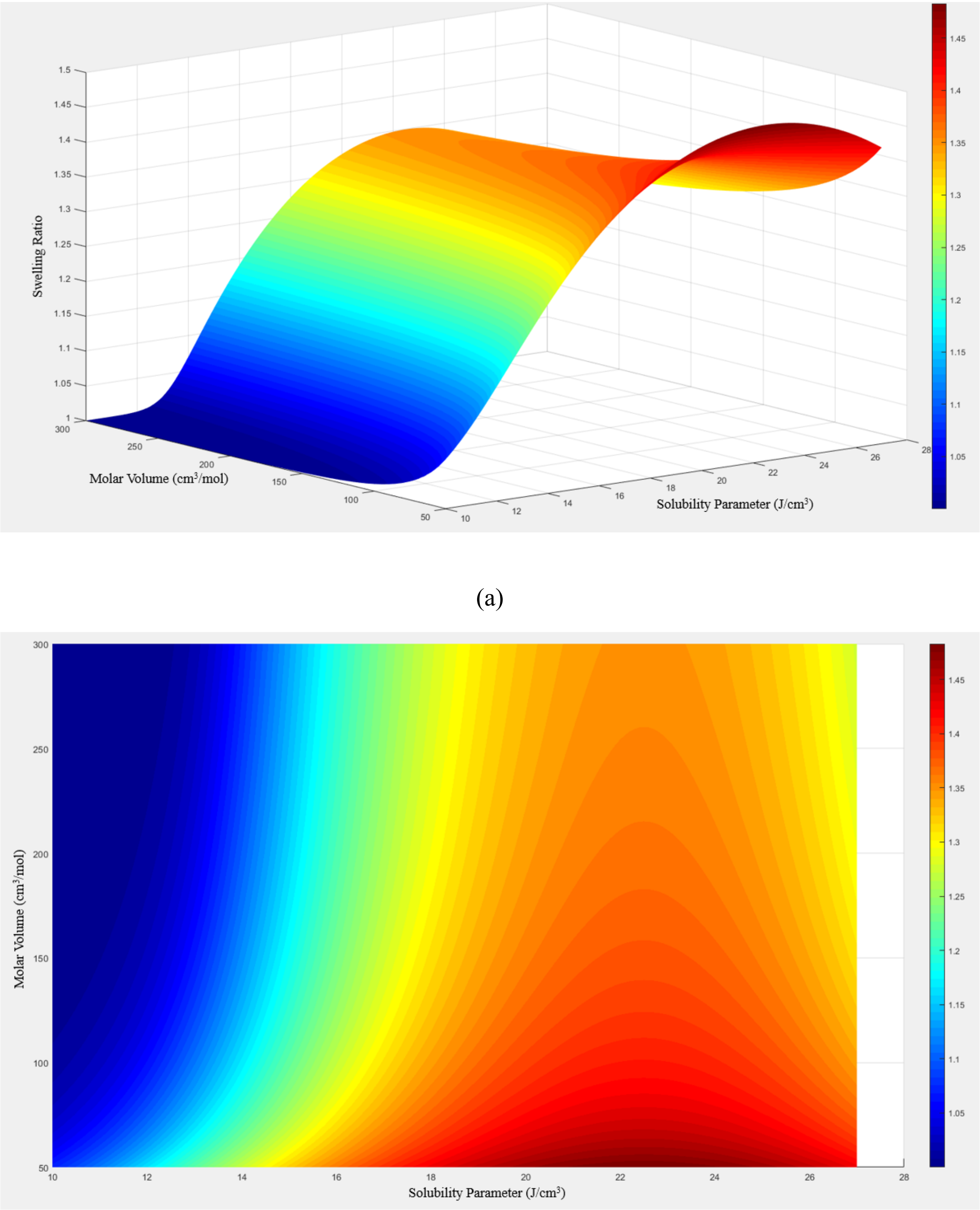

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Figure 3-2 Predicted swelling ratio of average type II kerogen as a function of solubility parameters and molar volumes of different solvents: (a) 3-D distribution; (b) contour distribution.

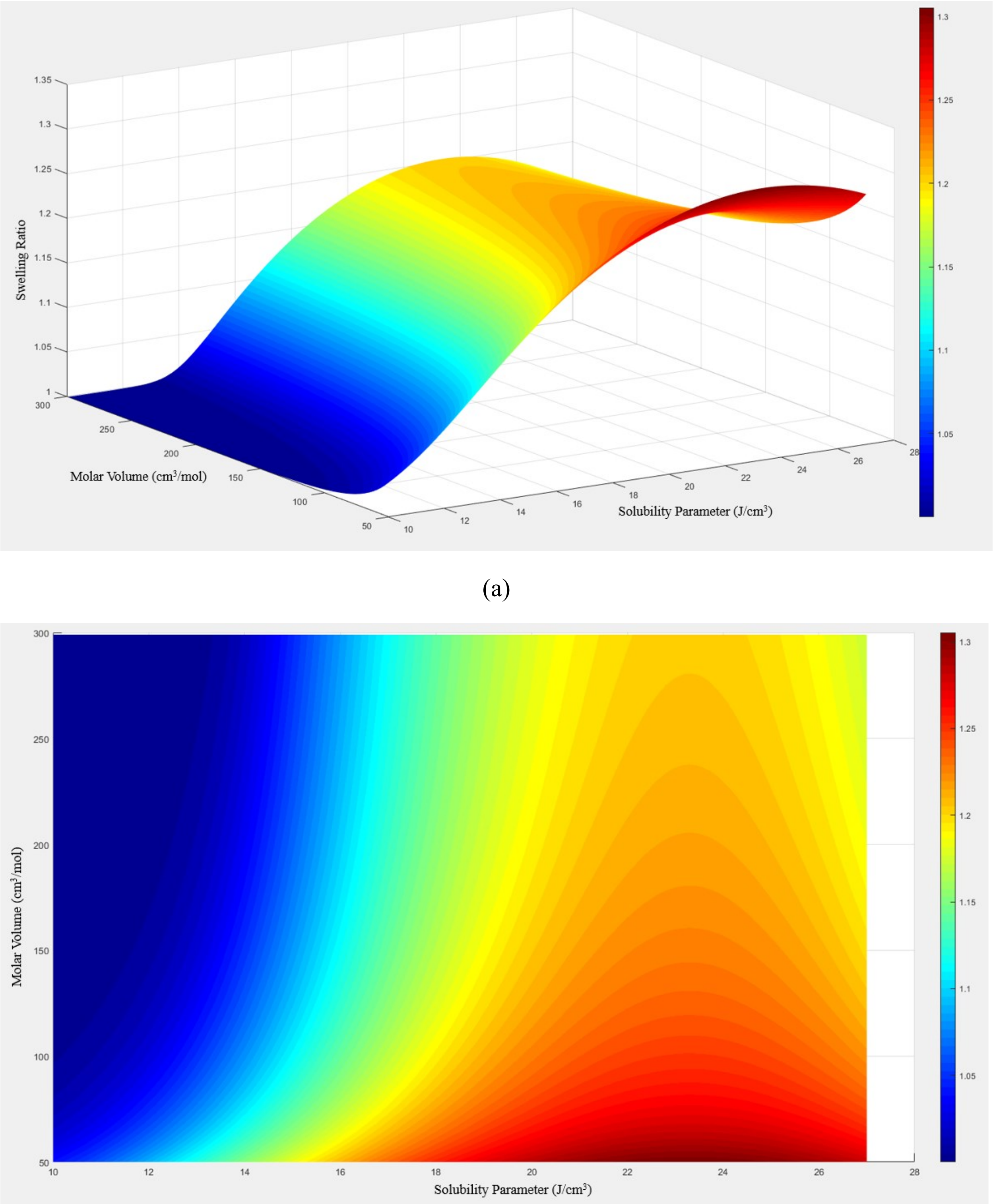

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Figure 3-3 Predicted swelling ratio of average type IIIC kerogen as a function of solubility parameters and molar volumes of different solvents: (a) 3-D distribution; (b) contour distribution.

3.2.2. Effect of Solvent Molecular Shape on Kerogen Swelling Ratio

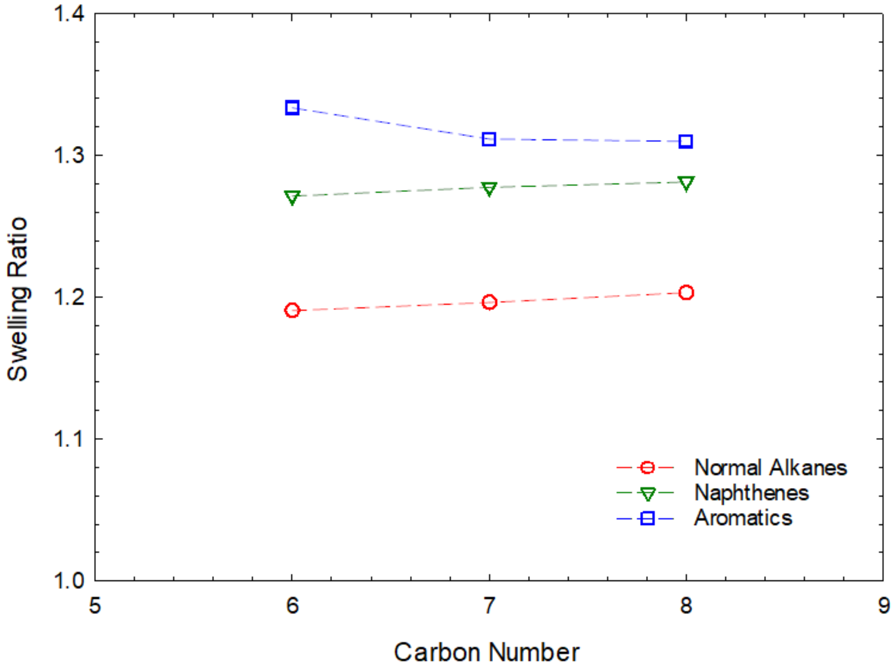
In this part, solvents with the same carbon number but different molecular shapes are selected to investigate the effect of solvent molecular shape on kerogen swelling ratio. The solubility parameter and molar volume of the selected solvents are shown in Table 3-6 and the calculated swelling ratios of different kerogen are shown in Table 3-7. Figure 3-4 shows the swelling ratio of different types of kerogens ((a) Draupne Type II Kerogen; (b) average type II kerogen; (c) type IIIC kerogen) as a function of carbon numbers. The red line, green line and blue line show the swelling ratios of kerogen in normal alkanes, naphthenes and aromatics, respectively. Compared with normal alkanes and naphthenes with the same carbon number, the swelling ratio of kerogen in aromatic solvents is larger. This can be attributed to the π-π interaction between the aromatic solvents and the aromatic molecules in kerogen network[6]. It can be also seen that the naphthenes induce a larger swelling ratio than normal alkanes do, which is different from the calculated results on Kimmeridge kerogen reported by Huang *et al.*[6] in 2020.

Table 3-6 Solubility parameters and molar volumes of different solvents at 25°C[3, 7]

Carbon Number	Solvent Name	Solubility Parameter (J/cm^3)	Molar Volume (cm^3/mol)
6	n-hexane	14.9	130.6
	cyclohexane	16.8	108.7
	benzene	18.7	89.4
7	n-heptane	15.2	147.0
	cycloheptane	17.2	121.3
	toluene	18.2	106.9
8	n-octane	15.5	163.4
	cyclooctane	17.5	134.4
	o-xylene	18.4	121.2

Table 3-7 Calculated swelling ratios of different kerogen by absorbing different solvents

Carbon Number	Solvent	Swelling Ratio		
		Draupne Type II Kerogen	**Average Type II Kerogen**	**Average Type IIIC Kerogen**
6	n-hexane	1.1907	1.1897	1.0879
	cyclohexane	1.2715	1.2956	1.1581
	benzene	1.3337	1.3731	1.2146
7	n-heptane	1.1965	1.1951	1.0898
	cycloheptane	1.2777	1.3010	1.1611
	toluene	1.3117	1.3438	1.1924
8	n-octane	1.2034	1.2022	1.0931
	cyclooctane	1.2814	1.3035	1.1623
	o-xylene	1.3101	1.3392	1.1885



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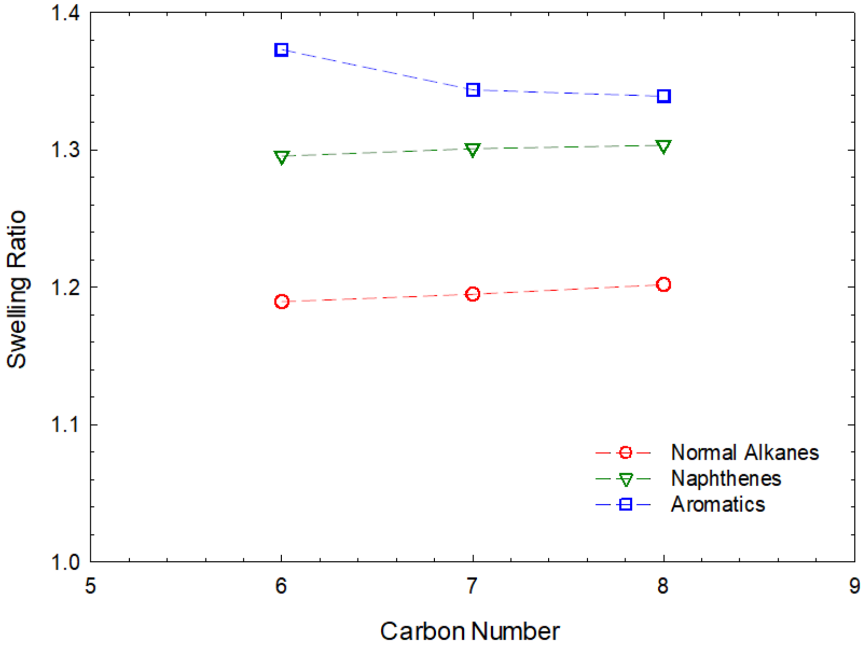

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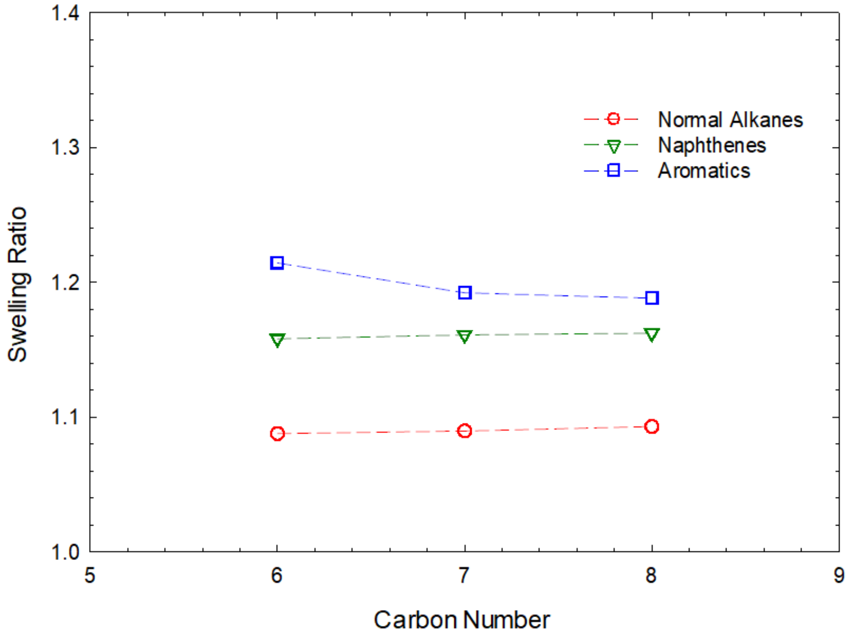


(c)

Figure 3-4 Swelling ratio of different types of kerogens as a function of carbon numbers: (a) Draupne Type II Kerogen; (b) average type II kerogen; (c) type IIIC kerogen.

3.2.3. Effect of Sulfur Content on Kerogen Swelling Ratio

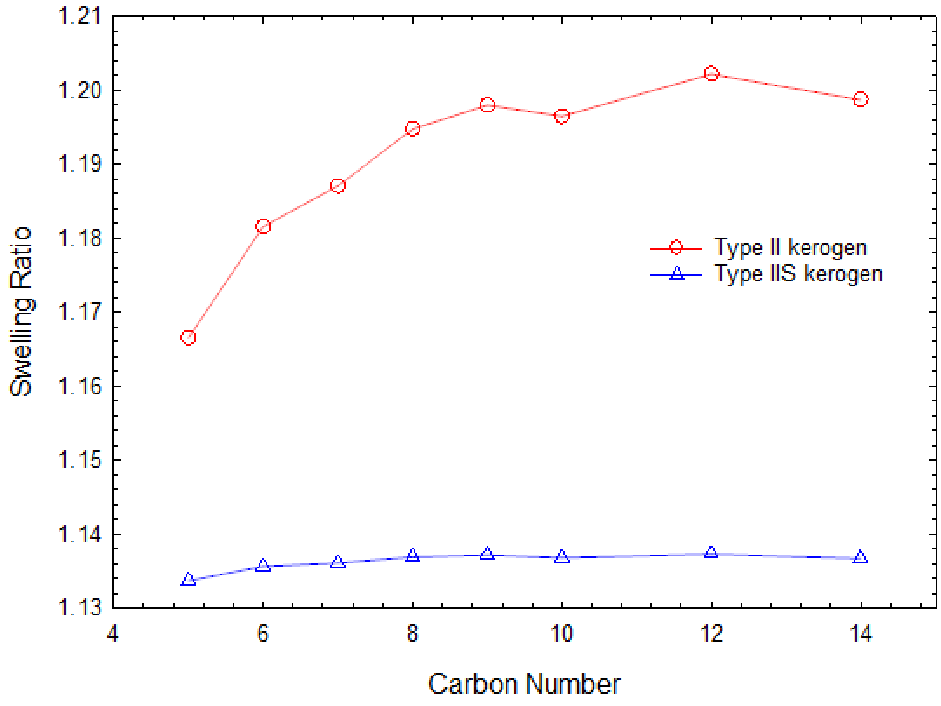
It has been proved that type II kerogen with a high sulfur content (8%-14wt% organic sulfur[8], named type IIS kerogen) begins to generate oil at lower thermal maturity than typical type II kerogen[8], which suggests that the high-sulfur kerogen may have different thermodynamic properties. In this part, 16 solvents are selected to study the effect of sulfur content in kerogen on kerogen swelling ratio. The thermodynamic properties of type II and type IIS kerogen with the same percentage of fractional conversion are shown in table 3-8[9] and the molar volume and solubility parameter of solvents are shown in table 3-9[3, 4, 7]. Figure 3-5 (a), Figure 3-5 (b) and Figure 3-5 (c) show the comparison of the swelling ratios of type II and type IIS kerogen in normal alkanes, naphthenes and aromatics. We can see from Figure 3-5 that the swelling ratios of both type II and type IIS kerogen in aromatic components are larger than those in normal alkanes and naphthenes. Compared with normal alkanes, the swelling ratios of both type II and type IIS kerogen in naphthenes are larger. It can be also seen that the swelling ratio of type IIS kerogen is smaller than the regular type II kerogen. The reduction of the swelling ratio of type IIS kerogen is more obvious when the solvent is aromatic. This result indicates that type IIS kerogen has a lower capacity to retain hydrocarbons than regular type II kerogen, which explains why high-sulfur kerogen begins to generate oil at lower thermal maturity.

Table 3-8 Thermodynamic parameters of the regular type II kerogen and type IIS kerogen[9]

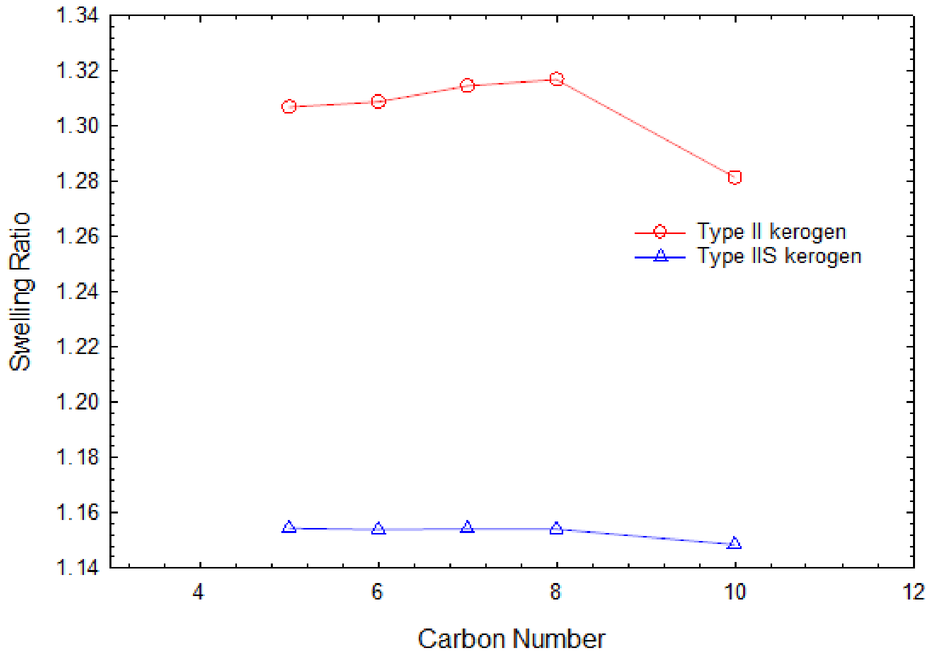
Property	**Solubility Parameters (δ_0) (J/cm^3)**	**Cross-link Density (N_e/v_0) (mol/cm^3)**	**Native Swelling Fraction (v_{eq})**
Type II Kerogen	22.1	0.12	0.76
Type IIS Kerogen	22.1	0.93	0.87

Table 3-9 Solubility parameters and molar volumes of different solvents at 25ºC[3, 4, 7]

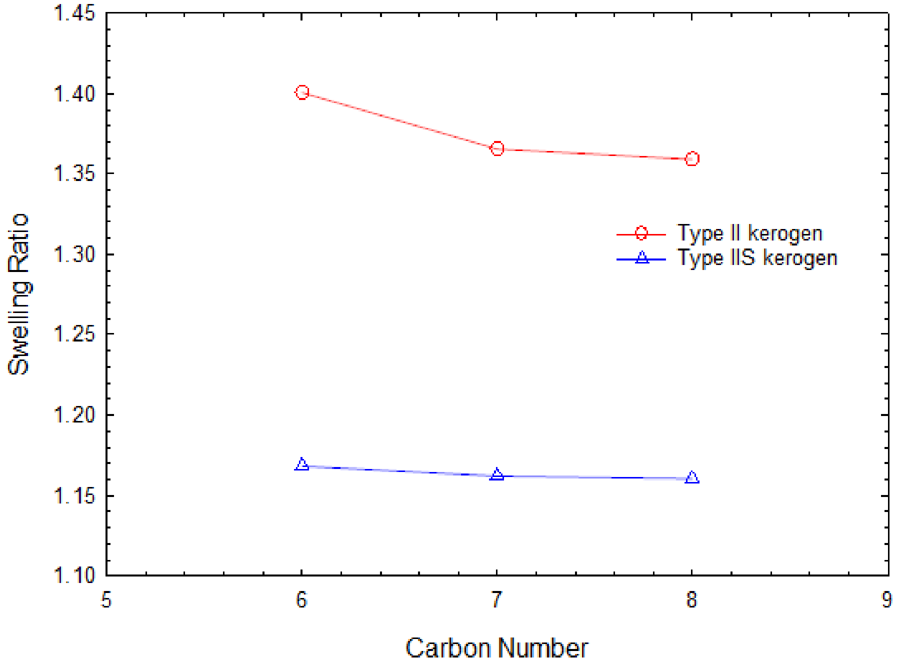
Solvent Name	Solubility Parameter (J/cm^3)	Molar Volume (cm^3/mol)
n-pentane	14.4	114.2
n-hexane	14.9	130.6
n-heptane	15.2	147
n-octane	15.5	163.4
n-nonane	15.7	179.7
n-decane	15.8	195.9
n-dodecane	16.1	228.9
n-tetradecane	16.2	261.6
cyclopentane	16.4	94.7
cyclohexane	16.8	108.7
cycloheptane	17.2	121.3
cyclooctane	17.5	134.4
cyclodecane	17.1	164.3
benzene	18.7	89.4
toluene	18.2	106.9
o-xylene	18.4	121.2



(a)



(b)



(c)

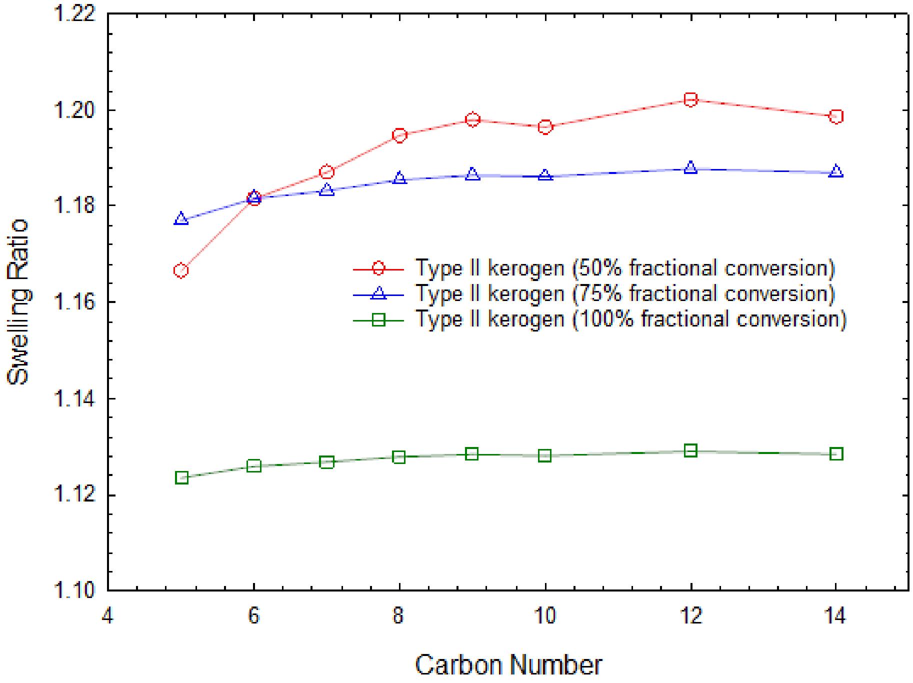
Figure 3-5 Comparison between the swelling ratio of type II and type IIS kerogen in: (a) normal alkanes; (b) naphthenes; (c) aromatics.

3.2.4. Effect of Thermal Maturity on Kerogen Swelling Ratio

Type II kerogen with three different percentages of fractional conversion (50%, 75% and 100%) are selected to study the effect of thermal maturity on kerogen swelling ratio. The solvents and their solubility parameters and molar volumes used in the calculations are listed in Table 3-9[3, 4, 7] and the thermodynamic properties of kerogens with different thermal maturity are shown in Table 3-10[9]. It can be seen from Table 3-10 that the solubility parameter of type II kerogen increases slightly with an increase in the thermal maturity, indicating an increase in aromaticity of kerogen. On the other hand, an obvious increase can be observed in the cross-linked density with an increase in the thermal maturity. Figure 3-6 (a), Figure 3-6 (b) and Figure 3-6 (c) show the comparison of the swelling ratios of type II kerogen with different percentage of fractional conversions in normal alkanes, naphthenes and aromatics. It can be observed that the low-maturity type II kerogen exhibits larger swelling ratios in different types of solvents and the lighter saturate components induce a smaller swelling ratio.

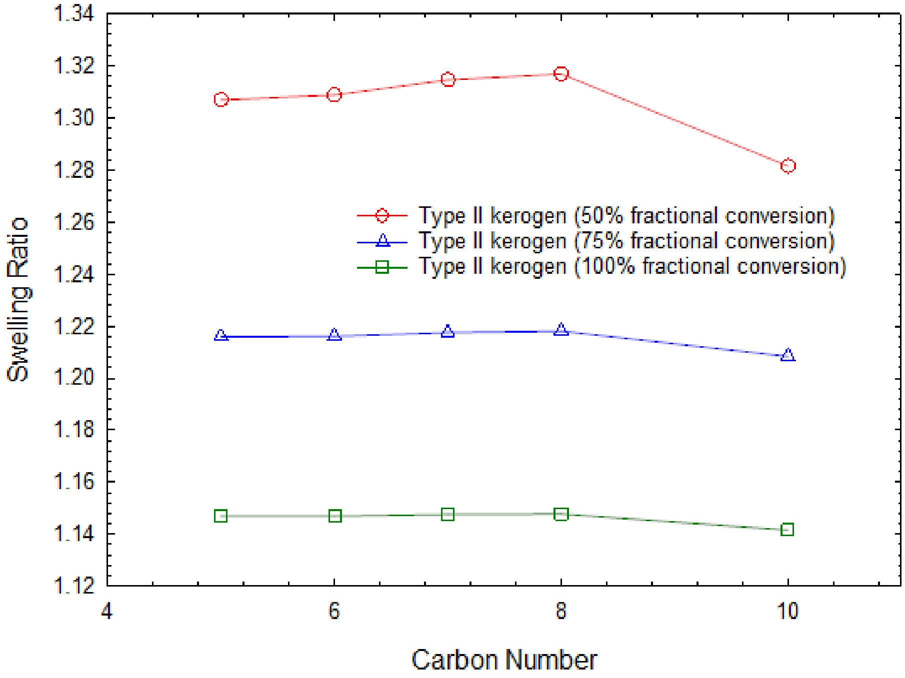
Table 3-10 Thermodynamic parameters of the type II kerogen with 50%, 75% and 100% fractional conversions[9].

Property	**Solubility Parameters (δ_0) (J/cm^3)**	**Cross-link Density (N_e/v_0) (mol/cm^3)**	**Native Swelling Fraction (v_{eq})**
Type II Kerogen (50% fractional conversion)	22.1	0.12	0.76
Type II Kerogen (75% fractional conversion)	22.6	0.52	0.82
Type II Kerogen (100% fractional conversion)	23.1	0.93	0.87



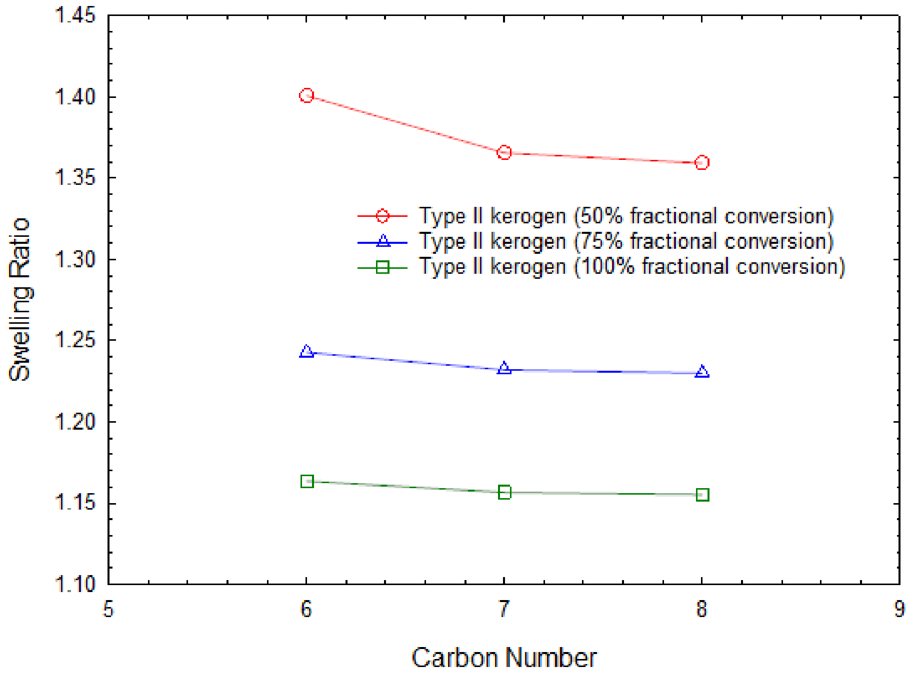
1.22
1.20
1.18
1.16
1.14
1.12
1.10
Swelling Ratio
4
6
8
10
12
14
Carbon Number
Type II kerogen (50% fractional conversion)
Type II kerogen (75% fractional conversion)
Type II kerogen (100% fractional conversion)

(a)



1.34
1.32
1.30
1.28
1.26
1.24
1.22
1.20
1.18
1.16
1.14
1.12
Swelling Ratio
4
6
8
10
Carbon Number
Type II kerogen (50% fractional conversion)
Type II kerogen (75% fractional conversion)
Type II kerogen (100% fractional conversion)

(b)



(c)

Figure 3-6 Comparison of the swelling ratios of type II kerogen with different percentages of fractional conversion in: (a) normal alkanes; (b) naphthenes; (c) aromatics.

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CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1. Conclusions

In this study, the extended FRRS model[1] is implied to properly predict the swelling behavior of kerogen. The FRRS code we have programmed is first successfully validated by kerogen swelling tests[1, 2] and then applied to predict the swelling ratios of different types of kerogens induced by different solvents. From the calculation results, we can draw the following conclusions:

- The swelling ratio of kerogen follows a bell-shaped trend with the change of solvent solubility parameter and molar volume, which is in qualitative agreement with the experimental data[3] and the prediction results from Huang *et al.* [4].
- Swelling ratio of kerogen increases with an increasing solubility parameter of solvent and reaches a maximum when the solubility parameter of solvent is close or equal to the solubility parameter of kerogen, and then decreases with the further increase in the solubility parameters.
- The swelling ratio of kerogen decreases with the increasing molar volume of solvents.
- Compared with normal alkanes, naphthenes lead to larger swelling ratios of kerogen.
- Aromatics induce larger swelling ratios of kerogen compared with normal alkanes and naphthenes.
- The swelling ratio of type IIS kerogen is smaller than the regular type II kerogen. This trend is more obvious when the solvent is aromatic. The lower swelling ratio indicates that type IIS kerogen has a lower capacity to retain hydrocarbons than regular type II kerogen, which explains why high-sulfur kerogen begins to generate oil at lower thermal

maturity.

- The swelling ratio of type II kerogen decreases with an increasing thermal maturity.

4.2. Recommendations

- In this work, we only consider the phase equilibrium between oleic phase and kerogen phase. However, it is shown that kerogen also generates water during its maturation process. Thus, a three-phase aqueous-oil-kerogen equilibrium calculation algorithm may be necessary to better honor the effect of water's presence on the phase behavior in shale reservoirs.
- The kerogen swelling tests conducted in the literature are conducted on pure components. Experimental data of kerogen swelling in solvent mixtures is required to further validate this model.

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