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Liquid–Liquid Equilibria in Some Binary and Ternary Mixtures with Tetraethylene Glycol

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Liquid–liquid equilibria (LLE) for tetraethylene glycol + heptane or + decalin and tetraethylene glycol + decane, + benzene, or + ethylbenzene over a temperature range of 293–330.5 K were used to estimate the interaction parameters between a new solvent group (tetraethylene glycol) and the main groups of CH_2 (paraffinic $> CH_2$), ACH (aromatic $\geq$ 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

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 + TEG (tetraethylene glycol), decane + benzene + TEG, decane + ethylbenzene + TEG, and decalin + TEG over the temperature range 293–330.5 K have been studied by Al-Qattan (*1*). The results were used to determine the UNIFAC interaction parameters between the solvent and CH_2, ACH, $ACCH_2$, and CHNA 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 chemicals used in this study were decane (99+%), Fluka, decalin (98+%), Fluka, ethylbenzene (99+%), BDH, benzene (99+%), Fluka, heptane (99+%), Fluka, and tetraethylene glycol (99+%), Fluka.

Procedure. The experimental apparatus used for extraction consists of a glass vessel with a water jacket in order to maintain a constant temperature. The temperature was controlled within ±0.5 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.

Table 1. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Heptane (1) + Tetraethylene Glycol (2)

	phase I x_1^{I}		phase II x_1^{II}	
T/K	exptl	calcd	exptl	calcd
293.0	0.9589	0.9633	0.0049	0.0064
302.5	0.9400	0.9375	0.0036	0.0036
312.0	0.9240	0.9197	0.0037	0.0035
322.0	0.9137	0.9166	0.0038	0.0038

Table 2. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the System Decalin (1) + Tetraethylene glycol (2)

	phase I x_1^{I}		phase II x_1^{II}	
T/K	exptl	calcd	exptl	calcd
303.0	0.9692	0.9785	0.0063	0.0094
313.0	0.9400	0.9327	0.0083	0.0130
321.5	0.9289	0.9537	0.0098	0.0156
330.5	0.9225	0.9279	0.0198	0.0198

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 × 0.003 175-m column was packed with 3% by volume OV-70 80/100 chromosorb Q 11. 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.

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:

$$\gamma_i^{I} x_i^{I} = \gamma_i^{II} x_i^{II} \tag{1}$$

$$z_i = z_i^{I} + z_i^{II} \tag{2}$$

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Table 3. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the Ternary System Decane (1) + Ethylbenzene (2) + Tetraethylene Glycol (3)

	phase I				phase II			
	x_1^I		x_2^I		x_1^{II}		x_2^{II}	
T/K	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
298.5	0.8726	0.8561	0.1078	0.1078	0.0009	0.0007	0.0109	0.0142
	0.6923	0.6923	0.2664	0.2664	0.0016	0.0011	0.0349	0.0679
	0.5651	0.5204	0.4348	0.4461	0.0009	0.0009	0.0398	0.0679
312.0	0.9476	0.9440	0.0524	0.0558	0.0034	0.0019	0.0116	0.0097
	0.4085	0.3353	0.5915	0.6119	0.0038	0.0016	0.0788	0.1197
	0.9500	0.9865	0.0000	0.0000	0.0041	0.0035	0.0000	0.0000
	0.5404	0.5052	0.4308	0.4308	0.0018	0.0099	0.0139	0.0488
323.0	0.9113	0.9039	0.0887	0.0961	0.0130	0.0017	0.0095	0.0119
	0.7577	0.7277	0.2423	0.2592	0.0432	0.0025	0.0387	0.0417
	0.3330	0.3033	0.5746	0.5746	0.0035	0.0026	0.1247	0.1411
	0.5216	0.4963	0.4146	0.4146	0.0028	0.0019	0.0757	0.0806
	0.3602	0.1906	0.6398	0.6772	0.0037	0.0026	0.0000	0.1621

Table 4. Experimental and Calculated Liquid–Liquid Equilibrium Compositions for the Ternary System Decane (1) + Benzene (2) + Tetraethylene Glycol (3)

	phase I				phase II			
	x_1^I		x_2^I		x_1^{II}		x_2^{II}	
T/K	calcd	exptl	calcd	exptl	calcd	exptl	calcd	exptl
302.0	0.7670	0.8260	0.0629	0.0629	0.0029	0.0017	0.0218	0.0249
	0.5320	0.5990	0.2672	0.2672	0.0030	0.0024	0.1241	0.1257
	0.5031	0.5011	0.4165	0.4165	0.0032	0.0026	0.1796	0.1954
	0.7920	0.8710	0.0000	0.0000	0.0038	0.0021	0.0000	0.0000
318.0	0.8611	0.8815	0.0651	0.0651	0.0024	0.0015	0.0285	0.0262
	0.5690	0.6126	0.2615	0.2615	0.0024	0.0017	0.1321	0.1185
	0.3789	0.3532	0.5652	0.5652	0.0038	0.0035	0.2782	0.2788
	0.4623	0.4817	0.4065	0.4065	0.0031	0.0024	0.2050	0.1911
	0.8710	0.9002	0.0000	0.0000	0.0037	0.0021	0.0000	0.0000
327.5	0.9328	0.9067	0.0671	0.6999	0.0022	0.0014	0.0169	0.0213
	0.7295	0.6843	0.2645	0.2645	0.0036	0.0024	0.1221	0.1150
	0.5346	0.5138	0.4016	0.4016	0.0040	0.0030	0.1817	0.1803

Table 5. Root Mean Square Deviation for the Measured System for Tetraethylene Glycol (TEG)

system	F/%
heptane + TEG	0.185
decalin + TEG	0.730
decane + benzene + TEG	2.140
decane + ethylbenzene + TEG	4.004

Table 6. Interaction Parameters for the UNIFAC Method (a_{nm}) for Tetraethylene Glycol (TEG)

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

group	A_{nm}	A_{mn}	B_{nm}	B_{mn}
CH_2 + TEG	85.29	487.2	−1.609	2.919
ACH + TEG	408.50	−157.4	−9.000	5.523
$ACCH_2$ + TEG	25.72	146.6	−4.094	2.216
CHNA + TEG	−49.27	169.9	−2.224	−0.897

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 tetraethylene glycol (TEG). The equilibrium data for the binary systems were used to determine the interaction parameters for the TEG 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 TEG and between the $ACCH_2$ and TEG groups. The dependence of the interaction parameters on temperature was expressed by

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

where T is the temperature (K) 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*)

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

where i = 1 and 2 for binary or 1, 2, and 3 for ternary, j = phase I or II, k = 1, 2, ..., n (tie lines), 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 + TEG, decaline + TEG, decane + benzene + TEG, and decane + ethylbenzene + TEG over the temperature range 293–330.5 K, and the results were used to calculate the UNIFAC interaction parameters for the groups CH_2 + TEG, ACH + TEG, $ACCH_2$ + TEG, and CHNA + TEG 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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