Liquid−Liquid Equilibria for Benzene + Cyclohexane + *N*,*N*-Dimethylformamide + Potassium Thiocyanate

Hongxing Dong, Xiaoguang Yang, and Jin Zhang*

The College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, P. R. China

Experimental liquid−liquid equilibrium (LLE) data were measured for benzene + cyclohexane + *N*,*N*-dimethylformamide (DMF) + potassium thiocyanate (KSCN) at atmospheric pressure and 303.15 K. The experimental data was correlated using the Othmer−Tobias correlation. The selectivity coefficients of DMF + KSCN for benzene are 2 to 11 in this work. The results revealed that the selectivity coefficients increased with the decrease in concentration of benzene in the raffinate and increased with the increase of the mass fraction of KSCN in the DMF + KSCN mixture. Considering the high selectivity for benzene, DMF + KSCN may be used as a potential extracting solvent for the separation of benzene and cyclohexane.

Introduction

As a very important bulk chemical, cyclohexane is mainly produced by catalytic hydrogenation of benzene, and the removal of the unreacted benzene from the reactor's effluent stream is a very important process.[1,2] However, the separation of benzene and cyclohexane mixtures has been proved one of the most difficult tasks in the petrochemical industry because of their close boiling points, approximately equal molecular volumes, and easy formation of azeotropic mixture.[1,3,4] Conventional distillation cannot achieve the task in practice. Special distillation such as azeotropic distillation and extractive distillation are usually employed for benzene/cyclohexane separation,[5,6] while these two processes suffer from complexity and high energy consumption. Furthermore, the technology of pervaporation (PV), emerging as an economical and simple alternative to many organic/organic separation applications,[7,8] has still not been employed for this benzene + cyclohexane separation in industry.

Liquid−liquid extraction is another alternative industrial separation process for homogeneous liquid mixtures. An appropriate extractant should have a good selectivity for benzene, a low volatility for loss reduction, easy regeneration, and minimum corrosion characteristics in addition to being environmentally friendly. Certainly, the industrial solvents must be cheap enough. Previous work shows that ethylene carbonate can be used as a suitable solvent in the recovery of aromatics, such as toluene and *m*-xylene from alkane mixtures.[9] The obtained liquid−liquid equilibrium (LLE) results for the mixture (ethylene carbonate + benzene + cyclohexane) show that benzene can be extracted from the (benzene + cyclohexane) mixture and the selectivity coefficient of ethylene carbonate is much higher at the low temperature.[10] However, there is still a limitation that the temperature should be above the melting point of ethylene carbonate. Furthermore, ionic liquids have a good selectivity for aromatics versus alkanes and are widely researched for the extraction of benzene from the benzene + cyclohexane mixture. Ionic liquids as the extractant have attracted much attention since the 1990s. Meindersma has used [emim] Tf_2N as the extractant for the benzene + cyclohexane separation, and the selectivity coefficient can be 17.7.[11] Wang et al. studied the performance of 1-methyl-3-methylimidazolium dimethylphosphate ([C_1min][DMF]), or 1-ethyl-3-methylimidazolium diethylphosphate ([C_2min][DEP]), on extracting benzene from cyclohexane at atmospheric pressure and (298.2 and 313.2) K.[12] Lu et al. determined LLE for benzene + cyclohexane + 1-butyl-3-methylimidazolium hexafluorophosphate.[13] However, ionic liquids are so expensive that they are difficult to be applied industrially. So it is necessary to look for an economical and simple extractant for the separation.

Ethirajulu et al. have reported studies on the selectivity improvement of *N*,*N*-dimethylformamide (DMF) using ethylene glycol as a cosolvent.[14] In this work, the complex solvent system, potassium thiocyanate (KSCN) dissolved in DMF, is found to be a good extractant for the separation of benzene from cyclohexane because the solvent is highly selective and very cheap. Phase equilibrium data are required for the evaluation of solvent combinations and design of extraction equipment, so the experimental LLE data were measured for benzene + cyclohexane + DMF + KSCN at 303.15 K and atmospheric pressure.

Experimental Section

Materials. The chemicals used in this study were benzene, cyclohexane, KSCN, and DMF. DMF with a nominal minimum mass fraction of 0.995 was used, received from Tianjin Guangfu Institute of Fine Chemicals without further purification. Benzene and cyclohexane with a nominal minimum mass fraction of 0.995 were used, received from Tianjin Fuyu Fine Chemicals Company. The nominal mass fractions of water for benzene and cyclohexane were both less than $5 \cdot 10^{-3}$. KSCN was provided by Tianjin Fucheng Chemical Reagent Factory. The purity of KSCN was above 0.985 in mass fraction.

Apparatus and Procedures. Complex solvents KSCN and DMF in ratios of 10:90, 15:85, 16:84, and 17:83 were prepared by dissolving a certain amount of KSCN in DMF solvent under stirring. LLE experiments were carried out in a conical flask with 100 mL volume in a thermostat. The temperature was controlled to 303.15 K with ± 0.1 K. The benzene + cyclohexane solution with the benzene mole fraction from 0.12

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* Corresponding author. E-mail address: zj343311973@126.com. Tel.: 86-1512408443.

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Table 1. LLE Data in Mass Fraction for Benzene (1) + Cyclohexane (2) + DMF (3) + KSCN (4) at 303.15 K and the Selectivity (*S*) and Distribution (*k*) Coefficients of Benzene versus Cyclohexane

extract phase				raffinate phase					
$\omega_{1,\mathrm{I}}$	$\omega_{2,\mathrm{I}}$	$\omega_{3,\mathrm{I}}$	$\omega_{4,\mathrm{I}}$	$\omega_{1,\mathrm{II}}$	$\omega_{2,\mathrm{II}}$	$\omega_{3,\mathrm{II}}$	$\omega_{4,\mathrm{II}}$	*S*	*k*
				$\omega(4)/\omega(3) = 10:90$					
0.054	0.043	0.722	0.181	0.122	0.757	0.109	0.012	7.79	0.44
0.102	0.057	0.672	0.168	0.175	0.703	0.110	0.012	7.19	0.58
0.149	0.071	0.624	0.156	0.219	0.644	0.124	0.014	6.17	0.68
0.207	0.084	0.567	0.142	0.257	0.595	0.133	0.015	5.71	0.81
0.249	0.093	0.526	0.131	0.311	0.460	0.206	0.023	3.96	0.80
0.299	0.126	0.460	0.115	0.349	0.408	0.218	0.024	2.77	0.86
				$\omega(4)/\omega(3) = 15:85$					
0.050	0.030	0.737	0.184	0.139	0.802	0.054	0.006	9.62	0.36
0.100	0.048	0.682	0.170	0.199	0.736	0.059	0.007	7.71	0.50
0.151	0.062	0.629	0.157	0.241	0.691	0.062	0.007	6.98	0.63
0.202	0.077	0.577	0.144	0.275	0.638	0.078	0.009	6.09	0.73
0.246	0.088	0.533	0.133	0.321	0.587	0.083	0.009	5.11	0.77
0.301	0.112	0.470	0.117	0.369	0.516	0.103	0.011	3.76	0.82
				$\omega(4)/\omega(3) = 16:84$					
0.053	0.028	0.735	0.184	0.153	0.832	0.013	0.001	10.29	0.35
0.082	0.031	0.710	0.177	0.222	0.747	0.028	0.003	8.90	0.37
0.102	0.033	0.692	0.173	0.265	0.703	0.029	0.003	8.20	0.38
0.130	0.037	0.667	0.167	0.312	0.615	0.066	0.007	6.93	0.42
0.142	0.041	0.654	0.164	0.359	0.538	0.093	0.010	5.19	0.40
				$\omega(4)/\omega(3) = 17:83$					
0.054	0.024	0.692	0.231	0.165	0.833	0.001	0.001	11.36	0.33
0.073	0.025	0.677	0.226	0.241	0.743	0.014	0.002	9.00	0.30
0.095	0.028	0.658	0.219	0.279	0.707	0.013	0.001	8.60	0.34
0.112	0.029	0.644	0.215	0.324	0.658	0.016	0.002	7.84	0.35

to 0.69 was put in the conical flask and kept at the temperature of 303.15 K. Then the complex solvent was added into the solution, and the volume ratio of (benzene + cyclohexane) to (DMF + KCNS) is 1. The system, benzene + cyclohexane + DMF + KSCN, was stirred for 1 h and kept still for 4 h at atmospheric pressure and 303.15 K. The time used here for equilibrium and phase splitting was fixed according to results from our previous experiments. The samples were carefully taken from each phase and analyzed.

The compositions of the raffinate (cyclohexane-rich phase) and extract phase were detected by gas chromatography. The gas chromatography was Shimadzu GC-14C. The injected volume was 0.2 μL. The injection temperature was 180 °C. Detection was performed by a flame ionization detector (FID) operating at 190 °C. The other analysis conditions include the following: a packed column, GDX-502, 1.5 m × 3 mm; column temperature, 175 °C; nitrogen pressure, 72 kPa; air pressure, 62 kPa; hydrogen pressure, 52 kPa; using the addition internal standard method.[15] Benzene was used as the internal standard. The sample constitute was given by the N3000 GC workstation according to the area of each chromatograph peak. The weight correction factors of cyclohexane and DMF were measured by a standard sample. Once the amount of benzene component had been determined, the mass fraction of cyclohexane and DMF was calculated via weight correction factor for the raffinate and extract phase samples. The KSCN cannot be detected by GC-14C. The mass fraction of KSCN was calculated via mass balance for raffinate and extract phase samples, respectively. With the low volatility of KSCN, a block of glass wool was put in the vaporizing chamber, to avoid pollution of the chromatographic column. Two samples were made for each phase, and triplicate injections were made for each sample in the GC analysis. The uncertainty of compositions was within 0.001 for the same sample. The greatest error of LLE data in these experiments was found to be less than 0.03. When the mass fraction of KSCN in the DMF + KSCN increases, the error of LLE data becomes larger and larger, and the measurement of data becomes difficult. Sometimes, if the KSCN was salted out from the extract phase when sampling, the measurement is not accurate, and the data need to be detected again.

Results and Discussion

It was found that KSCN was salted out from the complex solvent when the mixing ratio of KSCN and DMF was over 17:83. So, the experiments were not accomplished when the mixing ratio of KSCN and DMF was beyond 17:83.

The experimental results were summarized in Table 1 and displayed on the triangular diagrams, shown in Figures 1 to 4. It can be seen that the benzene mass fraction increases in the extract phase and the cyclohexane decreases in the raffinate

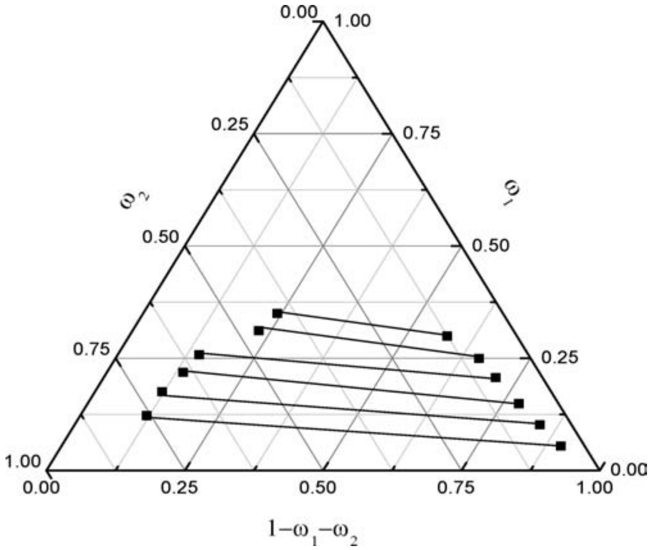

Figure 1. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + KSCN (4) quaternary system at 303.15 K, when the KSCN and DMF are in a ratio of 10:90. ω_1 refers to the mass fraction of benzene in the sample; ω_2 refers to the mass fraction of cyclohexane in the sample.

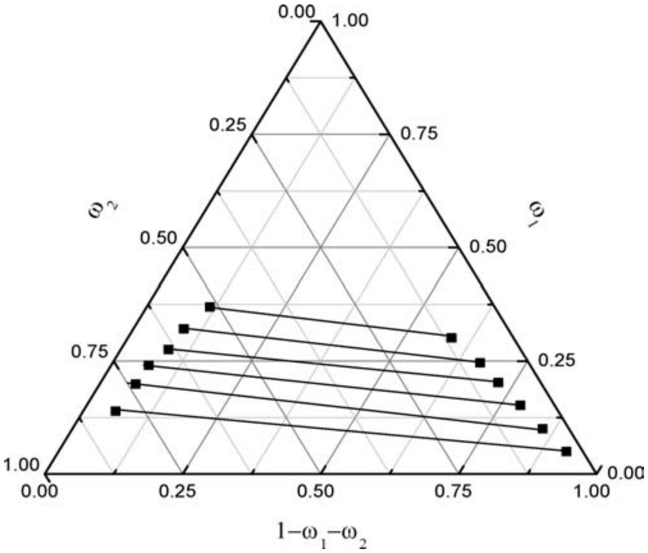

Figure 2. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + KSCN (4) quaternary system at 303.15 K, when the KSCN and DMF are in a ratio of 15:85. ω_1 refers to the mass fraction of benzene in the sample; ω_2 refers to the mass fraction of cyclohexane in the sample.

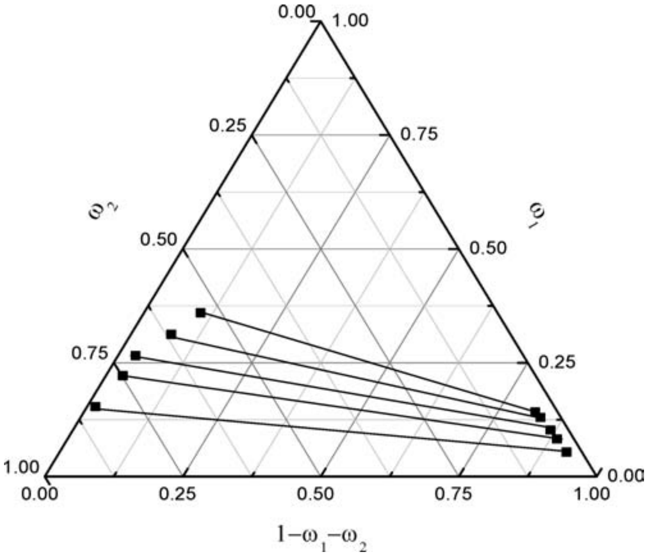

Figure 3. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + KSCN (4) quaternary system at 303.15 K, when the KSCN and DMF are in ratio of 16:84. ω_1 refers to the mass fraction of benzene in the sample; ω_2 refers to the mass fraction of cyclohexane in the sample.

phase when the benzene concentration increases in the raffinate phase, if the salt concentration in the extraction agent is maintained at the same level.

Selectivity (*S*) and distribution coefficients are important in assessing the feasibility of utilizing a solvent in liquid−liquid extraction. The following eqs 1 and 2 were used to calculate selectivity and distribution coefficients of benzene, respectively.

$$S = \frac{\omega_{1,\mathrm{I}}/\omega_{1,\mathrm{II}}}{\omega_{2,\mathrm{I}}/\omega_{2,\mathrm{II}}} \tag{1}$$

$$k = \omega_{1,\mathrm{I}}/\omega_{1,\mathrm{II}} \tag{2}$$

where $\omega_{1,\mathrm{I}}$ and $\omega_{2,\mathrm{I}}$ refer to the mass fraction of benzene and cyclohexane in the extract phase, respectively. $\omega_{1,\mathrm{II}}$ and $\omega_{2,\mathrm{II}}$ refer to the mass fraction of benzene and cyclohexane in the raffinate phase, respectively. The selectivity and distribution coefficients computed from the tie line data are presented in Table 1 as well.

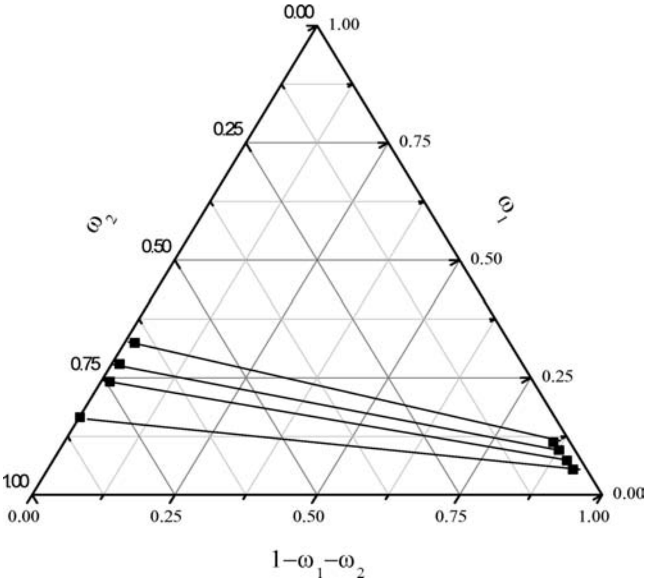

Figure 4. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + KSCN (4) quaternary system at 303.15 K, when the KSCN and DMF are in ratio of 17:83. ω_1 refers to the mass fraction of benzene in the sample; ω_2 refers to the mass fraction of cyclohexane in the sample.

Table 2. Constants of the Othmer−Tobias Correlation and the Correlation Factor (R^2) for the Systems Studied in This Work at 303.15 K (Based on Mass Fraction)

$\omega(4)/\omega(3)$	*N*	*a*	*b*	R^2	SD
10:90	6	−0.1175	0.6906	0.9690	0.08
15:85	6	0.1750	0.8771	0.9976	0.02
16:84	5	−0.5826	0.2745	0.9920	0.02
17:83	4	−0.4625	0.2252	0.9251	0.03

The experimental data can be correlated by applying the Othmer−Tobias correlation,[16,17] depicted in eq 3, for each of the above mixtures at the test temperature:

$$\ln\left(\frac{1-\omega_{3,\mathrm{I}}}{\omega_{3,\mathrm{I}}}\right) = a + b\ln\left(\frac{1-\omega_{2,\mathrm{II}}}{\omega_{2,\mathrm{II}}}\right) \tag{3}$$

where *a* and *b* are the fitting parameters of the Othmer−Tobias correlation. $\omega_{3,\mathrm{I}}$ is the DMF mass fraction in the extract phase. The values of *a*, *b*, and correlation factor R^2 are given in Table 2 at 303.15 K for the systems under study. The linearity of the Othmer−Tobias plots and the value of the R^2 (close to 1.0) reveal the degree of the consistency of the experimental data of this work. The standard deviations (SDs) of the studied systems are listed in Table 2 for reference.

To assess the separation effect of the complex solvent, the selectivity coefficients for separating benzene/cyclohexane were shown in the Figure 5. Only DMF was used as the extractant; tie-line data were reported by literature.[14] We computed the selectivity coefficients according to the tie-line date and display in the Figure 5. As shown in Figure 5, the selectivity coefficient of the complex solvent decreases with the increasing mass fraction of benzene in the raffinate phase at the same salt concentration of the complex solvent. The results are similar to those of Lu et al.,[13] Wang et al.,[12,18] and Letcher and Deenadayalu.[19] Additionally, the selectivity coefficient increases with the increasing salt concentration at the same mass fraction of benzene in the raffinate. The highest selectivity coefficient is 11.36 in our work. Compared with pure DMF which was reported by literature,[14] the complex solvents KSCN and DMF in ratios of 10:90, 15:85, 16:84, and 17:83 were better as an extractant.

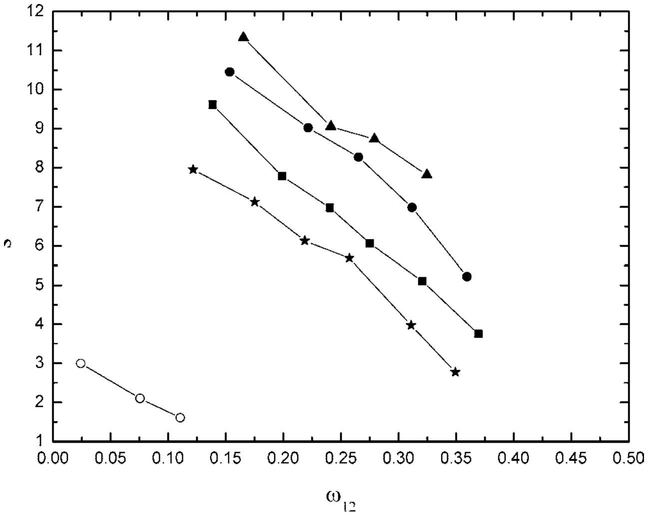

Figure 5. Effects of mass fraction of benzene in the raffinate phase to the selectivity (*S*) coefficient under different salt concentrations. ★, KSCN and DMF in a ratio of 10:90; ■, KSCN and DMF in a ratio of 15:85; ●, KSCN and DMF in a ratio of 16:84; ▲, KSCN and DMF in a ratio of 17:83. ○, only DMF was used as the extractant (the selectivity coefficient was calculated by literature).[14] ω_{12} refers to the mass fraction of benzene in the raffinate phase (cyclohexane-rich phase).

From the experimental results, it can be seen that the DMF + KSCN complex solvent can be used as an efficient extractive agent to separate benzene from cyclohexane.

Conclusions

In this work, a novel complex solvent, DMF + KSCN, was used as the extractive agent for extracting benzene from cyclohexane. The LLE data at 303.15 K for the systems were experimentally determined. The novel complex solvent's performance has been evaluated with the selectivity and distribution coefficients. The linearity of the Othmer−Tobias plots and the values of the correlation factor (R^2 very close to 1.0) proved the consistency of the experimental measurements for the systems as well as the low SDs. The novel complex solvent has a very high selectivity and may be used as a potential extracting solvent for the separation of benzene and cyclohexane.

Supporting Information Available:

Details are given on the addition internal standard method. This material is available free of charge via the Internet at http://pubs.acs.org.

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