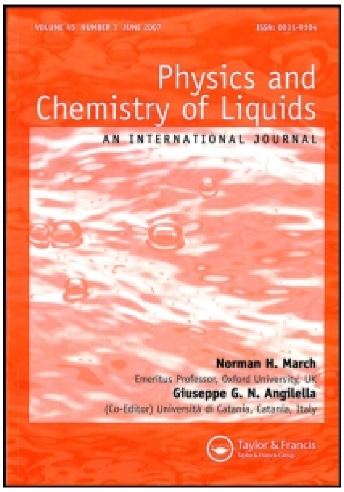

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Vapor–liquid equilibria of some binary mixtures formed by methylethylketone at 94.7 kPa

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Bubble temperatures at 94.7 kPa, for the binary mixtures formed by methylethylketone (MEK) with cyclo-hexanone, tetrahydrofuran, *ortho*- and *meta*-xylenes, bromobenzene, chlorobenzene, epichlorohydrin, nitrobenzene, and *iso*- and *tert*-butanols have been measured by means of a Swietoslawski-type ebulliometer. The data could be represented well by the Wilson model.

Keywords: Vapor–liquid equilibria; Methylethylketone; Wilson model

1. Introduction

The preference of isobaric operations near the ambient, particularly with reference to large scale separation operations and the necessitated application of isobaric vapor–liquid equilibrium data for the design and the operation of separations does not warrant any fresh emphasis. Methylethylketone (MEK) is a very important solvent frequently used in the surface-coating, adhesive, and printing ink industries. MEK's use as an extraction solvent in the pharmaceutical production and as an intermediate in the preparation of catalysts and anti-oxidants, and processing of cocaine are also well known. Expecting a potential use in the industrial separation of mixtures involving MEK as one of the components, and in continuation of our recent phase equilibrium studies [1–3], bubble point temperatures of the binary mixtures have been measured. The experiments have been conducted at 94.7 kPa. We could not locate any published phase equilibrium data on the systems chosen for the present study.

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2. Experimental

2.1. *Method*

A Swietoslawski-type ebulliometer, similar to the one described by Hala *et al.* [4], described in our earlier paper [3] was used in the present set of experiments. The total pressure of the system was maintained at 94.7 ± 0.1 kPa. The equilibrium temperatures were measured to an accuracy of ±0.1 K, by means of a calibrated platinum resistance thermometer. The liquid mixtures were prepared by mixing suitable masses of the pure components with the help of an electronic balance precise to ±0.0001 g. The samples were stirred well before being placed in the ebulliometer. The heating rate was adjusted to yield the desired condensate drop rate of 30 drops/min, in accordance with the suggestion of Hala *et al.* [4]. The bubble temperature was recorded after the steady drop rate and constant temperature were maintained for at least 30 min. The constancy of the liquid phase composition during each experiment was ensured by verifying the identity of the chromatograms obtained by injecting the liquid mixture sample to a gas chromatogram at the beginning and the end of each phase equilibrium experiment. Each measurement was repeated several times, till at least two consecutive observations were within the stated limits of the experimental uncertainties of ±0.1 K in the temperature, ±0.1 kPa in the pressure, and ±0.0001 in the liquid phase mole fraction.

2.2. *Materials*

AR grade chemicals used in this study were further purified according to the easiest possible methods described in Riddick *et al.* [5]. The purity of the chemicals was confirmed by measuring their density and refractive index at 298.15 K. The values measured in this work compare favorably with the literature data as shown in table 1.

3. Results and discussion

The experimental liquid phase mole fraction (x_1) *versus* temperature (T) data, summarized in table 2, are fitted to the Wilson equation [6] in the form

$$\ln \gamma_1 = -\ln(x_1 + \Delta_{12}x_2) + x_2\left[\left\{\Delta_{12}/(x_1 + \Delta_{12}x_2)\right\} - \left\{\Delta_{21}/(x_2 + \Delta_{21}x_1)\right\}\right] \qquad (1)$$

$$\ln \gamma_2 = -\ln(x_2 + \Delta_{21}x_1) + x_1\left[\left\{\Delta_{21}/(x_2 + \Delta_{21}x_1)\right\} - \left\{\Delta_{12}/(x_1 + \Delta_{12}x_2)\right\}\right] \qquad (2)$$

where

$$\Delta_{12} = \left(V_1^{\mathrm{L}}/V_2^{\mathrm{L}}\right)\exp[-(\lambda_{12} - \lambda_{11})/RT] \qquad (3)$$

$$\Delta_{21} = \left(V_1^{\mathrm{L}}/V_2^{\mathrm{L}}\right)\exp[-(\lambda_{12} - \lambda_{22})/RT] \qquad (4)$$

V_1^{L} and V_2^{L} are the pure liquid molar volumes, $[(\lambda_{12} - \lambda_{11})/R]$ and $[(\lambda_{12} - \lambda_{22})/R]$ are the Wilson parameters, and λ's being the energies of interaction between the molecules

Table 1. Comparison of the density (ρ) and the refractive index (n) of the pure liquids used in this study with the literature data from Riddick *et al.* [5] at 298.15 K.

	$\rho\,(\mathrm{kg\,m^{-3}})$		n	
Substance	This work	Riddick *et al.* [5]	This work	Riddick *et al.* [5]
Methylethylketone	799.7	799.70	1.3769	1.37685
Cyclohexanone	945.0[a]	945.20[a]	1.4510[a]	1.45097[a]
Tetrahydrofuran	889.2[a]	889.20[a]	1.4072[a]	1.40716[a]
ortho-Xylene	875.9	875.94	1.5030	1.50295
meta-Xylene	860.1	860.09	1.4946	1.49464
Bromobenzene	1488.1	14788.20	1.0100[b]	1.01000[b]
Chlorobenzene	1100.9	1100.90	1.5219	1.52185
Epichlorohydrin	1174.6	1174.55	1.4358	1.43580
Nitrobenzene	1198.3	1198.33	1.5500	1.54997
iso-Butanol	797.8	797.80	1.3939	1.39389
tert-Butanol	781.2	781.20	1.3852	1.38520

[a] Reference temperature: 293.15 K.
[b] Reference temperature: 303.15 K.

denoted by the subscripts. The optimum Wilson parameters are obtained minimizing the objective function defined as

$$\varphi = \Sigma\left[\left(P_{\mathrm{cal}}/P_{\mathrm{expt}}\right) - 1\right]^2 \tag{5}$$

where P_{cal} and P_{expt} are the calculated and experimental total pressures. The Nelder–Mead optimization technique described by Kuester and Mize [7] was used. The vapor phase non-ideality is considered in accordance with the method given by Tsonopoulos [8]. The saturated vapor pressures of the pure substances are calculated from the Antoine equation with the constants noted in table 3. Prior to use, the Antoine equation with the constants noted in table 3, has been tested. All the available literature vapor pressure data of each substance are noted. It is examined whether the Antoine equation with the set of constants noted in table 3 for the substance can predict the experimental data to be within the claimed accuracy of the particular set of data or within an average absolute deviation of 0.5%. The equation was subsequently used to calculate the boiling temperature of the pure liquid at the total pressure (94.7 kPa) chosen for the present study, and compared with that observed in the present set of experiments. In all cases, the departures are within the experimental accuracy of the set of measurements or an average absolute relative deviation of 0.5%. The Antoine equation for vapor pressure, with the set of constants (for the 11 liquids noted in table 3) representing the data well has therefore been used. The molar volumes of the pure liquids derived from the density measurements of this study (recorded in table 1) were used as the input to obtain the optimum Wilson parameters. The results of representation of the phase equilibrium data by the Wilson [6] equation, summarized in table 4, indicate that the data and the representation are quite good.

Table 2. Vapor–liquid equilibria of selected binary mixtures.

x_1	T(K)	y_1	x_1	T(K)	y_1	x_1	T(K)	y_1	x_1	T(K)	y_1	x_1	T(K)	y_1	x_1	T(K)	y_1
Methylethyl-ketone(1) + Cyclo-hexanone(2)			Tetrhydrofuran(1) + Methylethyl-ketone(2)			Methylethyl-ketone(1) + *ortho*-Xylene(2)			Methylethyl-ketone(1) + *meta*-Xylene			Methylethyl-Ketone(1) + *iso*-Butanol			Methylethyl-ketone(1) + *tert*-Butanol		
0.0000	426.55	0.0000	0.0000	351.25	0.0000	0.0000	415.65	0.0000	0.0000	410.45	0.0000	0.0000	379.95	0.0000	0.0000	354.25	0.0000
0.1617	401.85	0.5755	0.1551	346.55	0.2422	0.1520	398.25	0.4692	0.1538	392.85	0.4782	0.1464	370.65	0.3754	0.1530	352.25	0.2110
0.3254	384.95	0.7990	0.3151	344.75	0.4008	0.2910	386.25	0.6950	0.3170	379.85	0.7187	0.2863	365.85	0.5492	0.2932	350.85	0.3655
0.4357	376.55	0.8737	0.4530	343.25	0.5360	0.4500	375.45	0.8374	0.4826	372.85	0.8116	0.4452	361.85	0.6822	0.4450	349.85	0.5033
0.6347	364.95	0.9462	0.6235	341.45	0.6981	0.6080	366.75	0.9169	0.6128	364.05	0.9049	0.6074	358.45	0.7902	0.6076	349.25	0.6305
0.7354	360.45	0.9674	0.7682	339.95	0.8253	0.7420	360.55	0.9578	0.7460	358.95	0.9471	0.7558	355.55	0.8763	0.7525	349.15	0.7400
0.8746	355.15	0.9875	0.8689	338.95	0.8982	0.9090	354.05	0.9891	0.9114	353.75	0.9842	0.8858	353.25	0.9447	0.8950	349.75	0.8656
1.0000	351.25	1.0000	1.0000	337.55	1.0000	1.0000	351.25	1.0000	1.0000	351.25	1.0000	1.0000	351.25	1.0000	1.0000	351.25	1.0000
Methyethyl-ketone(1) + Bromobenzene(2)			Methylethyl-ketone(1) + Chlorobenzene(2)			Methylethyl-ketone(1) + Epichlorohydrin(2)			Methylethyl-ketone(1) + Nitrobenzene(2)								
0.0000	427.25	0.0000	0.0000	403.05	0.0000	0.0000	389.35	1.0000	0.0000	481.65	0.0000						
0.1654	393.65	0.6668	0.1630	377.35	0.5746	0.1587	381.95	0.3233	0.1400	412.85	0.8732						
0.3281	377.25	0.8415	0.3214	370.25	0.6990	0.3034	375.65	0.5428	0.2970	390.85	0.9514						
0.4678	368.35	0.9053	0.4480	365.95	0.7721	0.4656	369.05	0.7290	0.4490	377.65	0.9765						
0.6101	364.95	0.9414	0.6140	360.95	0.8537	0.6354	362.65	0.8601	0.6150	367.65	0.9893						
0.7378	357.75	0.9627	0.7680	365.75	0.9188	0.7771	357.75	0.9316	0.7540	360.35	0.9949						
0.8755	354.15	0.9810	0.9080	353.35	0.9701	0.8394	355.85	0.9552	0.9080	354.25	0.9986						
1.0000	351.25	1.0000	1.0000	351.25	1.0000	1.0000	351.25	1.0000	1.0000	354.25	1.0000						

Table 3. Antoine constants for the equation $\ln(P/\text{kPa}) = A - B/[(T(\text{K}) + C]$.

Substance	A	B	C
Methylethylketone	14.5813	3150.41	−36.65
Cyclohexanone	14.0539	3444.16	−63.60
Tetrahydrofuran	14.0894	2687.34	−46.90
orto-Xylene	14.0982	3395.57	−59.45
meta-Xylene	14.1198	3366.99	−58.04
Bromobenzene	13.7799	3312.98	−67.71
Chlorobenzene	14.0502	3295.11	−55.60
Epichlorohydrin	15.1815	3668.29	−43.75
Nitrobenzene	14.3520	4008.37	−72.04
iso-Butanol	14.8538	2874.72	−100.30
tert-Butanol	14.8374	2658.28	−95.45

Table 4. Representation of the measurements by Wilson Model.

System	$[(\lambda_{12} - \lambda_{11})/R]$ (K)	$[(\lambda_{12} - \lambda_{22})/R]$ (K)	Std. dev. in T (K)
Methylethylketone(1) + Cyclohexanone(2)	76.26	−76.58	0.14
Tetrahydrofuran(1) + Methylethylketone(2)	761.18	−324.76	0.09
Methylethylketone(1) + *ortho*-Xylene(2)	−134.03	165.84	0.16
Methylethylketone(1) + *meta*-Xylene(2)	−37.85	117.69	0.05
Methylethylketone(1) + Bromobenzene(2)	−92.77	414.58	0.11
Methylethylketone(1) + Chlorobenzene(2)	734.72	−175.12	0.04
Methykethylketone(1) + Epichlorohydrin(2)	557.15	−266.60	0.12
Methylethylketone(1) + Nitrobenzene(2)	697.76	−291.00	0.16
Methylethylketone(1) + *iso*-Butanol(2)	351.96	−87.23	0.05
Methylethylketone(1) + *tert*-Butanol(2)	−317.16	262.34	0.03

Std. dev. in $T = [\sum(T_{\text{expt}} - T_{\text{cal}})^2/n]^{0.5}$ where 'n' is the number of observations.

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