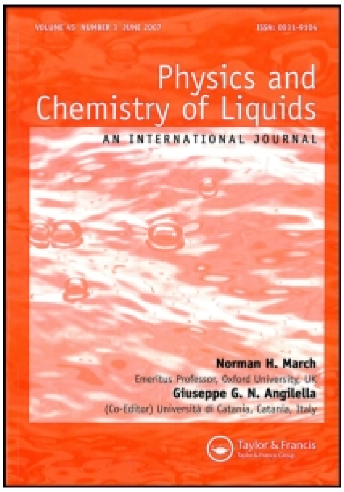

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VAPOR-LIQUID EQUILIBRIA IN THE BINARY SYSTEM FORMED BY METHYLTERTIARYBUTYLETHER WITH BENZENE AT 490 AND 709 mm Hg

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Isobaric vapor-liquid equilibria over the entire composition range are obtained from the measurement of the liquid phase composition *versus* boiling temperatures by means of a Swietoslawski type ebulliometer at 490 and 709 mm Hg for the methyl-tertiary-butylether(1) + benzene(2) system. The experimental composition (x) *versus* temperature (t) values could be represented well by both the Wilson and NRTL models. The optimum Wilson parameters have been used to calculate the excess Gibbs free energy.

Keywords: Vapor-liquid equilibria; methyltertiarybutylether; benzene; excess Gibbs free energy

INTRODUCTION

The present investigation is in continuation of our study of the thermophysical properties of binary liquid mixtures containing an ether as one of the components and benzene/substituted benzene as the other. Vapor-liquid equilibrium data for anisole + benzene and anisole + chlorobenzene; and anisole + nitrobenzene have been reported by Viswanathan *et al.* [1, 2]. Excess enthalpy measurements on the three

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systems are given by Viswanathan *et al.* [3]. This paper presents our measurements on the composition (x) *versus* equilibrium temperature (t) relationships for the methyltertiarybutylether(1) + benzene (2) system at 490 and 709 mm Hg. No published phase equilibrium information on this system could be located in the open literature for comparison purposes.

EXPERIMENTAL

Method

The measurements are carried out using a Swietoslawski type ebulliometer, very similar in design to the one described in Hala *et al.* [4]. The ebulliometer is connected to a vacuum system and the pressures are measured by means of a mercury-in-glass manometer in the line to an accuracy of ± 1 mm Hg. The temperatures are measured by means of a platinum resistance thermometer to an accuracy of ± 0.1 deg.C. The measurements are carried out at two subatmospheric pressures of 490 and 709 mm Hg. The equilibrium boiling temperatures are measured for the entire composition range at each of the two chosen pressures. Mixtures of different composition are prepared gravimetrically and placed in the ebulliometer. The heating rate is adjusted to yield the desired condensate drop rate of aroud 30 per minute recommended by Hala *et al.* [4]. The equibrium temperature, as indicated by the steady drop rate and constancy of the temperature, maintained for atleast 30 minutes, is recorded for different compositions at each pressure.

Materials

Methyltertiarybutylether procured from Fluka, with a purity guaranteed to be greater than 99% and HPLC grade benzene supplied by Spectrochem (Bombay, India) have been used without any further purification. From a comparison of the physical properties with the literature data, presented in Table I, the pure liquids used in this study are expected to be of 99.5% purity.

TABLE I Comparison of the physical properties of the pure liquids with the literature data

Component	*Density at* 303.15 *K* *g/mL* *Value*	*Reference*	*Refractive-index at* 293.15 *K* *Value*	*Reference*
Methyl-tert-butylether	0.7425	This work	1.3690	This work
	0.7418	Timmermans [6]	1.3690	API [7]
Benzene	0.8684	This work	1.5010	This work
	0.86829	Ridick *et al.* [8]	1.50112	Riddick *et al.* [8]

RESULTS AND DISCUSSION

The measured $(x-t)$ data are correlated by means of the Wilson and NRTL equations. The details of the equations and treatment of the data are given earlier by Viswanathan *et al.* [1]. The gas phase is assumed to be ideal and hence the fugacity coefficient is taken as unity. The total pressure at each data point is calculated from

$$P_{\text{Cal}} = \gamma_1 P_1 x_1 + \gamma_2 P_2 x_2 \tag{1}$$

where x_i, P_i, and γ_i represent the mole fraction, vapor pressure and activity coefficient respectively. The vapor pressures of the pure components are computed from the Antoine constants noted in Table II. The phase equilibrium data are presented in Tables III and IV. The optimum model parameters in each case are obtained by minimizing the sum of squares of the deviation in total pressure using the Nelder-Mead optimization technique described in detail in Kuester and Mize [5]. Table V lists the optimum model parameters along with the root mean square deviation.

The excess Gibbs free energies (G^E) are calculated at 298.15 K using the Wilson model and presented in Table VI. The methyltertiarybutylether + benzene system shows greater deviation from ideality

TABLE II Antoine constants

Component	*A*	*B*	*C*	*Reference*
Methyl-tert-butylether	6.89117	1126.59	225.86	Aim and Ciprian [9]
Benzene	6.90565	1211.03	220.79	Dean [10]

TABLE III VLE data for methyl-tert-butylether(1) + benzene(2) at 490 mm Hg

		Wilson equation			*NRTL equation*		
x_1	*t/deg.C*	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.0640	63.6	0.1468	1.1267	1.0007	0.1489	1.1202	1.0005
0.1338	61.0	0.2774	1.1048	1.0030	0.2809	1.1023	1.0024
0.2055	58.6	0.3882	1.0851	1.0069	0.3923	1.0856	1.0057
0.2862	56.1	0.4922	1.0661	1.0130	0.4961	1.0686	1.0111
0.3962	53.6	0.5823	1.0497	1.0211	0.5854	1.0531	1.0185
0.4500	52.5	0.6577	1.0365	1.0306	0.6597	1.0401	1.0276
0.5000	51.0	0.6995	1.0295	1.0372	0.7008	1.0330	1.0342
0.5739	49.4	0.7558	1.0208	1.0372	0.7562	1.0238	1.0453
0.6567	47.8	0.8126	1.0131	1.0613	0.8120	1.0154	1.0596
0.7588	46.2	0.8753	1.0062	1.0797	0.8739	1.0075	1.0801
0.8286	44.6	0.9143	1.0031	1.0934	0.9128	1.0038	1.0961
0.9041	43.3	0.9536	1.0009	1.1092	0.9525	1.0012	1.1151

TABLE IV Vapor liquid equilibria for the methyl-tertiary-butylether(1) + benzene(2) system at 709 mm Hg

		Wilson equation [11]			*NRTL equation* [12]		
x_1	*t/deg.C*	y_1	γ_1	γ_2	y_1	γ_1	γ_2
0.0640	75.4	0.1411	1.1202	1.0007	0.1407	1.1161	1.0005
0.1338	72.8	0.2684	1.0993	1.0029	0.2684	1.0989	1.0023
0.2055	70.0	0.3776	1.0807	1.0066	0.3783	1.0828	1.0055
0.2862	67.6	0.4812	1.0627	1.0124	0.4825	1.0664	1.0107
0.3692	65.2	0.5717	1.0471	1.0201	0.5733	1.0515	1.0179
0.4500	63.2	0.6480	1.0345	1.0291	0.6495	1.0389	1.0267
0.5000	62.5	0.6905	1.0279	1.0354	0.6919	1.0320	1.0330
0.5739	61.0	0.7481	1.0197	1.0456	0.7491	1.0231	1.0437
0.6567	59.1	0.8063	1.0124	1.0583	0.8068	1.0149	1.0576
0.7588	57.4	0.8708	1.0059	1.0756	0.8708	1.0073	1.0775
0.8286	55.8	0.9112	1.0029	1.0885	0.9516	1.0011	1.1113

TABLE V The model parameters

Model	*Parameters (K)*	*Percent average absolute deviation in pressure*
Wilson	$(\lambda_{12}-\lambda_{11})/R = 9.02$ $(\lambda_{12}-\lambda_{22})/R = 421.66$	0.8
NRTL	$g_{12} = -295.71$ $g_{21} = 663.98$ $\alpha_{12} = 0.12$	0.8

compared to the anisole + benzene system, the results of which have already been published by Viswanathan *et al.* [1]. Both the Wilson and NRTL models represent the data adequately.

TABLE VI Excess Gibbs free energy for the methyl-tertiary-butylether(1) + benzene (2) system at 298.15 K

x_1	G^E $(J \cdot mol^{-1})$
0.0500	18.8757
0.1000	35.3423
0.1500	49.4844
0.2000	61.3832
0.2500	71.1157
0.3000	78.7551
0.3500	84.3713
0.4000	88.0311
0.4500	89.7983
0.5000	89.7336
0.5500	87.8956
0.6000	84.3395
0.6500	79.1190
0.7000	72.2850
0.7500	63.8861
0.8000	53.9699
0.8500	42.5807
0.9000	29.7620
0.9500	15.5522

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