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LIQUID–LIQUID EQUILIBRIUM IN THE TOLUENE –METHYL ETHYL KETONE–WATER SYSTEM

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ABSTRACT

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For the toluene–methyl ethyl ketone–water system the liquid–liquid equilibrium tie-line data have been determined at 40 and 0 °C and the binodal curve for this system has been determined at 40, 0 and −10 °C. The tie-line data at 40 and 0 °C could be correlated with good accuracy using NRTL and UNIQUAC model equations.

INTRODUCTION

A mixture of methyl ethyl ketone (MEK) and toluene in approximately 50 : 50 ratio (by volume) is widely used as a solvent in the dewaxing and/or deoiling operation(s) of a lube refinery (Anonymous, 1976). The bulk solvent after dewaxing/deoiling operations is recovered in various flash columns and finally the residual solvent is separated in stripper and azeotropic columns. In an actual operation the solvent recovered from the oil filtrate and slack wax in primary flash columns gets richer in MEK while the so-called dry solvent recovered finally from the downstream columns gets richer in toluene with an overall water content of 4.0 to 10.0 mol.% in the circulating solvent. This water, which comes through the steam strippers and leaks in coolers and steam heaters, chokes the chillers and filters because of ice formation and decreases the throughput. Further, the water concentration in the solvent depends on the MEK content of the solvent. It is essential to determine liquid–liquid equilibrium (LLE) data for this system at the

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temperature around which the solvent is stored or solvent–water mixture coming from the strippers is allowed to settle into two liquid phases. The LLE data for the toluene–MEK–water system are not available in the literature either at this temperature (about 40 °C) or at lower temperatures at which wax crystallization occurs. The purpose of the present study was therefore to determine the LLE data for this system at 40, 0 and −10 °C so as to obtain an indication of how much water is likely to separate at these temperatures from the water originally present in the solvent before recycling. However, at −10 °C the tiny water droplets, resulting from the entrainment due to mixing, became solidified making it difficult for the two equilibrium phases to separate. Because of this experimental difficulty the LLE data have been determined at 40 °C and 0 °C and the results correlated by NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations.

EXPERIMENTAL DETAILS

Materials

MEK and toluene were obtained from S.D. Fine Chemicals Ltd., India and from BDH, India respectively. The purities of MEK and toluene were better than 99 wt.% and 99.5 wt.% as determined by gas chromatography and further checked by measurement of refractive index and density values as given in Table 1. The values obtained agreed quite closely with those reported in the literature for the purities mentioned. Toluene and MEK were further dried using molecular sieves in order to reduce their moisture content to a minimum.

Determination of liquid–liquid equilibria

For determination of liquid–liquid equilibrium at 40 °C and 0 °C single-stage batch equilibrium runs were carried out in a double-walled mixer–set-

TABLE 1

Physical properties of the solvents used

	MEK	Toluene
Refractive Index at 20 °C		
Measured	1.3789	1.4963
Literature (Weast, 1984)	1.3788	1.4961
Density at 20 °C, kg l^{-1}		
Measured	0.8050	0.8672
Literature (Weast, 1984)	0.8054	0.8669

tler having a capacity of about 250 ml and having a thermometer pocket and a syringe stirrer. The desired temperature was maintained to within 0.1°C with the aid of a thermostatic bath. Varying quantities of MEK, toluene and water were used in the mixer–settler and the contents were stirred for 20 min. The phases were then allowed to settle for about 2 h before they were withdrawn separately for analysis. The phases were weighed and analysed using a Perkin-Elmer Sigma 300 Gas Chromatograph with a thermal conductivity detector and an LIC-100 Laboratory Integrator. The analysis was carried out on Propak-Q (2 m × 2 mm i.d.) at 250°C with hydrogen as the carrier gas. Some of the phases in which there were chances of further phase separation due to variation in the solubility with temperature were collected in a known quantity of anhydrous methanol, before analysis. The accuracy of the analysis was checked with synthetic blends, which established a maximum relative error of less than 2%.

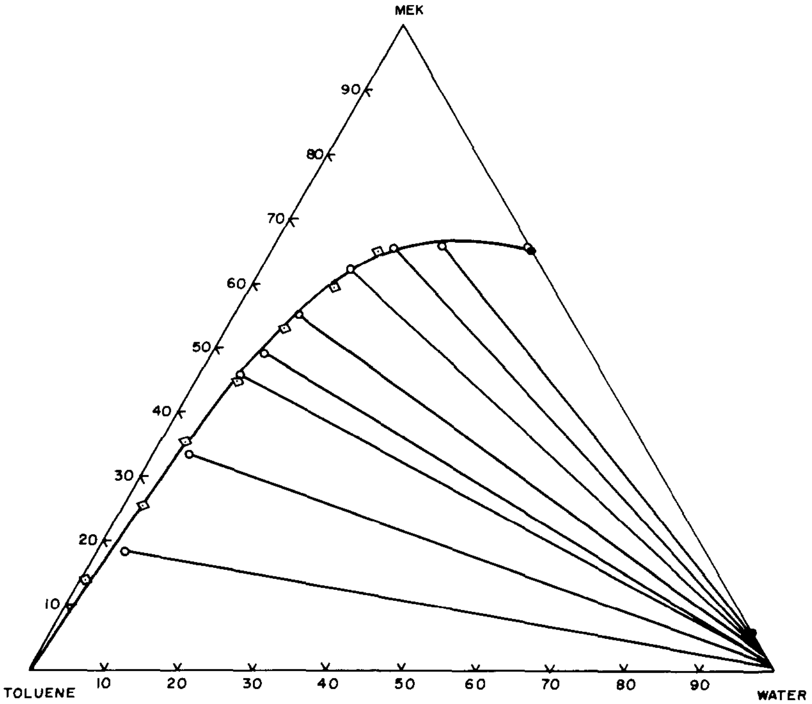

Fig. 1. Liquid–liquid equilibrium diagram and binodal curve for toluene(1)–MEK(2)–water(3) system at 40°C (concentrations in mol.%). ○, tie-line data; □, binodal curve data; ●, smoothed data (Sorensen and Arlt, 1979).

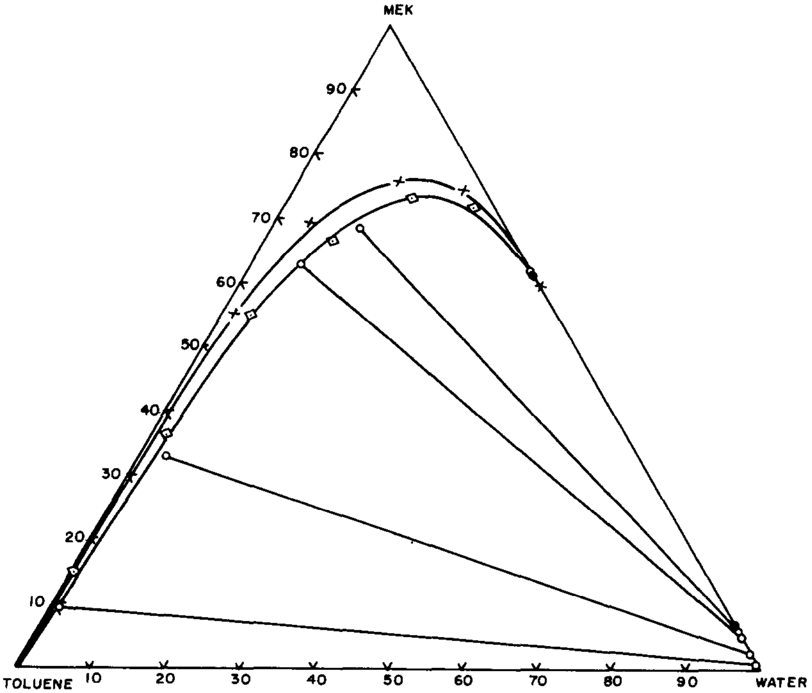

Fig. 2. Liquid–liquid equilibrium diagram at 0 ° C and binodal curves at 0 and − 10 ° C for toluene(1)–MEK(2)–water(3) system (concentrations in mol.%). ○, tie-line data; □, binodal curve data at 0 ° C; ×, binodal curve data at − 10 ° C; ●, smoothed data at 0 ° C (Sorensen and Arlt, 1979).

Determination of binodal curves

The binodal curves for the system were determined at 40, 0 and − 10 ° C by the titration method (Alders, 1959). The apparatus used was a double-walled flat-bottom tube having a capacity of about 120 ml and provided with a detachable adapter having a thermometer pocket. A magnetic stirrer was used to mix the contents. The desired temperatures were maintained within 0.1 ° C by circulating the chilled liquid from a thermostatic bath.

Varying amounts of MEK and toluene were used in the titration tube and the solubility of water in these mixtures was determined by observing the haze points. The whole system was sealed during the determination to keep the contents away from atmospheric moisture. In the present study the accuracy of determination of binodal curves (see Fig. 2) is within ±4%.

RESULTS AND DISCUSSION

The experimental LLE tie-line data for the toluene(1)–MEK(2)–water(3) system at 40 and 0 ° C are given in Tables 2 and 3 respectively whereas the

TABLE 2

Experimental and calculated LLE data for toluene(1)–MEK(2)–water(3) at 40 °C

Toluene (mol.%)			MEK (mol.%)			Water (mol.%)		
Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC
Raffinate phase compositions								
77.91	78.37	78.56	18.29	18.90	19.14	3.80	2.73	2.30
61.67	61.74	61.87	33.78	33.91	34.04	4.55	4.35	4.09
48.71	48.32	48.36	46.03	45.46	45.36	5.26	6.22	6.28
36.24	36.11	36.01	55.45	55.07	54.77	8.31	8.82	9.22
25.77	25.80	25.65	62.43	61.77	61.55	11.80	12.43	12.79
18.09	18.35	18.13	65.88	65.06	65.43	16.03	16.58	16.43
11.54	11.05	10.48	65.14	66.14	67.78	23.32	22.81	21.74
43.34	43.80	43.44	49.00	49.35	49.23	7.66	7.10	7.32
43.81	43.71	43.68	49.34	49.22	49.05	6.85	7.07	7.27
42.88	43.00	42.94	49.47	49.79	49.62	7.65	7.21	7.43
0.00	0.00	1.00	66.01	66.17	64.99	33.99	33.83	34.01
Corresponding extract phase compositions								
0.01	0.070	0.011	0.69	0.27	0.68	99.30	99.66	99.31
0.01	0.054	0.011	0.98	0.76	1.33	99.01	99.18	98.66
0.01	0.042	0.011	2.09	1.49	1.93	97.90	99.47	98.06
0.01	0.033	0.011	2.54	2.52	2.54	97.45	97.44	97.44
0.01	0.027	0.010	3.16	3.60	3.13	96.83	96.37	96.86
0.02	0.023	0.009	3.58	4.28	3.62	96.40	95.69	96.37
0.02	0.021	0.007	4.11	4.62	4.22	95.87	95.36	95.77
0.02	0.038	0.011	2.16	1.85	2.16	97.82	98.11	97.82
0.02	0.038	0.011	2.16	1.84	2.15	97.82	98.12	97.84
0.02	0.038	0.011	2.21	1.89	2.19	97.77	98.07	97.80
0.00	0.000	0.002	5.54	5.21	5.38	94.46	94.79	94.61

experimentally determined binodal curves (organic phase only) at 40, 0 and −10 °C are given in Table 4. Graphical representations of ternary equilibria are presented in Figs. 1 and 2 at 40 and 0 °C respectively. In Fig. 2 the binodal curve at −10 °C is also plotted. From the ternary LLE data at 40 and 0 °C the NRTL and UNIQUAC parameters of the three binary pairs were estimated using the method of Sorensen (1980). The model parameters, along with the root mean square deviation (RMSD) values, are given in Table 5. The RMSD between the experimental and calculated extract and raffinate phase compositions were calculated using

$$\mathrm{RMSD} = 100\left[\sum_{k}\sum_{i}\sum_{j}\left(x_{ijk} - \hat{x}_{ijk}\right)^2/6M\right]^{1/2} \qquad (1)$$

TABLE 3

Experimental and calculated LLE data for toluene(1)–MEK(2)–water(3) at 0 °C

Toluene (mol.%)			MEK (mol.%)			Water (mol.%)		
Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC
Raffinate phase compositions								
89.63	89.75	89.49	9.18	9.33	9.05	1.19	0.92	1.46
63.33	63.66	63.67	32.95	33.58	33.44	3.72	2.76	2.89
19.65	19.85	19.79	68.55	68.50	68.97	11.80	11.65	11.24
30.46	29.98	30.17	62.91	61.84	62.09	6.63	8.18	7.74
0.00	0.00	0.00	62.16	62.42	62.17	37.84	37.58	37.83
Corresponding Extract phase compositions								
0.01	0.0230	0.006	0.72	0.21	0.49	99.27	99.76	99.50
0.01	0.0187	0.008	2.47	1.24	2.08	97.52	98.74	97.92
0.01	0.0112	0.010	5.83	6.50	6.34	94.16	93.49	93.65
0.01	0.0129	0.010	4.99	4.63	5.02	95.00	95.36	94.97
0.00	0.0000	0.000	12.09	12.37	11.98	87.91	87.67	88.02

It is seen that both the UNIQUAC and NRTL models correlate the equilibrium data at 40 and 0 °C very well.

For comparison purposes ternary LLE data at 40 and 0 °C were also predicted by using UNIQUAC and NRTL models with binary parameters as reported in the literature; these parameters were based on vapor–liquid equilibrium (VLE) and LLE data. For toluene–MEK, the parameters reported are based on VLE data (Gmehling et al., 1979) whereas for the two partially miscible pairs, i.e. water–toluene and water–MEK, the parameters

TABLE 4

Experimentally determined binodal curves (organic phase only) for the toluene(1)–MEK(2)–water(3) system at 40, 0 and −10 °C (concentrations in mol.%)

40 °C			0 °C			−10 °C		
Toluene	MEK	Water	Toluene	MEK	Water	Toluene	MEK	Water
85.34	13.77	0.89	84.64	14.67	0.69	85.35	14.25	0.40
72.01	25.43	2.56	61.70	36.49	1.81	62.69	36.47	0.84
61.27	35.15	3.58	41.07	54.85	4.08	42.88	55.43	1.69
49.63	45.00	5.37	24.35	66.52	9.13	25.71	69.20	5.09
39.11	53.22	7.67	10.15	73.21	16.64	10.51	75.80	13.69
29.43	59.63	10.94	2.82	71.71	25.47	2.41	74.70	22.89
20.80	65.09	14.11	0.00	62.16	37.84	0.00	59.37	40.63
0.00	5.54	94.46	0.00	12.09	87.91	0.00	14.48	85.52
0.00	66.01	33.99						

TABLE 5

Model parameters (in kelvin) obtained from ternary LLE data and RMSD values at 40 and 0 °C

System	NRTL ($\alpha = 0.2$)		UNIQUAC	
	$\Delta g_{ij}/R$	$\Delta g_{ji}/R$	$\Delta u_{ij}/R$	$\Delta u_{ji}/R$
40 °C				
Toluene(1)–MEK(2)	−984.21	2287.50	9.64	−30.78
Toluene(1)–Water(3)	810.28	1732.60	677.43	392.86
MEK(2)–Water(3)	−25.19	1057.10	277.43	42.53
RMSD (mol.%)	0.4211		0.5817	
0 °C				
Toluene(1)–MEK(2)	−809.44	109.10	−71.89	79.42
Toluene(1)–Water(3)	967.23	1798.20	547.23	402.51
MEK(2)–Water(3)	55.79	698.98	374.08	−35.41
RMSD (mol.%)	0.5857		0.3933	

TABLE 6

Model parameters (kelvin) for the constituent binaries reported in the literature from their binary VLE/LLE data and corresponding RMSD values calculated at 40 and 0 °C.

System	Data type	Temperature (°C)	NRTL			UNIQUAC	
			$\Delta g_{ij}/R$	$\Delta g_{ji}/R$	α	$\Delta u_{ij}/R$	$\Delta u_{ji}/R$
40 °C							
Toluene(1)–MEK(2)	VLE	50	244.13	−111.75	0.303	203.36	−141.11
Toluene(1)–Water(3)	LLE	25	1313.30	2185.80	0.200	950.60	350.21
MEK(2)–Water(3)	LLE	40	−5.156	1001.30	0.200	322.64	20.80
RMSD (mol.%)			0.9783			0.7110	
0 °C							
Toluene(1)–MEK(2)	VLE	50	244.13	−111.75	0.303	203.36	−141.11
Toluene(1)–Water(3)	LLE	0	1401.30	1919.70	0.200	1030.40	289.19
MEK(2)–Water(3)	LLE	0	47.56	702.47	0.200	377.24	−38.04
RMSD (mol.%)			1.9440			0.8402	

were based on mutual binary solubility data (Sorensen and Arlt, 1979). The equilibrium data predicted at 40 and 0 °C from these binary parameters showed slightly higher RMSD values than those obtained from our own experimental data fit (cf. Tables 5 and 6).

CONCLUSIONS

The experimental equilibrium tie-line data for the system toluene(1)–MEK(2)–water(3) at 40 and 0 °C were correlated well using the NRTL and the UNIQUAC equations. The data were also predicted reasonably well by these equations when parameters reported in the literature from the binary data were used.

LIST OF SYMBOLS

Δg_{ij}, Δg_{ji}	NRTL parameters (J mol^{-1})
M	number of experimental tie lines
R	gas constant (J mol^{-1} K^{-1})
Δu_{ij}, Δu_{ji}	UNIQUAC parameters (J mol^{-1})
x_i	experimentally determined molar fraction

Greek Letters

α	NRTL non-randomness parameter

Superscripts

$\hat{}$	estimated values

Subscripts

i	components
j	phases
k	tie lines

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