JOURNAL OF CHEMICAL & ENGINEERING DATA

SHORT ARTICLE

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

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Supporting Information

ABSTRACT: Experimental liquid−liquid equilibrium (LLE) data were measured for benzene + cyclohexane + *N*,*N*-dimethylformamide (DMF) + ammonium thiocyanate (NH_4SCN) at atmospheric pressure and 298.15 K. The experimental data were correlated using the Othmer−Tobias correlation. The selectivity coefficients of DMF + NH_4SCN for benzene are 2 to 15 in this work. The results revealed that the selectivity coefficients increased with the decreasing of the concentration of benzene in the raffinate and increased with the increasing of the mass fraction of NH_4SCN in the DMF + NH_4SCN mixture. Considering the high selectivity for benzene, DMF + NH_4SCN may be used as a potential extracting solvent for the separation of benzene and cyclohexane.

INTRODUCTION

As a very important bulk chemical, cyclohexane is produced via catalytic hydrogenation of benzene, and thus the separation of the unreacted benzene from the product stream is inevitable.[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 (benzene: 353.25 K; cyclohexane: 353.85 K), approximately equal molecular volumes, low relative volatility in the whole composition range, and easy formation of an azeotropic mixture.[1−4] Conventional distillation cannot achieve the task in practice. Special distillation such as azeotropic distillation and extractive distillation are usually employed for benzene/cyclohexane separation,[5−10] while these two processes suffer from complexity and high energy consumption. Furthermore, to reduce the energy cost, pervaporation separation processes based on membrane and/or liquid-supported membranes have been studied extensively. Although the membranes tailored to such separation showed high selectivity,[4,11−13] it has still not been employed for this benzene + cyclohexane separation in industry.

Liquid−liquid extraction is another widely used industrial separation process for a homogeneous liquid mixture. The key is to find a suitable extractant which is highly selective to benzene and has 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.[14] The obtained LLE results for the mixture (ethylene carbonate + benzene + cyclohexane) show that benzene can be extracted from (benzene + cyclohexane) mixture and the selectivity coefficient of ethylene carbonate is much higher at the low temperature.[15] However, there is still a limitation that the temperature should be above the melting point of ethylene carbonate. Furthermore, ionic liquids have good selectivity for aromatics versus alkanes and are widely researched for extraction of benzene from cyclohexane. Ionic liquids as the extractant have attracted much attention since the 1990s. Wang et al. studied the performance of 1-methyl-3-methylimidazolium dimethylphosphate ([C_1min][DMF]), or 1-ethyl-3-methylimidazolium eiethylphosphate ([C_2min][DEP]), on extracting benzene from cyclohexane at atmospheric pressure and (298.2 and 313.2) K.[2] Meindersma et al. have used [emim]Tf_2N as the extractant for the benzene + cyclohexane separation, and the selectivity coefficient can be 17.7.[16] Lu et al. determined liquid−liquid equilibria for benzene + cyclohexane + 1-butyl-3-methylimidazolium hexafluorophosphate.[17] Samir et al. determined liquid−liquid equilibrium for cyclohexane + (benzene, + toluene, + ethylbenzene, or + *o*-xylene) + 4-methyl-*N*-butyl pyridinium tetrafluoroborate ([bmpy]BF_4).[18] 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 the studies on the selectivity improvement of DMF using ethylene glycol as a cosolvent.[19] KSCN as a cosolvent to improve the selectivity of DMF was reported by Dong et al.[20] In this work, the complex solvent which the NH_4SCN dissolves in DMF is confirmed to be a good extractant for the separation of benzene from cyclohexane for high selectivity and cheapness. Phase equilibrium data are required for the evaluation of solvent combinations, so the experimental liquid−liquid equilibrium data were measured for benzene + cyclohexane + DMF + NH_4SCN at 298.15 K and atmospheric pressure.

Received: May 26, 2010
Accepted: February 18, 2011
Published: March 08, 2011

dx.doi.org/10.1021/je1012026 | *J. Chem. Eng. Data* 2011, 56, 2664–2668

EXPERIMENTAL SECTION

Materials. The chemicals used in this study were benzene, cyclohexane, ammonium thiocyanate (NH_4SCN), and *N*,*N*-dimethylformamide (DMF). DMF with a nominal minimum mass fraction of 0.995 was used as 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 as received from Tianjin Fuyu Fine Chemicals Company. The nominal mass fractions of water for benzene and cyclohexane were both less than $5 \cdot 10^{-3}$. NH_4SCN was provided by Tianjin Guangfu Fine Chemicals Research Institution. The purity of NH_4SCN was above 0.985 in mass fraction.

Apparatus and Procedures. Complex solvents NH_4SCN and DMF in mass ratios of 5:95, 10:90, 15:85, and 20:80 were prepared by dissolving a certain amount of NH_4SCN in DMF solvent under stirring. Liquid–liquid equilibrium experiments were carried out in a conical flask with a 100 mL volume in a thermostat. The temperature was controlled to 298.15 K with ± 0.1 K. The benzene + cyclohexane solution with the benzene mole fraction from 0.23 to 0.74 was put in the conical flask and kept at the temperature of 298.15 K. Then the complex solvent was added into the solution, and the volume ratio of (benzene + cyclohexane) to (DMF + NH_4SCN) is 1. The system, benzene + cyclohexane + DMF + NH_4SCN, was stirred for 1 h and kept still for 4 h at atmospheric pressure and 298.15 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 453.15 K. Detection was performed by a flame ionization detector (FID) operating at 463.15 K. The others analysis conditions include: packed column, GDX-502, 2 m × 3 mm; column temperature, 448.15 K; using nitrogen as the carrier gas, and the nitrogen pressure, 72 KPa; air pressure, 62 KPa; hydrogen pressure, 52 KPa; internal standard method, and *n*-butyl alcohol served 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 benzene, cyclohexane, and DMF were measured by standard sample. Once the amount of *n*-butyl alcohol component had been determined, the mass fraction of benzene, cyclohexane, and DMF was calculated via the weight correction factor for the raffinate and extract phase samples. The NH_4SCN cannot be detected by GC-14C. The mass fraction of NH_4SCN was calculated via mass balance for raffinate and extract phase samples, respectively. With the low volatility of NH_4SCN, a block of glass wool was put in the vaporizing chamber, to avoid pollution of 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. With the mass fraction of NH_4SCN in the DMF + NH_4SCN increase, the errors of LLE data become more and more large, and the measurement of data becomes difficult.

RESULTS AND DISCUSSION

The experimental results are summarized in Table 1 and displayed on the triangular diagrams, shown in Figures 1 to 4 (we treated the NH_4SCN/DMF mixture as a single component when drawing the tie lines). It can be seen that the benzene mass fraction increases in the extract phase and the cyclohexane decreases in the raffinate phase when the benzene concentration increases in the raffinate phase, if the salt concentration in 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.

Table 1. Liquid–Liquid Equilibrium Data in Mass Fraction for Benzene (1) + Cyclohexane (2) + DMF (3) + NH_4SCN (4) at 298.15 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
$\omega(4)/\omega(3) = 5:95$									
0.055	0.104	0.692	0.149	0.051	0.847	0.062	0.040	8.77	1.08
0.102	0.124	0.640	0.134	0.108	0.785	0.090	0.017	6.00	0.95
0.138	0.118	0.614	0.130	0.152	0.691	0.126	0.031	5.34	0.91
0.178	0.137	0.558	0.127	0.207	0.564	0.181	0.048	3.53	0.86
$\omega(4)/\omega(3) = 10:90$									
0.082	0.060	0.673	0.185	0.112	0.782	0.065	0.041	9.52	0.73
0.119	0.070	0.641	0.170	0.172	0.679	0.087	0.062	6.70	0.69
0.157	0.075	0.589	0.179	0.253	0.560	0.126	0.061	4.63	0.62
0.208	0.091	0.545	0.156	0.313	0.450	0.162	0.075	3.29	0.66
0.250	0.100	0.489	0.161	0.381	0.368	0.206	0.045	2.40	0.66
$\omega(4)/\omega(3) = 15:85$									
0.075	0.041	0.641	0.243	0.127	0.801	0.046	0.026	11.45	0.59
0.104	0.042	0.624	0.230	0.189	0.696	0.059	0.056	9.06	0.55
0.146	0.044	0.556	0.254	0.292	0.597	0.079	0.032	6.80	0.50
0.173	0.049	0.548	0.230	0.362	0.505	0.103	0.030	4.90	0.48
0.209	0.045	0.521	0.225	0.422	0.394	0.127	0.057	4.31	0.50
0.266	0.058	0.468	0.208	0.499	0.316	0.159	0.026	2.90	0.53
$\omega(4)/\omega(3) = 20:80$									
0.081	0.029	0.617	0.273	0.147	0.761	0.034	0.058	14.77	0.55
0.095	0.031	0.592	0.282	0.213	0.707	0.040	0.040	10.39	0.45
0.116	0.025	0.571	0.288	0.300	0.584	0.055	0.061	9.21	0.39
0.147	0.028	0.547	0.278	0.368	0.471	0.068	0.093	6.77	0.40
0.183	0.032	0.503	0.282	0.445	0.392	0.075	0.088	5.11	0.41
0.221	0.031	0.464	0.284	0.501	0.294	0.097	0.108	4.23	0.44

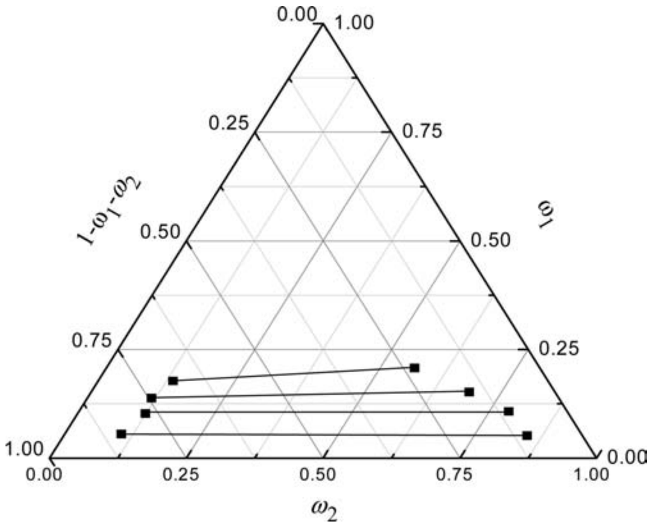

Figure 1. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + NH_4SCN (4) quaternary system at 298.15 K, with NH_4SCN and DMF in a ratio of 5:95.

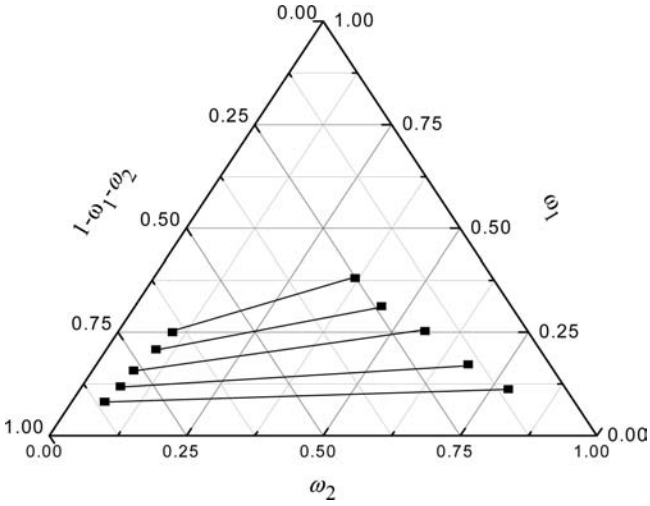

Figure 2. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + NH_4SCN (4) quaternary system at 298.15 K, with NH_4SCN and DMF in a ratio of 10:90.

The experimental data can be correlated by applying the Othmer–Tobias correlation,[21,22] depicted in eq 3, for each of the above mixtures at the test temperature:

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

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 and b and correlation factor R^2 are given in Table 2 at 298.15 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 are shown in Figure 5. Only DMF was used as the extractant; tie-line data was reported in the literature.[19] We computed the selectivity coefficients according to the tie-line data and display them in Figure 5. As shown in Figure 5, the selectivity coefficient of complex solvent decreases with the increasing mass fraction of benzene in the raffinate phase at the same salt concentration of complex solvent. The results are similar to those of Lu et al.,[17] Wang et al.,[2,23] and Letcher and Deenadayalu.[24] Additionally, the

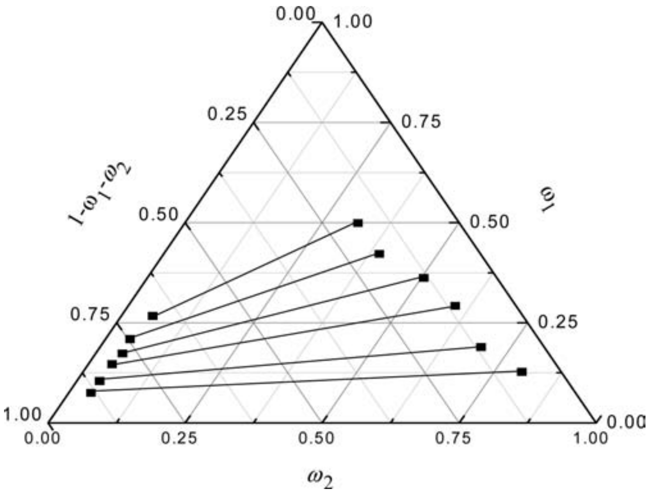

Figure 3. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + NH_4SCN (4) quaternary system at 298.15 K, with NH_4SCN and DMF in a ratio of 15:85.

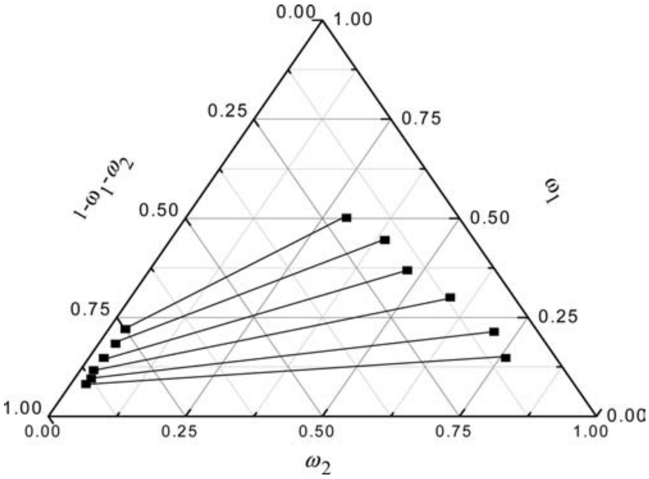

Figure 4. Tie-line data of the benzene (1) + cyclohexane (2) + DMF (3) + NH_4SCN (4) quaternary system at 298.15 K, with NH_4SCN and DMF in a ratio of 20:80.

Table 2. Constants of the Othmer–Tobias Correlation and the Correlation Factor (R^2), for the Systems Studied in This Work at 298.15 K (Based on Mass Fraction)

$\omega(4)/\omega(3)$	N	a	b	R^2	SD
5:95	4	−0.1363	0.3777	0.9780	0.04
10:90	5	−0.2325	0.4164	0.9802	0.05
15:85	6	−0.1667	0.3210	0.9515	0.07
20:80	6	−0.1527	0.2906	0.9645	0.05

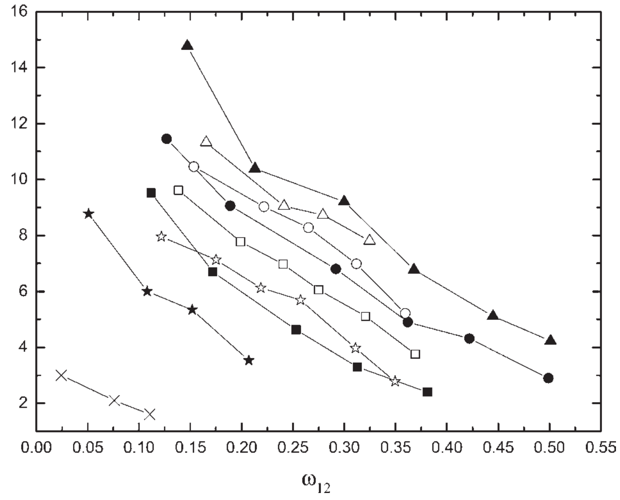

Figure 5. Effects of mass fraction of benzene in the raffinate phase to the selectivity (S) coefficient under different salt concentrations. ★, NH_4SCN and DMF in a ratio of 5:95; ■, NH_4SCN and DMF in a ratio of 10:90; ●, NH_4SCN and DMF in a ratio of 15:85; ▲, NH_4SCN and DMF in a ratio of 20:80. ×, only DMF was used as the extractant (the selectivity coefficient was calculated by literature[19]). ☆, 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 (by literature[20]). ω_{12} refers to the mass fraction of benzene in the raffinate phase (cyclohexane-rich phase).

selectivity coefficient increases with the increasing salt concentration at the same mass fraction of benzene in the raffinate. The highest selectivity coefficient is 14.77 in our work. Compared with pure DMF which was reported by ref 19 and DMF with KSCN reported by ref 20, the complex solvents NH_4SCN and DMF in ratios of 5:95, 10:90, 15:85, and 20:80 were better as an extractant.

From the experimental results, it can be seen that the DMF + NH_4SCN complex solvent can be used as an efficient extractive agent to separate benzene from cyclohexane.

CONCLUSIONS

In this work, a novel complex solvent, DMF + NH_4SCN, was used as the extractive agent for extracting benzene from cyclohexane. The LLE data at 298.15 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) 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. 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.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Chemical shifts of the proton signals of DMF, NH_4SCN, and DMF with NH_4SCN (Table 1) and ^1H NMR spectra (Figures 1 to 9). This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

We acknowledge the financial support by the National Natural Science Foundation of China (20976032, 21076049), Fundamental Research Funds for the Central Universities (HEUCFZ1018), and Natural Science Foundation of Heilongjiang Province (E-200808).

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