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Vapor Pressures, Refractive Indexes, and Densities at 20.0 °C, and Vapor–Liquid Equilibrium at 101.325 kPa, in the *tert*-Amyl Methyl Ether–Methanol System

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The vapor pressures of *tert*-amyl methyl ether (TAME) in the range 21–86 °C and of methanol (MeOH) at 43–64 °C were measured by comparative ebulliometry. The isobaric vapor–liquid equilibrium in the title system was determined by a dynamic method using a recirculation still. The vapor–liquid equilibrium data were fitted to the Redlich–Kister equation. At 101.325 kPa the system forms a minimum-boiling azeotrope of composition 22.9 mol % (48.6 wt %) TAME with the boiling point of 62.26 °C.

Introduction

TAME is considered as a possible additive to gasoline because of its antiknock effect similar to the presently used methyl *tert*-butyl ether. TAME is produced by the reaction of methanol with isoamylenes (*1*). In order to obtain basic data for the design of separation units for the production of pure TAME, the vapor pressure of TAME and vapor–liquid equilibrium in the TAME–MeOH system were measured.

Experimental Section

Materials. Pure TAME was prepared from the technical product by distillation followed by rectification on a 60-plate bubble-cap column at 30:1 reflux ratio. The middle distillate portion ($^1/_5$ of the initial amount) was then dried with freshly cut metal sodium for several days and finally rectified on a column packed with Pyrex-glass helices at a reflux ratio of 20:1. The middle fraction (60%) was used for the experiments. Gas-chromatographic analysis (TCD and FID) showed that the purity of TAME was approximately 99%.

Methanol, AR grade (Lachema), was rectified in a 60-plate bubble-cup column. The distillate was then rectified from dissolved magnesium methoxide in the way described earlier (*2*). The purity of the middle portion used for experiments was checked by refractive index and density measurements.

Physical constants of the pure substances used for experiments are listed in Table I.

Apparatus and Procedure. A modified Sprengel-Ostwald pycnometer was used for the determination of liquid densities at 20.0 ± 0.005 °C. Appropriate buoyancy corrections were applied. Repeated measurements made it possible to obtain an uncertainty of less than 0.000 05 g/cm^3.

Refractive indexes were measured by means of a refractometer (Carl Zeiss, Jena) with prisms thermostated to 20.0 ± 0.02 °C. Refractive indexes of pure components and the concentration dependence of refractive indexes of binary mixtures were determined. Repeated refractive index measurements of a sample had a standard deviation of less than 0.000 02 refractive index unit. The final uncertainty in the determination of refractive index was ±0.000 03.

Saturated vapor pressures were measured by means of two standard Swietoslawski ebulliometers connected to a pressure-controlling assembly based on a mercury-filled U-tube with point contacts. The first ebulliometer contained pure solvent; the second ebulliometer was filled with water. The boiling points were measured by two calibrated platinum resistance thermometers, connected to a Mueller bridge (Leeds and Northrup). The temperature was measured with an accuracy of ±0.01 °C. The corresponding pressure in the system was calculated from the boiling point of water by using the smoothed data (*3*); the pressure was determined with an accuracy of ±0.05% of the measured value. At the beginning of the measurement several milliliters of the sample were boiled off into a cold trap for the absence of any significant elevation of boiling temperature. Vapor pressure measurement was done in the case of TAME in two runs, first starting from the lowest pressure to atmospheric pressure and then going downward; in the case of methanol only one run was performed.

Table I. Density (ρ) and Refractive Index (n_D) at 20.0 °C, and Boiling Point at 101.325 kPa, for TAME and Methanol

ρ, g/cm^3	n_D	bp, °C	ref
	TAME		
0.770 74	1.388 48	86.428	this work
0.770 3	1.388 5	86.3	*7,18*
	Methanol		
0.791 25	1.328 39	64.527	this work
0.791 0–0.791 5	1.328 4–1.328 8	64.51–64.70	*8–19*

The recirculation equilibrium still of Dvořák and Boublík (*4*) was sued for vapor–liquid equilibrium measurements. The still was connected to the assembly maintaining pressure at 101.325 kPa. The equilibrium temperature and pressure were determined in the same way as described for the vapor pressure measurements of pure substances. Samples of equilibrium phases were taken for refractometric analysis approximately 20 min after the boiling temperature was stabilized. The composition was determined from the interpolation tables (of refractive index vs. concentration) computed from eq 2. Estimated uncertainty in the determined mole fraction varied from ±0.0005 in the methanol-rich region to ±0.0050 in the TAME-rich region due to the shape of the refractive index concentration dependence for the binary.

Results and Discussion

Densities and refractive indexes determined at 20.0 °C and boiling points at 101.325 kPa (calculated from eq 1) for pure components are shown in Table I and are compared with literature data.

Results of vapor pressure measurements are given in Table II. The differences between the vapor pressures calculated from the Antoine equation

$$\log P(\text{kPa}) = A - B/(C + t(°\text{C})) \qquad (1)$$

and the experimental values are listed in the third column of the table. The coefficients A, B, and C of eq 1 evaluated by the weighted least-squares procedure (*5*) from the experimental data and the corresponding standard deviations are shown in Table III.

The refractive indexes (n_D) at 20.0 °C as a function of the weight fraction of TAME (w_1) are listed in Table IV along with

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Table II. Vapor Pressures of TAME and Methanol

t, °C	P, kPa	$P_{calcd} - P$, kPa
	TAME	
21.109	8.332	−0.002
21.128	8.331	0.006
27.070	11.075	−0.018
27.096	11.073	−0.002
32.140	13.922	−0.002
32.148	13.923	0.002
36.451	16.810	−0.000
36.449	16.807	0.001
40.928	20.311	0.000
40.912	20.299	−0.002
45.596	24.571	0.000
45.601	24.578	−0.002
50.137	29.387	−0.002
50.142	29.395	−0.005
54.591	34.814	0.005
54.587	34.815	−0.001
58.857	40.754	−0.001
58.852	40.751	−0.004
63.219	47.627	0.006
63.207	47.612	−0.008
70.048	60.227	0.007
70.057	60.245	0.009
76.615	74.710	0.007
76.616	74.707	0.013
83.738	93.395	−0.004
83.748	93.405	0.014
85.386	98.205	−0.015
86.027	100.126	−0.018
	Methanol	
43.003	40.742	−0.002
46.467	47.613	0.004
51.857	60.247	−0.002
56.977	74.736	−0.004
62.467	93.379	0.010
63.519	97.382	−0.007

Table III. Coefficients of the Antoine Equation and Standard Deviations in Pressure

compd	A	B	C	S, kPa
TAME	5.976 31	1208.391	217.907	0.008
methanol	7.157 60	1554.708	237.247	0.008

Table IV. Refractive Index of the TAME (1)-Methanol (2) Solutions at 20.0 °C

w_1	n_D	n_D(calcd) − n_D(exptl)
0.0974	1.334 55	0.000 04
0.1925	1.340 69	−0.000 06
0.2895	1.346 83	−0.000 04
0.3937	1.353 47	−0.000 06
0.4940	1.359 73	0.000 03
0.5942	1.366 00	0.000 04
0.6914	1.371 92	0.000 05
0.7992	1.378 20	0.000 04
0.9029	1.383 85	−0.000 03

the difference between refractive indexes calculated from the equation

$$n_D = w_1 n_{D1} + w_2 n_{D2} + w_1 w_2 (A_1 w_1 + A_2 w_2 - A_3 w_1 w_2) \quad (2)$$

and the experimental values. The coefficients A_k, calculated from the measured values, are A_1 = 0.01559, A_2 = 0.00386, A_3 = 0.01150.

Table V. Vapor-Liquid Equilibrium Data for the System TAME (1)-Methanol (2) at 101.325 kPa

exptl			calcd − exptl			
t, °C	x_1	y_1	Δt, °C	Δx_1	Δy_1	ΔP, kPa
63.354	0.0495	0.0865	−0.007	0.0005	−0.0004	0.043
63.044	0.0705	0.1131	−0.007	0.0006	−0.0005	0.046
62.535	0.1265	0.1666	−0.008	0.0005	−0.0007	0.049
62.303	0.1857	0.2063	−0.011	0.0004	−0.0007	0.073
62.250	0.2281	0.2299	−0.016	−0.0001	0.0003	0.101
62.307	0.2881	0.2562	−0.014	0.0000	0.0000	0.091
62.676	0.3995	0.2994	−0.010	−0.0009	0.0007	0.074
63.516	0.5358	0.3441	−0.007	0.0015	−0.0016	0.047
64.692	0.6513	0.3888	0.001	0.0013	−0.0005	−0.010
66.207	0.7417	0.4324	0.013	−0.0041	−0.0015	−0.096
67.498	0.7946	0.4701	0.005	−0.0077	0.0005	−0.030
69.136	0.8450	0.5138	−0.004	−0.0062	0.0015	0.029
71.617	0.8929	0.5794	−0.008	−0.0060	0.0039	0.064
75.073	0.9370	0.6750	−0.011	−0.0025	0.0098	0.085
78.504	0.9662	0.7779	−0.013	0.0007	0.0188	0.101
80.980	0.9805	0.8491	−0.009	0.0016	0.0188	0.071
83.302	0.9919	0.9213	−0.010	0.0027	0.0205	0.083

The vapor-liquid equilibrium data obtained for the studied system at 101.325 kPa are presented in Table V. The composition of the liquid (x_1) and the vapor (y_1) is expressed in TAME mole fraction. The data were correlated by a maximum likelihood regression minimizing the deviations in all the measured variables, each point having the same weight. Experimental errors in the determined liquid-phase mole fraction (x_1), vapor-phase mole fraction (y_1), temperature (t), and pressure (P) were estimated to be ±0.0005-0.0050, ±0.0005-0.0050, ±0.020 °C, and ±0.101 kPa, respectively. The computer program from ref *6* was employed. The three-constant Redlich-Kister equation

$$\ln \gamma_1 = x_2^2 \sum_{k=0}^{2} A_k (x_1 - x_2)^{k-1} (2kx_1 + x_1 - x_2)$$

$$\ln \gamma_2 = x_1^2 \sum_{k=0}^{2} A_k (x_1 - x_2)^{k-1} (-2kx_2 - x_2 + x_1) \quad (3)$$

was used to describe the composition dependence of liquid-phase activity coefficients (γ_i). Because we failed to find values of virial coefficients of TAME or its critical constants, ideal behavior of the vapor-phase and independence of the liquid-phase fucagity on pressure were assumed. Thus, we employed the relationship

$$y_i P = \gamma_i x_i P_i^\circ \quad (4)$$

The resulting parameters of the Redlich-Kister equation for the TAME-MeOH system are A_0 = 1.3692, A_1 = 0.0225, and A_2 = 0.1745. The differences between the values calculated from eq 3 and 4 and the measured ones are also given in Table V. The standard deviations for x_1, y_1, t, and P are ±0.0035, ±0.0094, ±0.011 °C, and ±0.077 kPa, respectively.

In order to verify the consistency of the measured data, the data were also correlated by minimizing only the deviations in x_1, t, and P (by using the same estimates of experimental errors and the correlation expression as above). Consistent data should yield similar results. The standard deviations resulting from this correlation were ±0.0020, ±0.0106, ±0.003 °C, and ±0.021 kPa in x_1, y_1, t, and P, respectively. On the basis of comparison of the standard deviations in y from the two correlations, as well as results of the correlation of the complete set of data, we can conclude that the data can be considered consistent.

The TAME-MeOH system shows positive deviations from ideality with a minimum-boiling azeotrope. The azeotrope contains 22.9 mol % (48.6 wt %) TAME and boils at 62.26 °C at 101.325 kPa. These values are in good agreement with the data published by Evans and Edlund (*7*) (50 wt % TAME and 62.3 °C) which represent to our knowledge the only available information on vapor-liquid equilibrium in the TAME-methanol system.

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Glossary

A, B, C	constants of the Antoine equation
A_k	constants of the Redlich-Kister equation
d	density
n_D	refractive index
P	pressure
x, y	mole fraction in liquid and vapor, respectively
w	weight fraction
γ	activity coefficient

Registry No. TAME, 994-05-8; methanol, 67-56-1.

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Excess Thermodynamic Properties for Water/Ethylene Glycol

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Isothermal P-x data at 60 °C and heat-of-mixing data at 50 °C are reported for the binary system water/ethylene glycol. These data, together with P-x data at 50 °C and H^E data at 25 °C from the literature, are reduced to provide correlations for H^E, G^E, and S^E as functions of both composition and temperature.

The heat-of-mixing measurements reported here for water/ethylene glycol at 50 °C combine with the comprehensive data set at 25 °C of Touhara and Nakanishi (*1*) to establish the temperature dependence of H^E. The vapor/liquid equilibrium measurements reported for 60 °C augment a comparable set of P-x data at 50 °C published earlier (*2*), and together they form the basis for correlation of G^E.

The ethylene glycol was 99$^+$ mol % reagent from MCB Manufacturing Chemists, Inc. The water was doubly deionized. For P-x measurements in the static VLE apparatus of Gibbs and Van Ness (*3*) both reagents were thoroughly degassed. The isothermal dilution calorimeter used for the H^E measurements was essentially that of Winterhalter and Van Ness (*4*). We have found that for aqueous systems the usual procedure of loading the calorimeter at room temperature with undegassed reagents is unsatisfactory, because subsequent heating to 50 °C and mixing lead to the evolution of dissolved gases. Loading the calorimeter with reagents at temperatures greater than 50 °C and then sealing it solves the problem.

Results and Correlation

Table I presents the experimental values of total vapor pressure at 60 °C as a function of composition; Table II gives values of H^E at 50 °C.

Table I. P-x Data for Water (1)/Ethylene Glycol (2) at 60 °C[a]

x_1	x_2	P/kPa
0.0	1.0000	0.214
0.0188	0.9812	0.543
0.0487	0.9513	1.058
0.1008	0.8992	1.997
0.1497	0.8503	2.892
0.1989	0.8011	3.813
0.2479	0.7521	4.760
0.2973	0.7027	5.790
0.3477	0.6523	6.678
0.3975	0.6025	7.724
0.4478	0.5522	8.718
0.4982	0.5018	9.721
0.4987	0.5013	9.717
0.5487	0.4513	10.713
0.5989	0.4011	11.751
0.6489	0.3511	12.746
0.6988	0.3012	13.757
0.7489	0.2511	14.836
0.8003	0.1997	15.880
0.8504	0.1496	16.879
0.9001	0.0999	17.906
0.9495	0.0505	18.923
0.9797	0.0203	19.428
1.0000	0.0	19.931

[a] $B_{11} = -930$, $B_{22} = -1697$, $B_{12} = -1050$, $V_1{}^L = 18$, $V_2{}^L = 58$.

Correlation of all data is through the four-parameter Margules equation, written for H^E as

$$H^E/(x_1x_2RT) = A_{21}'x_1 + A_{12}'x_2 - (C_{21}'x_1 + C_{12}'x_2)x_1x_2 \tag{1}$$

and for G^E as

$$G^E/(x_1x_2RT) = A_{21}x_1 + A_{12}x_2 - (C_{21}x_1 + C_{12}x_2)x_1x_2 \tag{2}$$

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