Fluid Phase Equilibria, 46 (1989) 95–102
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ISOBARIC VAPOUR–LIQUID EQUILIBRIA OF THE SYSTEMS: BENZENE–TRIETHYLENE GLYCOL, TOLUENE–TRIETHYLENE GLYCOL AND BENZENE-*N*-METHYLPYRROLIDONE

S.K. GUPTA, B.S. RAWAT *, A.N. GOSWAMI, S.M. NANOTI and R. KRISHNA
Indian Institute of Petroleum, Dehra Dun 248 005 (India)

(Received January 8, 1987; accepted in final form August 4, 1988)

ABSTRACT

Gupta, S.K., Rawat, B.S., Goswami, A.N., Nanoti, S.M. and Krishna, R., 1989. Isobaric vapour–liquid equilibria of the systems: benzene–triethylene glycol, toluene–triethylene glycol and benzene–*N*-methylpyrrolidone. *Fluid Phase Equilibria,*: 46: 95–102.

Isobaric vapour–liquid equilibria have been determined at 101.325 kPa for three binary mixtures: benzene–triethylene glycol, toluene–triethylene glycol and benzene–*N*-methylpyrrolidone. The data have been correlated with reasonable accuracy using the NRTL, Wilson and UNIQUAC equations using a non-linear regression approach based on the maximum-likelihood principle.

INTRODUCTION

Triethylene glycol (TEG) and *N*-methylpyrrolidone (*N*-MP) are used industrially as solvents for the selective removal of aromatic hydrocarbons such as benzene and toluene from naphtha (Somekh, 1963; Muller and Hoehfeld, 1971). The vapour–liquid equilibrium (VLE) data for binary mixtures of benzene–TEG and toluene–TEG are not available in the literature; for the mixture benzene–*N*-MP, isothermal VLE data are reported by Fabries et al. (1977) at temperatures ranging from 20 to 100 °C and by Gierycz et al. (1985) for 60.1 and 80 °C.

Knowledge of VLE data is required for the design of extractive distillation and solvent recovery columns in the separation processes of aromatics, and it is the objective of the present paper to generate isobaric VLE data for the three binary mixtures mentioned.

---

* To whom all correspondence should be addressed.

0378-3812/89/$03.50

EXPERIMENTAL DETAILS

Chemicals

Pure benzene and toluene were obtained from BDH, India. TEG and *N*-MP were procured from Aldrich Chemicals, U.S.A., and BDH Chemicals, U.K., respectively. TEG and *N*-MP were distilled under vacuum and their middle fractions were collected for use in the study. The purities of all the above chemicals were checked by measuring their densities and refractive indices, which indicated a minimum purity of 99%.

Experimental procedure

For all three systems the VLE data were determined in a Smith and Bonner still (Smith and Bonner, 1949). The still was slightly modified by providing a closed magnetic stirrer. The procedural details have been described earlier by Rawat et al. (1980).

Analysis of TEG in the vapour phase

Since there is a large difference between the boiling points of TEG and of the hydrocarbons used, the amount of TEG present in the vapour phase was so small that is posed a problem of analysis. Therefore, a titration method (Gyenes, 1967) was used; this involved the acetylation of the hydroxyl groups by acetic anhydride in the presence of perchloric acid, which acted as a catalyst. Ethyl acetate was used as a solvent. The detailed procedure is reported in the literature (Fritz and Schenk, 1959; Gyenes, 1967). About 2 ml of the vapour sample were collected in a conical flask after equilibrating the phases for about 3 h. The sample was titrated as indicated above. The method is sensitive enough to determine small traces of glycols to an accuracy of about ±0.4%. This accuracy was verified using various synthetic mixtures prepared in the concentration range 0.1–5.0 wt.% TEG.

Analysis of N-*MP*

The concentration of *N*-MP in the vapour phase was determined by a gas–liquid chromatographic technique. The accuracy of the values determined was checked by analysis of synthetic mixtures.

RESULTS AND DISCUSSION

The VLE data (P, t, x, y) for all three binaries are presented in Table 1. For phase equilibrium data reduction, the following thermodynamic relation

TABLE 1

Experimental VLE data for systems benzene(1)–TEG(2), toluene(1)–TEG(2) and benzene(1)–*N*-MP(2) at 101.325 kPa

Benzene(1)–TEG(2)			Toluene(1)–TEG(2)			Benzene(1)–*N*-MP(2)		
Temperature (° C)	Liquid phase composition (x_1)	Vapour phase composition (y_1)	Temperature (° C)	Liquid phase composition (x_1)	Vapour phase composition (y_1)	Temperature (° C)	Liquid phase composition (x_1)	Vapour phase composition (y_1)
155.6	0.068	0.9900	169.4	0.0815	0.9802	146.9	0.1217	0.8242
139.0	0.097	0.9949	141.4	0.1497	0.9933	140.2	0.1514	0.8650
135.2	0.1079	0.9953	122.0	0.2920	0.9976	124.6	0.2360	0.9280
112.7	0.1841	0.9989	117.0	0.4012	0.9984	110.0	0.3660	0.9658
92.6	0.3294	0.9996	115.0	0.5127	0.9987	103.9	0.4550	0.9760
85.4	0.4457	0.9998	114.2	0.6126	0.9988	98.3	0.5493	0.9840
83.3	0.5573	0.9998	114.0	0.7063	0.9989	92.6	0.6634	0.9902
82.5	0.6575	0.9999	113.0	0.7876	0.9991	88.8	0.7471	0.9935
82.0	0.7400	0.9999	112.5	0.8644	0.9993	85.7	0.8335	0.9961
81.8	0.8173	0.9999	112.1	0.9353	0.9995	82.7	0.9173	0.9982
81.5	0.8849	0.9999						

was used

$$\phi_i y_i P = \gamma_i x_i \phi_i^s P_i^s \exp\left[v_i^L (P - P_i^s)/RT\right] \tag{1}$$

The data of the three binaries were correlated by NRTL (Renon and Prausnitz, 1968). Wilson (1964) and UNIQUAC (Abrams and Prausnitz, 1975) equations. The correlation parameters for these equations were obtained following the procedure described by Prausnitz et al. (1980) using a non-linear regression approach based on the maximum-likelihood principle. The best correlation parameters in each case were obtained by minimizing the following objective function, S

$$S = \sum_{i=1}^{m} \left[\frac{(P_i^c - P_i^e)^2}{\sigma_P^2} + \frac{(T_i^c - T_i^e)^2}{\sigma_T^2} + \frac{(x_i^c - x_i^e)^2}{\sigma_x^2} \right] \tag{2}$$

The superscripts c and e indicate calculated and experimental values respectively. The estimated variances in pressure, temperature and liquid phase mole fraction are calculated using the values

$$\sigma_P = 1 \text{ mmHg} \qquad \sigma_T = 0.05\,^\circ\text{C} \qquad \sigma_x = 0.001 \tag{3}$$

In the regression, the vapour phase compositions were not included in view of the fact that the concentration of high boiling-point constituents in the vapour phase is very small and consequently subject to large relative errors.

The second virial coefficients required for calculating the vapour phase fugacity coefficients in eqn. (1) were calculated using the method of Hayden and O'Connell (1975); the physical properties of pure components used in this calculation step are presented in Table 2. The properties for benzene and toluene were taken from the literature (Gmehling et al., 1980; Prausnitz et al., 1980). For TEG and *N*-MP the properties taken from the literature included the dipole moment (Riddick and Bunger, 1970), UNIQUAC structural parameters (Sorensen and Arlt, 1979), solvation and association parameters (Fredenslund et al., 1977) and Antoine constants (Marsden, 1963; Gierycz et al., 1985). The critical constants for *N*-MP and TEG were calculated using the method of Hakuta and Hirata (1970). The radius of gyration values for *N*-MP and TEG were calulated using the method suggested by Fredenslund et al. (1977). The liquid molar volumes of the pure components required in eqn. (1) were calculated at the desired temperatures using values of the critical compressibility factor (Table 2) in the Rackett equation (Rackett, 1970).

The calculated correlation parameters for the three binaries corresponding to NRTL, Wilson and UNIQUAC equations are presented in Table 3, together with the corresponding values of the root mean square deviations. As seen from Table 3 the results of benzene–TEG, toluene–TEG and

TABLE 2

Characteristics of the components used in calculating predicted vapour–liquid equilibrium values

Component	P_c (bar)	RD (Å)	μ (D)	T_c (K)	Z_c	η	Antoine constants			UNIQUAC parameters	
							A	B	C	r_k	q_k
Benzene	48.98	3.004	0.00	562.16	0.2710	0.00	6.879870	1196.760	219.161	3.19	2.40
Toluene	41.09	3.443	0.36	591.79	0.2640	0.00	6.950870	1342.310	219.187	3.92	2.97
N-MP	48.66	3.337	3.88	712.03	0.2539	0.90	7.362566	1874.715	215.508	3.98	3.20
TEG	31.58	4.322	5.58	751.04	0.2197	1.55	8.702614	2852.623	210.398	5.59	4.89

Solvation parameter:
Aromatics with *N*-MP (ketone) 0.50
Aromatics with TEG (alcohol) 0.00

TABLE 3

Correlation parameters for the systems studied

System	Equation	Parameter (K)		t [a] (°C)	p [a] (mmHg)	x [a] (mole fraction)	y [a] (mole fraction)
Benzene –TEG	NRTL	$\Delta g_{12}/R$	1309.53	0.21	3.70	0.0028	0.0005
		$\Delta g_{21}/R$	−245.27				
		α	0.22				
	Wilson	$\Delta\lambda_{12}/R$	164.25	0.36	6.68	0.0098	0.0005
		$\Delta\lambda_{21}/R$	1759.36				
	UNIQUAC	$\Delta u_{12}/R$	213.77	0.17	3.18	0.0027	0.0005
		$\Delta u_{21}/R$	−1.27				
Toluene –TEG	NRTL	$\Delta g_{12}/R$	177.09	0.22	4.36	0.0024	0.0008
		$\Delta g_{21}/R$	357.55				
		α	−1.04				
	Wilson	$\Delta\lambda_{12}/R$	284.96	0.20	3.95	0.0062	0.0008
		$\Delta\lambda_{21}/R$	1158.25				
	UNIQUAC	$\Delta u_{12}/R$	159.26	0.30	5.86	0.0024	0.0008
		$\Delta u_{21}/R$	40.16				
Benzene *N*-MP	NRTL	$\Delta g_{12}/R$	61.63	0.09	1.76	0.0019	0.0043
		$\Delta g_{21}/R$	57.62				
		α	−6.26				
	Wilson	$\Delta\lambda_{12}/R$	63.32	0.13	2.41	0.0023	0.0036
		$\Delta\lambda_{21}/R$	114.62				
	UNIQUAC	$\Delta u_{12}/R$	−44.23	0.14	2.48	0.0024	0.0036
		$\Delta u_{21}/R$	112.78				

[a] Root mean square deviation.

benzene–*N*-MP systems are best represented by UNIQUAC, Wilson and NRTL equations, respectively. Considering the large differences in boiling points of the binary systems, the deviations are within an acceptable range.

LIST OF SYMBOLS

Δg^{12}, Δg^{21}	NRTL parameters (J mol^{-1})
m	number of experimental points
P	pressure (mmHg)
P_c	critical pressure (bar)
q	UNIQUAC area parameter
r	UNIQUAC volume parameter

R	gas constant
RD	mean radius of gyration (Å)
S	objective function, eqn. (2)
t	temperature (°C)
T	absolute temperature (K)
T_c	critical temperature (K)
v	liquid molar volume ($m^3\ mol^{-1}$)
x	liquid phase mole fraction
y	vapour phase mole fraction
Z_c	critical compressibility factor

Greek Letters

α	NRTL parameter
γ	activity coefficient
Δu^{12}, Δu^{21}	UNIQUAC parameters ($J\ mol^{-1}$)
$\Delta\lambda_{12}$, $\Delta\lambda_{21}$	Wilson parameters ($J\ mol^{-1}$)
η	association parameter
μ	dipole moment (D)
σ^2	variance
ϕ	fugacity coefficient

Superscripts

c	calculated value
e	experimental value
s	saturated condition

Subscripts

i	ith component

REFERENCES

Abrams, D.S. and Prausnitz, J.M., 1975. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. AIChE J., 21: 116–128.

Fabries, J.-F., Gustin, J.-L. and Renon, H., 1977. Experimental measurements of phase equilibrium properties for systems containing n-heptane, benzene, *N*-methylpyrrolidone and monoethanol amine. Representation by NRTL equation. J. Chem. Eng. Data, 22(3): 303–308.

Fredenslund, Å., Gmehling, J. and Rasmussen, P., 1977. Vapor–Liquid Equilibria using UNIFAC. Elsevier, Amsterdam.

Fritz, J.S. and Schenk, G.H., 1959. Acid-catalyzed acetylation of organic hydroxyl groups. Anal. Chem. 31(11): 1808–1812.

Gierycz, P., Rogalaski, M. and Malanowski, S., 1985. Vapour–liquid equilibria in binary systems formed by *N*-methylpyrrolidone with hydrocarbons and hydroxyl derivatives. Fluid Phase Equilibria, 22(1): 107–122.

Gmehling, J., Onken, U. and Arlt, W., 1980. Vapor–Liquid Equilibrium Data collection, Aromatic Hydrocarbons, Vol. 1 Part 7, DECHEMA Chem. Data Ser. DECHEMA, Frankfurt, p. 295.

Gyenes, I., 1967. Titrations in Non-aqueous Media. van Nostrand, Princeton, p. 294.

Hakuta, T. and Hirata, M., 1970. Estimation of critical constants. J. Chem. Eng. Japan, 3(1): 5–8.

Hayden, J.G. and O'Connell, J.P., 1975. A generalized method for predicting second virial coefficients. Ind. Eng. Chem. Proc. Des. Dev., 14: 209–216.

Marsden, C., 1963. Solvents Guide. Cleaver-Hume Press, London, p. 542.

Muller, E. and Hoehfeld, G., 1971. Aromatics recovery by extractive distillation with N-methylpyrrolidone. 8th World Petrol. Congr., 4: 213–219.

Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert C.A., Hsieh, R., and O'Connell, J.P., 1980. Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria. Prentice-Hall, Englewood Cliffs.

Rackett, H.G., 1970. Equation of state for saturated liquids. J. Chem. Eng. Data, 15(4): 514–517.

Rawat, B.S., Goswami, A.N. and Krishna, S., 1980. Isobaric vapour–liquid equilibria of the ternary system hexane–benzene–sulpholane. J. Chem. Tech. Biotechnol., 30: 557–562.

Renon, H. and Prausnitz, J.M., 1968. Local compositions in thermodynamic excess function for liquid mixtures. AIChE J., 14: 135–144.

Riddick, J.A. and Bunger, W.B., 1970. Organic Solvents. Wiley-Interscience, New York, 3rd edn., Vol. II, pp. 454, 475.

Smith, T.E. and Bonner, R.F., 1949. Vapor–liquid equilibrium still for partially miscible liquids. Ind. Eng. Chem., 41: 2867.

Somekh, G.S., 1963. How to improve aromatics extraction. Part 1: ethylene glycols. Hydrocarbon Process. Petrol. Refiner, 42(7): 161–164.

Sorensen, J.M. and Arlt, W., 1979. Liquid–Liquid Equilibrium Data Collection, Binary Systems, Vol. V, Part 1, DECHEMA Chem. Data Ser. DECHEMA, Frankfurt, pp. 279, 338.

Wilson, G.M., 1964. Vapor–liquid equilibrium. XI. A new expression for the excess free energy of mixing. J. Am. Chem. Soc., 86: 127–130.