VAPOUR-LIQUID EQUILIBRIUM IN THE METHYL TERT-BUTYL ETHER-n-HEXANE AND METHYL TERT-BUTYL ETHER-TOLUENE SYSTEMS*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

Vapour-liquid equilibrium data in binary methyl tert-butyl ether-n-hexane and methyl tert-butyl ether-toluene mixtures were determined experimentally. The data were described thermodynamically by the one-constant Redlich-Kister equation.

In connection with the investigation of certain separation processes, we have studied in our work the phase vapour-liquid equilibrium in binary methyl tert-butyl ether--toluene and methyl tert-butyl ether-n-hexane systems. No experimental data on these systems have so far been published in the available literature.

EXPERIMENTAL

Pure substances. Technical methyl tert-butyl ether (MTBE) was firstly rectified on a 40-plate packed column. Then it was refluxed for 2 hours in nitrogen atmosphere containing 4 g/dm^3 LiAlH$_4$ and rectified again. The measured density is d (20°C) = 0·7405 gcm^{-1} (ref.[1] 0·7405) and refractive index n_D^{20} 1·3690 (ref.[1] 1·3689). n-Hexane (HX) was prepared by the reaction between preliminarily rectified n-propyl bromide and sodium; n-propyl bromide was slowly added to a 25% excess of Na at a rate of 3 cm^3/min. After the consumption of the calculated amount of n-propyl bromide, the reaction mixture was heated for 5 hours. The product was distilled off and rectified. The measured density is d (20°C) = 0·6596 gcm^{-3} (ref.[2] 0·65953) and refractive index n_D^{20} 1·3750 (ref.[2] 1·3750). AR-grade (Lachema Brno) toluene (TL) was rectified with Na. The measured density is d (20°C) = 0·8668 gcm^{-3} (ref.[2] 0·8672) and refractive index n_D^{20} 1·4965 (ref.[2] 1·4970). Other quantities (constants in the Antoine equation, critical properties, accentric factor) were taken from the literature[3,4]. Critical properties of MTBE were estimated by the Lydersen method[10]. All pure substances were kept above an A4 molecular sieve to remove traces of possible wetness.

The vapour-liquid equilibrium was measured by the dynamic method in the Gillespie still. The boiling point temperature was determined by the Anschütz thermometer with a ±0·05°C

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accuracy. During the isothermal measurement[5,6] the constant boiling point temperature in the Gillespie still was maintained by an electronic regulator[7] with a thermistor sensor controlling the solenoid valve, whereas during the isobaric measurement the constant pressure was achieved by maintaining constant the boiling point temperature of redistilled water in a parallelly connected ebulliometer. The boiling point temperature of redistilled water was measured by calibrated mercury standards.

Analysis of equilibrium phases. System MTBE–TL: the composition of equilibrium phases was determined from the refractive index measured on an Abbe refractometer (Carl Zeiss, Jena, model G); the measuring prism was thermostated to 20°C by an U3 ultrathermostat. System MTBE–HX: the composition of equilibrium phases in this system was determined from the density, which was measured in 10 ml pycnometers at 20°C.

RESULTS

Results of our isobaric and isothermal experimental measurements of the vapour–liquid equilibrium in both systems investigated are given in Tables I and II.

The data were described through concentration dependences of the activity coefficients of components, which were calculated from the relation

$$\gamma_i = y_i P \Theta_i / (x_i P_i^0)\,, \tag{1}$$

where γ_i is the activity coefficient of component i in the liquid phase, y_i is the mole fraction of component i in the vapour phase, P is the total pressure, P_i^0 is the vapour

TABLE I

Vapour–Liquid Equilibrium in the MTBE(1)–HX(2) System

x_1	y_1	P, kPa	Δy_1	x_1	y_1	t, °C	Δy_1
60°C, $A_{12} = 0{\cdot}17^a$				96 kPa, $A_{12} = 0{\cdot}192^a$			
0·068	0·118	80·85	0·003	0·085	0·152	64·89	0·011
0·109	0·178	83·40	0·001	0·140	0·220	63·87	0·000
0·156	0·234	85·93	−0·007	0·196	0·300	62·61	0·007
0·205	0·306	89·07	0·002	0·299	0·406	60·88	−0·006
0·300	0·418	93·83	0·006	0·397	0·501	59·42	−0·010
0·400	0·504	98·33	−0·008	0·499	0·603	58·04	0·000
0·502	0·612	102·91	0·007	0·654	0·740	56·3	0·008
0·638	0·716	107·57	−0·002	0·820	0·862	54·86	−0·000
0·762	0·812	111·75	−0·003	0·882	0·914	54·24	0·005
0·896	0·925	116·14	0·006				

[a] Mean deviation 0·005.

pressure of component i, x_i is the mole fraction of component i in the liquid phase, Θ_i is the correction for the real behaviour of the vapour phase.

The state behaviour of the vapour phase was expressed through the virial equation of state with the second virial coefficient. The following relation holds for Θ_i[8]

$$\Theta_i = \exp \{[(2 \sum_{j=1}^{N} B_{ij} y_j - B) P - B_{ii} P_i^0 - V_i^L (P - P_i^0)]/RT)\} , \qquad (2)$$

where $B = \sum_{i=1}^{N} \sum_{j=1}^{N} B_{ij} y_i y_j$, B_{ij} $(i \neq j)$ is the cross virial coefficient, B_{ii} resp. B_{jj} are the virial coefficients of pure components i and j, V_i^L is the molar volume of pure liquid component i. The second virial coefficients of pure components were calculated by Pitzer and Curl[9] from the critical temperature T_c, critical pressure P_c and accentric factor ω. The critical properties of MTBE were not found in the literature and consequently they were estimated by the Lydersen method[10].

The second cross virial coefficient was calculated from the relation

$$B_{12} = (B^0 + \omega B^1) RT_{c12}/P_{c12} , \qquad (3)$$

in which

$$T_{c12} = (T_{c1} T_{c2})^{1/2} , \quad \omega_{12} = (\omega_1 + \omega_2)/2 ,$$
$$V_{c12} = (V_{c1}^{1/3} + V_{c2}^{1/3})^3/8 , \quad z_{c12} = (z_{c1} + z_{c2})/2 , \qquad (4)$$
$$P_{c12} = z_{c12} RT_{c12}/V_{c12} .$$

$B^0 = f_1(T/T_c)$ and $B^1 = f_2(T/T_c)$ are functions defined by Pitzer and Curl[9].

TABLE II

Vapour–Liquid Equilibrium in the MTBE(1)–TL(2) System

x_1	y_1	P, kPa	Δy_1	x_1	y_1	P, kPa	Δy_1
60°C, $A_{12} = 0·137$[a]							
0·097	0·430	29·52	0·001	0·579	0·896	77·75	0·005
0·177	0·591	38·12	−0·003	0·656	0·910	85·45	−0·007
0·243	0·682	45·13	0·001	0·695	0·935	89·10	0·003
0·317	0·753	52·47	0·003	0·773	0·954	96·28	0·004
0·489	0·854	68·95	0·000	0·818	0·962	101·03	0·001

[a] Mean deviation 0·003.

Both systems investigated exhibit low positive deviations from Raoult's law. The concentration dependence of the ratio of the activity coefficients was correlated by the one-constant Redlich–Kister equation

$$\ln\left(\gamma_1/\gamma_2\right) = A_{12}(1 - 2x_1) \tag{5}$$

which was found to be of sufficient accuracy. The constant A_{ij} in the correlation was calculated from experimental data by the least squares method and the minimized quantity was the logarithm of the ratio of both activity coefficients.

DISCUSSION

Our data on the binary MTBE–HX and MTBE–TL systems represent the only experimental informations on the phase equilibria in the above systems. Experimental data on MTBE are scarce in the literature; this follows, *e.g.*, from the fact that good data on its vapour pressure were published only recently by Ambrose and coworkers[3].

The thermodynamic consistency of our binary equilibrium data was evaluated by Redlich and Kister[11]. This test showed that the data are thermodynamically consistent and that the scatter of experimental values is comparable both with the estimated error[12] and with the scatter of data by other authors[13]. In view of the fact that the deviations from Raoult's law are very low, the neglection of the real behaviour of the vapour phase has a negative effect on the resulting thermodynamic consistency.

Differences between isobaric and isothermal data in the MTBE–HX system can be neglected. A similar result is encountered in the MTBE–TL system due to very low values of the heat of mixing. This quantity is equal to $\Delta H_M(\max) \approx 10\ \mathrm{J\ mol^{-1}}$ in the MTBE–TL system[14].

TABLE III

Vapour–Liquid Equilibrium in the MTBE(1)–HX(2)–TL(3) System at 60°C

x_1	x_2	x_3	y_1	y_2	y_3	Δy_1	Δy_2	Δy_3
0·029	0·526	0·445	0·073	0·763	0·163	0·009	−0·004	−0·005
0·046	0·752	0·202	0·084	0·840	0·076	−0·001	−0·005	−0·006
0·304	0·411	0·285	0·477	0·447	0·076	−0·001	0·005	−0·005
0·418	0·323	0·196	0·653	0·296	0·051	0·007	−0·009	0·002
0·554	0·181	0·256	0·748	0·190	0·062	−0·005	0·008	−0·003

The applicability of the calculated constants A_{12} and A_{13} and of the constant A_{23} determined from literature data (a binary HX–TL system[15]) was verified by several experiments in the ternary MTBE(1)–HX(2)–TL(3) system (Table III). The composition of equilibrium phases was determined chromatographically. The results indicate that the thermodynamic description of the ternary mixture can be obtained from the binary constants only.

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