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Liquid−Liquid Equilibria for the Cyclohexane + Benzene + Dimethylformamide + Ethylene Glycol System

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Liquid−liquid equilibrium data for the extraction of cyclohexane + benzene + dimethyl formamide with 10, 20, 30, and 50 mass % ethylene glycol were measured. The NRTL equation was used to correlate the experimental data and to predict the phase composition of the quaternary system. The agreement between the predicted and experimental results was good.

Introduction

Use of mixed solvents for extraction of aromatics from similar boiling nonaromatics has been drawing considerable attention in the past decade. The pioneering work in this area was by Muller and Hoehfeld (1973). They classified the solvents with high capacity and low selectivity as basic solvents and those with low capacity and high selectivity as blending solvents. They also gave a method of comparison of different solvents. Dimethylformamide (DMF) is a solvent with high solvent capacity but a low selectivity for aromatics and is used as a solvent for extraction of higher aromatics from lube distillates in the Redex process (Hancock, 1975). Surana and co-workers (1981) have studied the use of DMF for lower aromatics such as benzene, toluene, and xyelene, and Ethirajulu and Roy (1981) have reported studies on the selectivity improvement of DMF using ethylene glycol (EG) as a cosolvent. Phase equilibrium data are required for the evaluation of solvent combinations and design of extraction equipment. Experimentally determined phase equilibrium data are expensive and are seldom available for the conditions of operation required in a particular design problem. In many cases, it is necessary to extrapolate the available data and, where no data is available, to estimate the data from an appropriate correlation.

The most important requirements of a solvent used in liquid−liquid extraction are high solvent capacity and selectivity in addition to having properties such as low viscosity, high thermal stability, and easy regenerability. As it is difficult to find a solvent that has all these properties, an attempt is made to combine solvents having high capacity with those with high selectivity. Solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl pyrrolidone (NMP), aniline, phenols, and furfural, which have high solvent capacity are considered as basic solvents, and solvents such as ethylene glycol (EG), diethylene glycol, diethanolamine, and glycerol, which have high selectivity, are considered as blending solvents. Not much quantitative information is available in the literature on the use of mixed solvents for extraction of aromatics. The purpose of this work is to study the phase equilibrium in batch extraction of benzene from a cyclohexane + benzene mixture using a solvent combination having dimethyl formamide as basic solvent and ethylene glycol as blending solvent and to correlate the phase equilibrium data using a suitable thermodynamic model.

Table 1. Tie Line Data for the Cyclohexane (1) + Benzene (2) + Dimethylformamide (3) System, mass fraction (*w*)

glycol-rich phase			cyclohexane-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
		t = 30 °C			
0.2677	0.0219	0.7105	0.8907	0.0243	0.0850
0.3321	0.0652	0.6027	0.8112	0.0758	0.1130
0.3752	0.1018	0.5230	0.6542	0.1106	0.2352
		t = 40 °C			
0.3235	0.0163	0.6601	0.8050	0.0323	0.1626
0.3945	0.0356	0.5699	0.7111	0.0623	0.2266
		t = 50 °C			
0.4803	0.0101	0.5097	0.6901	0.0199	0.2901

Experimental Section

Materials. Analytical reagent grade (A.R.) cyclohexane used in the experiments was obtained from BDH (India), while A.R. grade benzene, dimethyl formamide, and ethylene glycol were obtained from E. Merck (India). The purity of all chemicals was checked by gas chromatography and was found to be higher than 99.5%.

Procedure. Mutual solubility curves have been determined by the titration method as suggested by Alders (1955). For determination of tie line data, cyclohexane, benzene, and the solvent were taken in such proportions that they formed a heterogeneous mixture. It was then allowed to equilibrate for 50 min at the required temperature. The preliminary studies have shown that this time was sufficient for attaining equilibrium. The phases were then separated and weighed. The solvent from each phase was removed by washing two to three times with a small quantity of water in a separating funnel. Extract and raffinate phases were dried using a small quantity of

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Table 2. Tie Line Data for the Cyclohexane (1) + Benzene (2) + Ethylene Glycol (3) System, mass fraction (w)

glycol-rich phase			cyclohexane-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
$t = 30$ °C					
0.0021	0.0348	0.9650	0.7400	0.2580	0.0020
0.0021	0.0860	0.9120	0.5300	0.4640	0.0040
0.0045	0.1720	0.8230	0.3300	0.6600	0.0050
0.0045	0.2210	0.7740	0.1610	0.8310	0.0080

Table 3. Tie Line Data for the Cyclohexane (1) + Benzene (2) + ($w_3 = 0.9$) Dimethylformamide (3) + ($w_4 = 0.1$) Ethylene Glycol (4) System, mass fraction (w)

glycol-rich phase			cyclohexane rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
$t = 30$ °C					
0.1983	0.0411	0.7605	0.8915	0.0698	0.0387
0.2321	0.0955	0.6723	0.7891	0.1601	0.0507
0.2699	0.1449	0.5851	0.6658	0.2150	0.1192
$t = 40$ °C					
0.2122	0.0535	0.7353	0.8478	0.0789	0.0732
0.2598	0.1090	0.6311	0.7202	0.1645	0.1154
0.2978	0.1421	0.5601	0.6185	0.2102	0.1713
$t = 50$ °C					
0.2396	0.0605	0.6999	0.8185	0.0898	0.0917
0.2878	0.1110	0.6012	0.7055	0.1588	0.1357
0.3313	0.1501	0.5186	0.5824	0.2063	0.2113

Table 4. Tie Line Data for the Cyclohexane (1) + Benzene (2) + ($w_3 = 0.8$) Dimethylformamide (3) + ($w_4 = 0.2$) Ethylene Glycol (4) System, mass fraction (w)

glycol-rich phase			cyclohexane-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
$t = 30$ °C					
0.1284	0.0610	0.8106	0.8354	0.0965	0.0681
0.1362	0.1365	0.7273	0.7001	0.1851	0.1148
0.1585	0.1814	0.6601	0.5631	0.2510	0.1859
0.1932	0.2317	0.5751	0.4105	0.2910	0.2985
$t = 40$ °C					
0.1345	0.0567	0.8088	0.8310	0.0812	0.0878
0.1655	0.1295	0.7050	0.6875	0.1751	0.1374
0.2045	0.1857	0.6098	0.5721	0.2332	0.1947
0.2303	0.2310	0.5387	0.4300	0.2744	0.2965
$t = 50$ °C					
0.1632	0.0410	0.7958	0.8375	0.0710	0.0914
0.1850	0.1067	0.7083	0.7250	0.1445	0.1305
0.1979	0.1410	0.6611	0.6123	0.1988	0.1889
0.2389	0.2110	0.5501	0.5455	0.2299	0.2246

Table 5. Tie Line Data for the Cyclohexane (1) + Benzene (2) + ($w_3 = 0.7$) Dimethylformamide (3) + ($w_4 = 0.3$) Ethylene Glycol (4) System, mass fraction (w)

glycol-rich phase			cyclohexane-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
$t = 30$ °C					
0.0395	0.0350	0.9255	0.7997	0.1401	0.0602
0.0872	0.0938	0.8290	0.6904	0.2204	0.0892
0.1131	0.2010	0.6859	0.5910	0.2950	0.1140
0.1288	0.2650	0.6062	0.4220	0.3912	0.1868
$t = 40$ °C					
0.0576	0.0899	0.8525	0.8057	0.1233	0.0710
0.0822	0.1665	0.7513	0.6579	0.2366	0.1055
0.1057	0.2285	0.6658	0.5321	0.3110	0.1569
0.1388	0.3011	0.5601	0.3710	0.3887	0.2403
$t = 50$ °C					
0.0412	0.0610	0.8978	0.8307	0.1096	0.0597
0.0715	0.1602	0.7683	0.6414	0.2288	0.1298
0.1117	0.2511	0.6372	0.4884	0.3023	0.2093
0.1393	0.2996	0.5611	0.3499	0.3632	0.2869

Table 6. Tie Line Data for the Cyclohexane (1) + Benzene (2) + ($w_3 = 0.5$) Dimethylformamide (3) + ($w_4 = 0.5$) Ethylene Glycol (4) System, mass fraction (w)

glycol-rich phase			cyclohexane-rich phase		
w_1	w_2	w_3	w_1	w_2	w_3
$t = 30$ °C					
0.0348	0.0543	0.9109	0.7054	0.1931	0.1015
0.0388	0.0960	0.8652	0.5588	0.3282	0.1130
0.0361	0.1406	0.8242	0.3810	0.4957	0.1233
0.0171	0.1540	0.8289	0.2704	0.5945	0.1351
$t = 40$ °C					
0.0374	0.0458	0.9168	0.7050	0.1850	0.1075
0.0371	0.0871	0.8758	0.5211	0.3562	0.1227
0.0290	0.1351	0.8359	0.3777	0.4949	0.1274
0.0189	0.1910	0.7901	0.2740	0.5936	0.1320
0.0019	0.2369	0.7612	0.1387	0.7011	0.1602
$t = 50$ °C					
0.0490	0.0756	0.8754	0.6933	0.1687	0.1380
0.0395	0.1210	0.8395	0.5694	0.2887	0.1419
0.0307	0.1582	0.8111	0.2811	0.5392	0.1797
0.0236	0.1953	0.7811	0.1634	0.6114	0.2252
0.0088	0.2411	0.7501	0.0585	0.6805	0.2610

calcium chloride and weighed. Masses of solvents in the phases was obtained by the difference in mass before and after washing. The composition of benzene and cyclohexane was determined by measuring the refractive index of the sample in a research model Abbe's refractometer with an accracy of 0.0001 units.

Results and Discussions

Experimental Data. The experimental tie line data for the system cyclohexane + benzene + dimethyl formamide at (30, 40, and 50) °C are given in Table 1, tie line data for the system cyclohexane + benzene + ethylene glycol at 30 °C are given Table 2, and tie line data for the system cyclohexane + benzene + dimethyl formamide + ethylene glycol at (30, 40, and 50) °C with DMF:EG mass % at 90:10, 80:20, 70:30, and 50:50 in Tables 3, 4, 5, and 6 respectively.

Data Correlation and Prediction. The NRTL model was used to predict the LLE data in the present work. The NRTL equation proposed by Renon and Prausnitz (1968) is an empirical model that is used to correlate the excess Gibbs free energy. It is a three-parameter equation that makes use of the local composition concept devoloped by Wilson (1964). The local mole fraction concept is modified by introducing the nonrandomness parameter, α, which can be set to a predetermined value ranging from 0.2 to 0.5 according to the recommendation of Renon and Prausnitz. The nonrandomness parameter is related inversely to the coordination number of the liquid by Guggenhaim's quasichemical theory (Guggenhaim, 1952). The multicomponent form of the NRTL equation is given by

$$g^{\mathrm{E}} = \sum_{i=1}^{M} x_i \frac{\sum_{j=1}^{M} \tau_{ji} G_{ji} X_j}{\sum_{k=1}^{M} G_{ki} X_k} \tag{1}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{2}$$

and

$$G_{ji} = \exp\,(-\alpha_{ji}\tau_{ji}) \tag{3}$$

Table 7. NRTL Parameters for Cyclohexane (1) + Benzene (2) + Dimethylformamide (3) + Ethylene Glycol (4)

mass % EG	t/°C	NRTL parameters 1-2	1-3	2-1	2-3	3-1	3-2	% dev
0	30	637.01	179.76	245.46	359.06	42.65	−80.16	0.41
	40	555.43	155.61	256.89	159.75	144.56	157.68	1.22
	50	398.80	400.45	368.85	369.70	−500.82	377.34	0.18
10	30	727.80	512.55	258.77	487.37	352.12	533.73	1.47
	40	599.22	479.56	335.63	509.97	471.75	483.52	1.51
	50	770.27	259.03	202.89	241.04	161.76	359.02	0.86
20	30	570.56	213.05	485.42	543.13	290.84	89.73	0.58
	40	548.07	273.85	486.42	532.97	314.32	131.76	0.30
	50	542.31	264.97	476.07	547.83	333.61	181.39	0.62
30	30	534.99	266.47	728.22	486.80	159.30	92.63	0.84
	40	546.57	176.19	654.62	358.40	270.38	225.39	0.37
	50	590.01	214.75	680.53	631.13	296.89	44.26	0.99
50	30	316.41	−171.80	881.41	344.29	347.94	434.28	0.48
	40	356.59	−125.54	871.23	375.59	466.00	460.18	1.05
	50	390.62	178.44	780.77	452.54	62.40	350.08	1.07

where g^E is the molar excess Gibbs energy, g_{ij} is the energy parameter in the NRTL equation (K), M is the number of components, R is the gas constant [cal/(mol·k)], T is the temperature (K), x_i is the mole fraction of component i, and α_{ij} is the nonrandomness parameter. Here the value of the nonrandomness parameter is taken as 0.2 as recommended by Renon and Prausnitz (1968). The NRTL equation was fitted to the experimental data for the cyclohexane + benzene + dimethyl formamide + ethylene glycol system. For each set of data the interaction parameters τ_{ji} and τ_{ij} were obtained using an iterative computer program using the Nelder−Mead search method to minimize the value of the objective function, F

$$F = \sum_{i=1}^{N}\sum_{l=1}^{2}\sum_{m=1}^{M}(x_{ilm} - x_{ilm})^2 \tag{4}$$

where $i = 1, 2, 3, ..., N$ (components), $l = 1, 2$ (phases), and $m = 1, 2, 3, ..., M$ (tie lines).

The interaction parameters for the NRTL equation determined as above for different experimental runs are listed in Table 7. Using these interaction parameters and an α value of 0.2, the mass percentage of benzene has been calculated. The deviation in terms of the benzene composition expressed as the ratio of the difference in the predicted value and the experimental value of mass percentage of benzene in the phases to the experimental value expressed as percentage is also shown in Table 7. It is seen from Table 7 that there is inconsistency in the temperature dependence of the NRTL parameters both with respect to the change in temperature at constant composition of EG as well as with respect to the change in mass of EG at the same temperature. It becomes necessary to explain this incoherent behavior, although the purpose of the paper is only to present the equilbrium data for the quarternary system that is likely to have some practical significance. This can be explained on the basis of the difference in the degree of miscibility of the components involved in the system as well as the change of solubility of the binary components with respect to temperature. A very important role is played by the nonrandomness parameter α_{ij}, which has been assumed to be constant for all the compositions and temperatures at which the experiments have been carried out. This parameter has been found to vary even at the same temperature from binary pair to pair. The binary parameters chosen were those that gave an optimum representation of the liquid−liquid equilbrium data and they are not unique. They will change according to the value assigned to the nonrandomness parameter α_{ij} and hence the inconsistent variation of parameters with respect to temperature.

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