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Short Communication

ISOBARIC VAPOUR–LIQUID EQUILIBRIA FOR THE TERNARY MIXTURE: METHYL ETHYL KETONE–WATER–TOLUENE

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ABSTRACT

Rawat, B.S., Gupta, S.K., Nanoti, S.M. and Krishna, R., 1987. Isobaric vapour–liquid equilibria for the ternary mixture: methyl ethyl ketone–water–toluene. *Fluid Phase Equilibria*, 38:155–161.

The vapour–liquid equilibrium was measured for methyl ethyl ketone–water–toluene ternary in the miscible region at 101.325 kPa pressure. The miscible liquid-phase compositions were chosen from the ternary solubility curve determined experimentally at 40 ° C. The experimental ternary vapour-phase compositions have been compared with values calculated by NRTL, modified UNIQUAC and UNIFAC model equations using binary data available in the literature.

INTRODUCTION

In the petroleum refining industry, solvent dewaxing and solvent deoiling processes are used in the Lube Oil block to produce lube oil base stocks and paraffin waxes, respectively. The most extensively used solvent is a mixture of methyl ethyl Ketone (MEK) and toluene. This solvent combination, generally in 50 : 50 volume ratio, is used to serve a dual purpose of providing higher selectivity (by MEK) and solubility (by toluene) in the oil–wax separation. Both solvent dewaxing and solvent deoiling operations have crystallization, filtration, solvent recovery and refrigeration sections. The crystallization and filtration sections are the most critical which are very expensive and determine the capacity of Lube Oil Block. To improve or maintain the performance of these two sections, it is essential to control the amount of water in the solvent mixture which otherwise chokes the chillers and filters due to ice formation and decreases the throughput. Generally, the combined recovered solvent mixture contains 1 to 2.5 wt.% water, which

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finds its way into the solvent through steam strippers and leaks in coolers and steam heaters. Refiners often find it difficult to remove this water in the solvent recovery system. In the present-day context, to improve further the efficiency of these industrial units it is necessary to remove or reduce this water content to about 0.2 wt.%. Therefore, in designing an optimum drying/stripping column the knowledge of vapour–liquid equilibria (VLE) is essential but to the authors knowledge data for the MEK–water–toluene system are not available in the literature. The objective of this study is to determine isobaric VLE data for this ternary mixture and compare them with those calculated by different predictive methods using equilibrium data of constituent binary mixtures available in the literature.

EXPERIMENTAL

Materials

Toluene and MEK, procured from M/s B.D.H., India and M/s Glaxo Laboratories, India, respectively, were of minimum 99.5% purity as checked by gas chromatography (GC). Both toluene and MEK were dried over molecular sieves before use. The physical properties of these chemicals also compare well with the literature values (Marsden, 1963).

Apparatus and procedure

The VLE studies for the ternary system were carried out in a modified Smith and Bonner type of still (Smith and Bonner, 1949) provided with a magnetic stirrer. The experimental details are described earlier by Rawat et al. (1980). For VLE measurements the liquid phase compositions were chosen from the ternary equilibrium solubility diagram (Fig. 1) determined at 40 °C by titration method (Alders, 1959).

The vapour phase always formed two liquid phases on cooling. The vapour samples were, therefore, made homogeneous by adding a known amount of anhydrous acetone. This homogeneous sample was then analysed by GC using a Perkin-Elmer Sigma 300 Gas chromatograph with thermal conductivity detector and LCI-100 Laboratory Integrator. The analysis was carried out on Porapak-Q (2M × 2 mm id) at 250 °C with hydrogen as the carrier gas. The accuracy of the analysis was checked with synthetic blends, which showed a maximum error of ~ 2%.

RESULTS AND DISCUSSION

The MEK–water–toluene ternary has two azeotropic (Marsden, 1963; Othmer et al., 1952) partially miscible binaries (water–toluene and

TABLE 1

Equilibrium ternary solubilities for MEK–water–toluene system at 40 ° C Data in mole fraction

MEK	Water	Toluene
0.2542	0.0190	0.7268
0.4603	0.0526	0.4871
0.4900	0.0766	0.4334
0.5545	0.0831	0.3624
0.6243	0.1180	0.2577
0.6514	0.2332	0.1154
0.6539	0.1662	0.1795
0.0077	0.9922	0.0001
0.0209	0.9790	0.0001
0.0216	0.9782	0.0002
0.0254	0.9744	0.0002
0.0316	0.9683	0.0001
0.0411	0.9587	0.0002
0.0359	0.9640	0.0001

MEK–water) and the third binary (MEK–toluene) is completely miscible and non-azeotropic. The formation of a ternary azeotrope is not reported in the literature. The mutual solubility (40 ° C) and azeotropic data for the partially miscible binaries are presented in Fig. 1 along with the equilibrium solubility data (Table 1) determined experimentally at 40 ° C. For the determination of ternary VLE in the miscible region the liquid phase compositions were chosen from Fig. 1.

The experimentally determined VLE data for MEK–water–toluene ternary are presented in Table 2. The ternary VLE data have been further calculated by NRTL (Renon and Prausnitz, 1968) and modified UNIQUAC (Anderson and Prausnitz, 1978) equations using the binary parameters obtained from the equilibrium data reported in the literature on the constituent binaries. The isobaric VLE data for MEK–water and MEK–toluene are reported by Ellis and Garbett (1960) and Steinhauser and White (1949), respectively. The liquid-phase activity coefficients required for the estimation of the binary parameters were calculated from the binary VLE data using the following equation (van Ness, 1964)

$$\gamma_i = \frac{Py_i}{P_i^0 x_i} \exp\left(\frac{(B_i - V_i^L)(P - p_i^0)}{RT} \right) \tag{1}$$

The VLE data for MEK–Water binary were chosen in the temperature range of 73.55–83.25 ° C. The three points in the infinite dilution region were omitted as they gave large deviations.

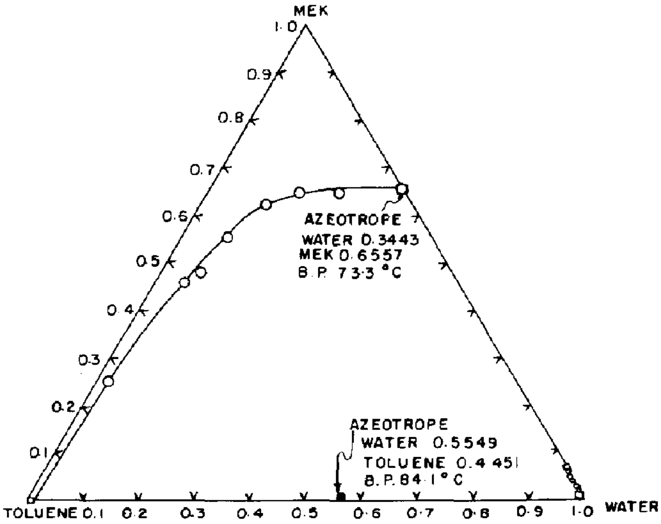

Fig. 1. Solubility limits for MEK(1)–water(2)–toluene(3) at 40 °C (concentrations in mole fractions).

The second virial coefficients for all the three components were calculated by the method of Hala (Hala et al., 1967) while the Critical constants were taken from the literature (Weast, 1984). The liquid molar volumes for water and toluene were also taken from the literature (Prausnitz et al., 1967) and for MEK they were calculated from the density values (Marsden, 1963) and fitted to a quadratic equation to compute the constants, *a*, *b* and *c*. The vapour-pressure data were calculated from Antoine equation using the constants reported in the literature (Dreisbach, 1955, 1961; Ohe, 1976).

TABLE 2

Experimental VLE data for the system: MEK(1)–water(2)–toluene(3) at 101.325 kPa. Data in mole fraction

Temperature (°C)	Liquid phase		Vapour phase	
	x_1	x_2	y_1	y_2
74.2	0.6783	0.2833	0.6002	0.3641
74.6	0.6819	0.2312	0.5802	0.3586
75.2	0.6848	0.1720	0.5563	0.3556
76.4	0.6814	0.1170	0.5772	0.3219
76.7	0.7127	0.1133	0.6013	0.3047
77.6	0.6510	0.0918	0.5687	0.3111
79.1	0.6248	0.0644	0.5750	0.2873
80.8	0.5328	0.0521	0.5294	0.2965
84.5	0.4963	0.0349	0.5402	0.2567

TABLE 3

Correlation parameters for the constituent binary systems

Equation	System $i-j$		
	MEK(1)–water(2)	MEK(1)–Toluene(3)	Water(2)–Toluene(3)
NRTL (Three parameters)			
$\Delta g_{ij}/R$	229.40	254.14	2100.54
$\Delta g_{ji}/R$	919.31	−67.21	839.88
α_{ij}	0.30	0.30	0.2
RMSD, y_i	0.0162	0.0090	–
Modified UNIQUAC (Two parameters)			
$\Delta u_{ij}/R$	596.39	133.30	194.19
$\Delta u_{ji}/R$	−42.40	−84.96	1151.71
RMSD, y_i	0.0127	0.0079	–

For water–toluene binary the activity coefficients were estimated from the mutual solubility (Seidell, 1940) data using the following relation

$$(\gamma_i x_i)^{\mathrm{I}} = (\gamma_i x_i)^{\mathrm{II}} \tag{2}$$

The NRTL and modified UNIQUAC binary parameters for all the three binaries were finally calculated from the Nelder and Mead (1964) simplex optimization technique. The values of the parameters as given in Table 3 were used to predict the ternary vapour compositions using the ternary forms of these equations. The root mean square deviation (*RMSD*)

$$RMSD = \sqrt{\sum (y_{i,\mathrm{exp}} - y_{i,\mathrm{cal}})^2/n} \tag{3}$$

between the experimental and calculated vapour-phase compositions for the two binaries and for the ternary are given in Tables 3 and 4. From these RMSD values it is apparent that NRTL equation provides the best prediction of the ternary results.

The ternary VLE data were also calculated from the ternary t–x data (Table 2) using UNIFAC (Fredenslund et al., 1975, 1977; Gmehling et al.,

TABLE 4

RMSD for prediction of ternary VLE by different model equations

Method	RMSD on vapour-phase mole fractions		
	MEK	Water	Toluene
NRTL	0.0079	0.0121	0.0072
Modified UNIQUAC	0.0187	0.0232	0.0078
UNIFAC	0.0816	0.0982	0.0190

1982) group contribution method. The large deviations in RMSD values (Table 4) show the limitation of the UNIFAC approach for this system.

LIST OF SYMBOLS

B_i	pure component second virial coefficient (m^3 mol^{-1})
Δg_{ij}, Δg_{ji}	NRTL parameters (J mol^{-1})
n	number of points
P_i^0	saturated vapour-pressure of pure component (Pa)
P	total pressure (Pa)
R	gas constant (J mol^{-1} K^{-1})
T	absolute temperature (K)
Δu_{ij}, Δu_{ji}	UNIQUAC parameters (J mol^{-1})
V_i^L	pure component molar volume (m^3 mol^{-1})
x_i	liquid-phase mole fraction
y_i	vapour-phase mole fraction

Greek letters

α	NRTL non randomness parameter
γ_i	liquid-phase activity coefficient of component i

Subscripts

i	ith component
j	jth component
cal	calculated value
exp	experimental value

Superscripts

I, II	two phases

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