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Liquid−Liquid Equilibria in Some Binary and Ternary Mixtures with *N*-Formylmorpholine

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Liquid−liquid equilibria (LLE) for *N*-formylmorpholine + heptane or + decalin and *N*-formylmorpholine + decane + benzene or + ethylbenzene over a temperature range of 293−338 K were measured. The results were used to estimate the interaction parameters between a new solvent group, NFM (*N*-formylmorpholine), and the main groups of CH_2 (paraffinic CH_2), ACH (aromatic CH), $ACCH_2$ (aromatic CCH_2), and CHNA (condensed naphthenic CH) as a function of temperature. The estimated interaction parameters of these groups have been used with other interaction parameters present in the literature to compare calculated values with the experimental LLE equilibrium measurements.

Introduction

N-Formylmorpholine (NFM) has been successfully used in industry for the extraction of aromatics from feedstocks such as fully hydrogenated pyrolysis gasoline, reformate gasoline, and hydrorefined coke oven oil (*1*). Some binary and ternary systems occurring in the extraction of such feedstocks are studied in this work.

The prediction of liquid−liquid equilibria (LLE) requires a knowledge of the activity coefficient as a function of composition. The UNIFAC group contribution method, described in detail by Fredenslund et al. (*2*), is a reliable method for prediction of liquid-phase activity coefficients.

The application of the UNIFAC method requires the determination of interaction parameters as a function of temperature which can be obtained from measurements of liquid−liquid equilibria (LLE) on binary and ternary systems. In the present work, LLE measurements for the four systems heptane + NFM, decane + benzene + NFM, decane + ethylbenzene + NFM, and decalin + NFM over the temperature range 293−338 K have been studied. The results were used to determine the UNIFAC interaction parameters between the solvent and CH_2 (paraffinic CH_2), ACH (aromatic CH), $ACCH_2$ (aromatic CCH_2), and CHNA (condensed naphthenic CH) groups as a function of temperature. These groups are some of the structural groups of hydrocarbon compounds found in petroleum fractions. The functional group parameters were calculated by Fredenslund et al. (*2*). Other hydrocarbon interaction parameters were obtained from Rahman et al. (*4*).

Experimental Section

Chemicals. The purities of chemicals used in this study in mole percent were for decane 99+, Fluka, decalin 98+, Fluka, ethylbenzene 99+, BDH, benzene 99+, Fluka, heptane 99+, Fluka, and *N*-formylmorpholine ($C_5H_9NO_2$) 99+, Fluka. They were used without further purification.

Procedure. The experimental apparatus used for extraction consists of a glass cell with a water jacket in order to maintain a constant temperature. The temperature was controlled within ±0.5 K inside the cell. The cell was connected to a water bath which was controlled within ±0.1 K. The mixture was prepared by mass, placed in the extraction vessel, and stirred for 1 h, and the mixture was then left to settle for 3 h. Samples were taken by a syringe from the upper and the lower phases through a sampling stopcock. A series of LLE measurements were made by changing either the temperature or the composition of the mixture. Increasing agitation or settling times did not affect the accuracy of measurement, indicating that equilibrium was attained.

Table 1. Experimental and Calculated Liquid−Liquid Equilibrium Mole Fractions for the Binary System Heptane (1) + *N*-Formylmorpholine (2)

	x_1^{I}		x_1^{II}	
T/K	exptl	calcd	exptl	calcd
303.0	0.9341	0.9280	0.2250	0.2650
308.0	0.9226	0.9265	0.0278	0.0336
313.0	0.8981	0.9066	0.0269	0.0270
318.0	0.8423	0.8345	0.0289	0.0242

Table 2. Experimental and Calculated Liquid−Liquid Equilibrium Mole Fractions for the Binary System Heptane (1) + *N*-Formylmorpholine (2)

	x_1^{I}		x_1^{II}	
T/K	exptl	calcd	exptl	calcd
293.0	0.9565	0.9698	0.0103	0.0103
302.5	0.9313	0.9317	0.0120	0.0137
312.0	0.8894	0.8693	0.0163	0.0212
338.0	0.7554	0.7640	0.0211	0.0140

The composition of the mixture was determined by means of a gas−liquid chromatograph (Varian-Vista-6000) equipped with a flame ionization detector and connected to a Varian-Vista-4290 data system. A 2 m long and 1/8 in. diameter column was packed with 3% by volume OV-70 80/100 chromosorb Q II. The column initial temperature was kept at 313 K, and a heating rate of 15 K·min^{-1} was used. The flow rate of helium carrier gas was kept constant at 30 cm^3·min^{-1}. The air flow rate was 300 cm^3·min^{-1}, and the hydrogen flow rate was 30 cm^3·min^{-1}. The final column temperature was kept at 523 K.

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Table 3. Experimental and Calculated Liquid–Liquid Equilibrium Mole Fractions for the Ternary System Decane (1) + Benzene (2) + *N*-Formylmorpholine (3)

	x_1^{I}		x_2^{I}		x_1^{II}		x_2^{II}	
T/K	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
298.0	0.4207	0.3671	0.3976	0.3976	0.0076	0.0000	0.2859	0.2862
	0.3488	0.3537	0.4773	0.4773	0.0159	0.0000	0.3659	0.3473
	0.4967	0.4532	0.3500	0.3500	0.0107	0.0042	0.2323	0.2269
	0.6875	0.5299	0.0973	0.0973	0.0043	0.0035	0.0564	0.0616
	0.7120	0.4709	0.0000	0.0000	0.0025	0.0016	0.0000	0.0000
313.0	0.3667	0.3707	0.4500	0.4500	0.0177	0.0087	0.3219	0.3326
	0.5652	0.4828	0.2190	0.2190	0.0049	0.0000	0.1365	0.1573
	0.4771	0.4704	0.3586	0.3586	0.0129	0.0086	0.2411	0.2630
	0.6989	0.6128	0.0946	0.0946	0.0047	0.0015	0.0613	0.0777
	0.6058	0.4994	0.1611	0.1611	0.0058	0.0024	0.1062	0.1316
	0.7317	0.5768	0.0000	0.0000	0.0016	0.0600	0.0000	0.0000
323.0	0.3719	0.4528	0.4310	0.4310	0.0205	0.0000	0.3563	0.3769
	0.5513	0.6069	0.2779	0.2779	0.0074	0.0000	0.1899	0.2014
	0.3877	0.4319	0.3969	0.3969	0.0112	0.0000	0.2305	0.2684
	0.6549	0.6448	0.1269	0.1269	0.0052	0.0000	0.0625	0.0531
	0.7322	0.6646	0.000	0.0000	0.0028	0.0000	0.0000	0.0000

Table 4. Experimental and Calculated Liquid–Liquid Equilibrium Mole Fractions for the Ternary System Decane (1) + Ethylbenzene (2) + *N*-Formylmorpholine (3)

	x_1^{I}		x_2^{I}		x_1^{II}		x_2^{II}	
T/K	exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd
298.5	0.4713	0.5516	0.4564	0.4484	0.0094	0.0062	0.1739	0.1531
	0.5965	0.6376	0.3378	0.3378	0.0053	0.0033	0.1085	0.1074
	0.8226	0.8211	0.1145	0.1145	0.0021	0.0001	0.0291	0.0308
313.0	0.5108	0.4843	0.3048	0.3049	0.0091	0.0076	0.1167	0.1311
	0.3321	0.2549	0.4022	0.4022	0.0127	0.0113	0.1951	0.1772
	0.3914	0.3510	0.3862	0.3862	0.0135	0.0138	0.1874	0.1678
	0.4497	0.4183	0.3491	0.3491	0.0101	0.0000	0.1698	0.1476
	0.3613	0.2937	0.3882	0.3882	0.0135	0.0136	0.2081	0.1788
	0.7564	0.7877	0.1456	0.1456	0.0027	0.0000	0.0337	0.0370
323.0	0.3630	0.5302	0.3868	0.3868	0.0136	0.0000	0.1862	0.0000
	0.4119	0.4639	0.3531	0.3531	0.0099	0.0000	0.1432	0.0992
	0.7120	0.7539	0.1146	0.1146	0.0035	0.0000	0.0307	0.0197

Single-phase samples of known composition were used to calibrate the gas chromatograph in the composition range of interest. Replicate analyses indicated that a precision of ±1 mol % was obtained of each component.

Triplicate samples of each phase were taken, and the average value was used. A maximum variation of ±0.001 mole fraction was observed. This was quite acceptable in the high mole fraction range; however, the solvent phase had lower mole fractions of the solutes, and higher errors can be expected. The heptane + *N*-methylpyrrilidone system was used to test the reproducibility of the experimental procedure. Comparison of mole fractions versus previous work carried out on the same equipment by Al-Zayed (*6*) gave an average deviation of 2.8 mol %. A comparison of published work by Ferreira (*5*) on the same system revealed an average deviation of 5 mol %.

Phase Equilibrium. If a liquid mixture of given composition and at a known temperature is separated into two phases, at equilibrium, the calculation of the composition of the two phases can be achieved through the following system of equations:

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \qquad (1)$$

$$z_i = z_i^{\mathrm{I}} + z_i^{\mathrm{II}} \qquad (2)$$

where z_i, z_i^{I}, and z_i^{II} are the numbers of moles of component *i* in the system and in phases I and II, respectively, and γ_i^{I} and γ_i^{II} are the corresponding activity coefficients of component *i* in phases I and II as calculated from the UNIFAC model. Equation 1, with the material balance equation (2), can be solved for the mole fraction (x) for component *i* in each liquid phase. This method of calculation gives a single tie line (*2*).

Results

The results for the binary and ternary mixtures studied are given in Tables 1–4. These results were used to calculate the interaction parameters of the hydrocarbon groups with *N*-formylmorpholine (NFM). The equilibrium data for the binary systems were used to determine the interaction parameters for the NFM group with the CH_2 and CHNA groups. The equilibrium data for the ternary systems were used to calculate the interaction parameters between the ACH and NFM and between the $ACCH_2$ and NFM groups. The dependence of the interaction parameters on temperature was expressed by

$$a_{\mathrm{nm}} = A_{\mathrm{nm}} + B_{\mathrm{nm}}(T/\mathrm{K} - 273.2) \qquad (3)$$

where T is the temperature and A_{nm} and B_{nm} are constants specific to each group. Table 6 gives the interaction parameters calculated from the binary and the ternary systems studied.

The phase equilibrium results obtained using the UNIFAC model with the interaction parameters are compared with the experimental results in Tables 1 and 2 for the binary systems and in Tables 3 and 4 for the ternary mixtures. Table 5 gives the root mean square deviation (RMS) for the binary and ternary systems defined by the objective function (*3*)

$$F = 100[\sum_k \min \sum_i \sum_j (x_{ijk,\mathrm{exptl}} - x_{ijk,\mathrm{calcd}})^2/M]^{1/2} \qquad (4)$$

where $i = 1$ and 2 for binary systems or 1, 2, and 3 for ternary systems, j = phase I or II, $k = 1, 2, ..., n$ (tie lines),

Table 5. Root Mean Square Deviation (*F*) for the Measured System for *N*-Formylmorpholine (NFM)

system	*F*/%
heptane + NFM	0.40
decalin + NFM	0.68
decane + benzene + NFM	8.02
decane + ethylbenzene + NFM	6.60

Table 6. Interaction Parameters for the UNIFAC Method (a_{nm}) for *N*-Formylmorpholine (NFM)

$$a_{nm} = A_{nm} + B_{nm}(T/K - 273.2)$$

group	A_{nm}	A_{mn}	B_{nm}	B_{mn}
CH_2 + NFM	165.0	164.0	−4.997	2.015
ACH + NFM	−158.6	239.3	7.625	−9.000
$ACCH_2$ + NFM	306.8	20.7	−2.846	−1.891
CHNA + NFM	−325.4	615.6	3.148	9.000

$M = 2ni$, and x = liquid mole fraction. Generally the RMS is quite low for the binary mixtures and increases slightly for ternary mixtures probably due to the increase of the number of groups and, consequently, the number of interaction parameters to be optimized.

Conclusions

Liquid–liquid equilibria have been measured for heptane + NFM, decalin + NFM, decane + benzene + NFM, and decane + ethylbenzene + NFM over the temperature range 293–338 K, and the results were used to calculate the UNIFAC interaction parameters for the groups CH_2 + NFM, ACH + NFM, $ACCH_2$ + NFM, and CHNA + NFM as a function of temperature. The accuracy of these parameters was verified by comparing the predicted phase equilibrium compositions from UNIFAC with the experimental results.

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