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Liquid–Liquid Equilibria of the Ternary System Thiophene + Octane + Dimethyl Sulfoxide at Several Temperatures

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Abstract Liquid–liquid equilibria (LLE) data of the ternary system thiophene + octane + dimethyl sulfoxide at 40°C, 50°C, and 60°C under atmospheric pressure were determined using an equilibrium cell with the standard curve method. The distribution of thiophene between extract and raffinate was measured and a practical formula of equilibria data for industrial extraction was proposed. NRTL model and UNIQUAC model were used to correlate and calculate LLE data of the system, and model parameters were determined using the simplex optimization method and imitative Newton method with a minimized objective function of mole fraction deviation. The rule of thermodynamic equilibria was used to deal with multi-roots problem in correlating process. Agreement between predicted and experimental data was satisfactory. The average absolute deviations of the NRTL and UNIQUAC models of thiophene mass fraction were 0.0040 and 0.0078, respectively. Both NRTL and UNIQUAC models were suitable for the calculation of LLE data of the ternary system thiophene + octane + dimethyl sulfoxide. The correlation accuracy of NRTL model is inferior to that of UNIQUAC model.

Keywords Liquid–liquid equilibria · Thiophene · Octane · Dimethyl sulfoxide · NRTL model · UNIQUAC model

Introduction

Sulfur is an undesirable component in gasoline since it creates corrosive combustion by-products, releases sulfur oxides into atmosphere, and increases deposits on fuel injection and combustion systems. Increasingly tight emission standards are or will be imposed worldwide aiming to reduce air pollution and greenhouse effect. Such standards are forcing the oil refiners over the world to produce low-sulfur gasoline starting now or soon.

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Hydrodesulfurization (HDS), a key process in existing petroleum refining operations, uses various catalysts to add hydrogen in order to reduce unwanted sulfur components. Unfortunately, the gasoline HDS is a high-cost process under high pressure (up to 500psig) and high temperature (250–400°C). For gasoline deep desulfurization, only using HDS technique also suffers from high octane number loss and low liquid product yield. Compared with HDS technique, a combined technique of extractive distillation (ED) + HDS can provide many advantages, such as low cost, low octane number loss, and high liquid product yield [1–3].

Component distribution between the two phases of extraction system can be estimated using proper thermodynamic models (NRTL, UNIQUAC, UNIFAC, etc.) [4]. Liquid–liquid equilibrium (LLE) data of sulfide (existing in gasoline) + hydrocarbons + solvent (selected) are necessary to estimate the model parameters used for the design and modeling of gasoline extraction distillation. Unfortunately, such data have been rarely reported in the literature.

The main aim of this work was to obtain the model parameters of the system studied and to evaluate the performance of the models (NRTL [5], UNIQUAC [6]) for gasoline extraction distillation. Thiophene was selected as typical sulfide existing in gasoline, dimethyl sulfoxide was experimentally selected as the solvent, and octane was selected as typical hydrocarbon in gasoline. Experimental LLE data were determined for the ternary system at 40°C, 50°C, and 60°C, respectively, under atmospheric pressure. The experimental data were correlated using the NRTL and UNIQUAC models for the activity coefficient. New model parameters for both models were estimated using the simplex minimization method and a composition-based objective function. The results were evaluated in terms of average absolute deviations between experimental and calculated mass fractions of thiophene.

Experiments

Chemicals

Dimethyl sulfoxide and octane (AR) were supplied by Tianjin Guangfu Fine Chemical Research Institute. Thiophene (AR) was purchased from J&K Chemical Ltd. and was used without further purification. Dimethyl sulfoxide was purified and dehydrated by 3A activated molecular sieve. The purity was checked by the gas chromatography (SP3420, FID) and was higher than 99.5% by mass fractions.

Equilibria Measurements

LLE measurements of the ternary system were made at different temperatures (40°C, 50°C, and 60°C, respectively) under atmospheric pressure. Liquid mixtures of known overall compositions in mass fractions were prepared and introduced into a glass equilibrium cell with a water jacket to maintain isothermal condition. The volume of the cell was about 60mL and was almost fully filled. The mixture was vigorously agitated by a magnetic stirrer. After several initial tries and taking samples at different time intervals, it was found that further increases in the agitation time (minimum time 2h) and the settling time (minimum time 3h) have no considerable effect on the equilibrium phase compositions. Therefore, the mixture was stirred for 2h at least and then left to settle for 3h for phase separation.

The cell temperature was regulated by circulating water from a thermostatic bath (CS501, from Shanghai Precision Science Instrument Co. Ltd.), which was equipped with a temperature controller. It is capable to maintain the temperature fluctuation within ±0.1°C

by a high precision digital thermometer. In the experiments, the actual fluctuation of the temperature was within ±0.05°C.

At the end of the settling period, three to four samples, carefully taken from the raffinate and extract phases, respectively, were analyzed by a gas chromatography (SP3420, Beijing Analysis Instrument Corp., FID). The estimated accuracy of the compositions in mass fractions was within ±0.01. Good separation of these components was obtained on a 50-m-long AT.OV-1 column (0.32mm in diameter and 0.5μm film thickness) and used with a programmed temperature analysis. First, the column temperature was increased from 80°C to 280°C at increment rate of 25°C/min and maintained at 280°C for 1min, then was further increased to 310°C at increment rate of 10°C/min and maintained at 310°C for 10min; injector temperature was 320°C and the detector temperature was 380°C; hydrogen was used as the carrier gas at 30mL/min; the volume of the injected liquid sample was 1μL.

Results and Discussion

Experimental Data

LLE data of the ternary system thiophene (1) + octane (2) +dimethyl sulfoxide (3) at 40°C, 50°C, and 60°C, respectively, under atmospheric pressure are presented in Table 1; x_i (i = 1, 2, 3) is the concentration of the ith component expressed in mass fraction.

Table 1 LLE data of thiophene (1) + octane (2) + dimethyl sulfoxide (3) system (ω,%).

t (°C)	Raffinate			Extract		
	x_1	x_2	x_3	x_1	x_2	x_3
40	1.0397	98.75	0.2133	1.4446	0.0872	98.47
	0.6485	99.01	0.3399	0.9266	0.1390	98.93
	0.5729	99.01	0.4127	0.8880	0.1689	98.94
	0.4459	99.10	0.4547	0.7499	0.1860	99.06
	0.3645	99.16	0.4788	0.6603	0.1959	99.14
	0.3372	99.17	0.4927	0.5567	0.2016	99.24
	0.2669	99.23	0.5007	0.5264	0.2049	99.27
	0.2610	99.23	0.5053	0.4406	0.2068	99.35
50	0.8347	98.95	0.2133	1.3622	0.0872	98.55
	0.6456	99.01	0.3399	1.0096	0.1390	98.85
	0.5140	99.07	0.4127	0.8237	0.1689	99.01
	0.4222	99.12	0.4547	0.6668	0.1860	99.15
	0.3522	99.17	0.4788	0.5436	0.1959	99.26
	0.3439	99.16	0.4927	0.4085	0.2016	99.39
	0.3025	99.20	0.5007	0.4531	0.2049	99.34
	0.1985	99.30	0.5053	0.4212	0.2068	99.37
60	0.7838	99.00	0.2133	1.2105	0.0872	98.70
	0.8078	98.85	0.3399	0.9911	0.1390	98.87
	0.5877	99.00	0.4127	0.8799	0.1689	98.95
	0.5089	99.04	0.4547	0.6436	0.1860	99.17
	0.4173	99.10	0.4788	0.5450	0.1959	99.26
	0.4252	99.08	0.4927	0.4670	0.2016	99.33
	0.3923	99.11	0.5007	0.4337	0.2049	99.36
	0.3077	99.19	0.5053	0.3899	0.2068	99.40

Data Correlation

The effectiveness of a solvent can be expressed by the selectivity, β, and the distribution coefficients, K_i [7]. The selectivity is calculated by the equation:

$$\beta = \frac{K_1}{K_2}, \tag{1}$$

where K_i, is the distribution coefficient of the ith component, which is calculated by the equation

$$K_i = \frac{x_i^{II}}{x_i^{I}}, \tag{2}$$

where the superscripts I and II represent raffinate and extract, respectively.

From the experimental data, the distribution coefficients of thiophene and octane and the selectivity coefficients of dimethyl sulfoxide solvent at different temperatures were calculated and plotted in Figs. 1 and 2. The horizontal axis of Fig. 2, R, is the ratio of solvent to oil. Figure 2 shows that dimethyl sulfoxide is a good solvent to separate tiophene from octane.

The NRTL and UNIQUAC models were used to correlate the experimental data of the ternary system. In fitting the UNIQUAC interaction parameters, the structural parameters r and q were used for the pure components. The values of the structural parameters r and q are presented in Table 2. The non-randomness parameter α_{ij} of the NRTL model was set to 0.3 [8]. The estimated results are given in Tables 3 and 4. The model parameters were determined using the simplex optimization method and imitative Newton method with a minimized objective function of mole fraction deviation [9]. The rule of thermodynamic equilibrium was used to deal with multi-roots problem in correlating process. The objective function, F, is given as

$$F = \min \sum_{i=1}^{N_P} \sum_{j=1}^{N_C} \left| \frac{\gamma_{ij}^{I}}{\gamma_{ij}^{II}} x_{ij}^{I} - x_{ij}^{II} \right|^2 \tag{3}$$

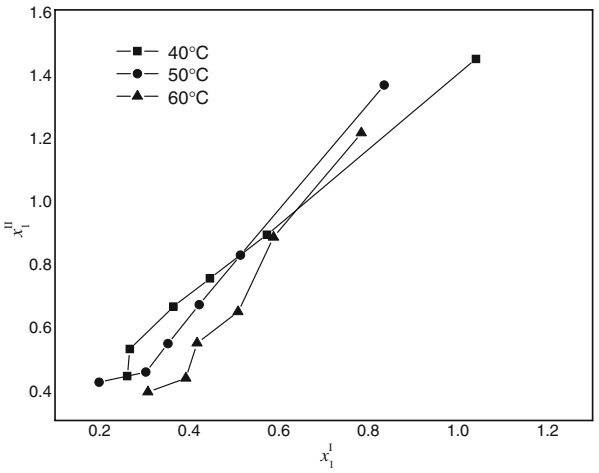

Fig. 1 Distribution curves of thiophene (1) + octane (2) + dimethyl sulfoxide (3) system

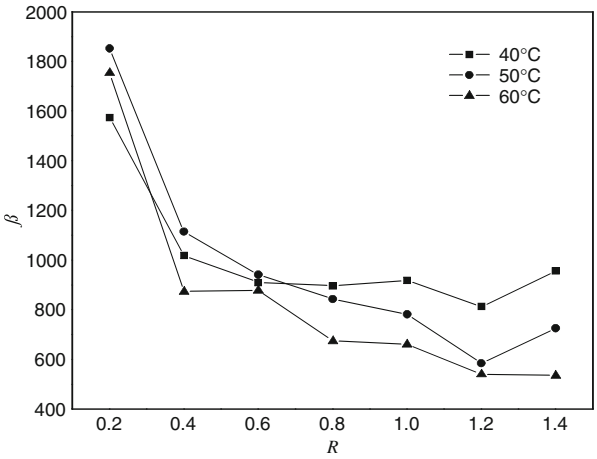

Fig. 2 Selectivity coefficients of thiophene (1) + octane (2) + dimethyl sulfoxide (3) system

where N_p is the number of experimental points, N_c the number of experimental components, and γ_i the activity coefficient.

Correlation Results

An attempt was made to examine the predicting capability of the NRTL and UNIQUAC models with the model parameters obtained above. The average absolute deviations of the calculated data and experimental data can be obtained by Eqs. 4 and 5, respectively.

$$\Delta x_i^{\mathrm{I}} = \sqrt{\sum_{k=1}^{N_P} \left(x_{ki}^{\mathrm{I}} - x_{ki}^{*\mathrm{I}}\right)^2 \Big/ N_{\mathrm{P}}} \tag{4}$$

$$\Delta x_i^{\mathrm{II}} = \sqrt{\sum_{k=1}^{N_P} \left(x_{ki}^{\mathrm{II}} - x_{ki}^{*\mathrm{II}}\right)^2 \Big/ N_P}. \tag{5}$$

The obtained average absolute deviations using the NRTL model and UNIQUAC model are given in Tables 5 and 6, respectively.

By observing Tables 5 and 6, we can conclude that both NRTL and UNIQUAC models are capable of reproducing the LLE data of these systems. Further comparing the correlation accuracy of Table 5 with that of Table 6, we can see that the NRTL model is inferior to UNIQUAC model.

Table 2 The structural parameters r and q of UNIQUAC model.

Solvents	r	q
Thiophene	2.8569	2.140
Octane	5.8466	4.936
Dimethyl sulfoxide	2.8266	2.472

Table 3 Estimated NRTL parameters.

t(°C)	Model parameters						F
	Δg_{12}	Δg_{13}	Δg_{21}	Δg_{23}	Δg_{31}	Δg_{32}	
40	−9,434.7	−1,395,137.5	2,160.9	−2,160.9	−42,822.3	8,078.5	0.2777
50	−9,881.0	−1,146,509.2	2,287.2	−5,932.7	−45,660.5	8,337.5	0.2698
60	−11,720.7	−1,181,988.3	4,184.4	−8,006.4	−57,415.6	8,975.0	0.2138

Table 4 Estimated UNIQUAC parameters.

t (°C)	Model parameters						F
	Δu_{12}	Δu_{13}	Δu_{21}	Δu_{23}	Δu_{31}	Δu_{32}	
40	23,979.39	−10,861.69	16,603.04	23,979.39	23,979.39	977.80	1.4778
50	22,882.88	−11,396.61	24,745.14	24,745.14	24,745.14	1,008.63	1.4071
60	−10,346.62	−10,827.80	25,510.88	25,510.88	25,510.88	637.87	4.4596

Table 5 Average absolute deviation of calculated results and experimental data of the ternary system(NRTL model).

t (°C)	Average deviation of composition					
	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
40	0.0046	0.2451	8.9513×10^{-4}	0.0072	0.0981	0.1905
50	0.0039	0.2873	8.6819×10^{-4}	0.0053	0.1135	0.1791
60	0.0036	0.2041	9.3005×10^{-4}	0.0064	7.7136×10^{-4}	0.2116
Average	0.0040	0.2455	8.9779×10^{-4}	0.0063	0.0708	0.1937

Table 6 Average absolute deviation of calculated results and experimental data of the ternary system (UNIQUAC model).

t (°C)	Average deviation of composition					
	Δx_1^{I}	Δx_2^{I}	Δx_3^{I}	Δx_1^{II}	Δx_2^{II}	Δx_3^{II}
40	0.0022	0.0048	0.0022	2.5000×10^{-4}	0.0018	2.6926×10^{-4}
50	0.0020	0.0046	0.0021	2.5000×10^{-4}	0.0018	2.6926×10^{-4}
60	0.0193	0.0274	0.0129	9.2534×10^{-4}	0.0018	1.9365×10^{-4}
Average	0.0078	0.0123	0.0057	4.7511×10^{-4}	0.0018	2.4406×10^{-4}

Conclusions

LLE data of the ternary system thiophene + octane + dimethyl sulfoxide at 40 °C, 50 °C, and 60 °C under atmospheric pressure have been measured using equilibrium cell with the standard curve method.

The NRTL and UNIQUAC models were used to correlate and calculate LLE data of the ternary system. The results were considered very satisfactory for both models. The model parameters were determined using the simplex optimization method and imitative Newton method with a minimized objective function of mole fraction deviation. The average absolute deviations of thiophene mass fraction calculated by NRTL and UNIQUAC models were 0.0040 and 0.0078 respectively. Both NRTL and UNIQUAC models are suitable for the calculation of the LLE data of the ternary system thiophene + octane + dimethyl sulfoxide. The correlation accuracy of NRTL model is inferior to that of UNIQUAC model.

F objective function
K distribution coefficients
N_p number of experimental points
u parameter for UNIQUAC (J/mol)
α non-randomness factor for NRTL
γ_i activity coefficient
g interaction parameter for NRTL (J/mol)
N_c number of experimental components
R the ratio of solvent to oil
x composition of liquid phase, mass fraction
β selectivity

Superscript:
I Raffinate
II Extract

Subscripts:
i, j, k component

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