J. Chem. Eng. Data **2004,** *49,* 11−17

Vapor−Liquid Equilibrium for Acetonitrile + Propanenitrile and 1-Pentanamine + 1-Methoxy-2-propanol[†]

Maria Antosik, Maria Gałka, and Stanisław K. Malanowski*

Instytut Chemii Fizycznej PAN, Kasprzaka 44, 01-224 Warszawa, Poland

The saturation pressures of acetonitrile (302 to 353) K, propanenitrile (309 to 353) K, 1-pentanamine (322 to 378) K, and 1-methoxy-2-propanol (331 to 373) K were measured by an ebulliometric method. The vapor−liquid equilibrium (p, T, x, y) was measured by an ebulliometric method for the systems acetonitrile + propanenitrile at (313.15, 323.15, and 343.15) K and 1-pentanamine + 1-methoxy-2-propanol at (333.15, 343.15, and 353.15) K. The experimental vapor pressures were correlated with the Antoine equation and, for pentanamine + 1-methoxy-2-propanol, also with the AEOS equation of state. The VLE data were correlated with the "γ/φ" method. For the system 1-pentanamine + 1-methoxy-2-propanol the prediction with the AEOS model has been proposed. In this system an almost tangent negative azeotrope is observed for temperatures below 350 K.

Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers. In this work, we report part of the experimental measurements that have been made under Project 805(B)/97. For the investigated systems the only available vapor−liquid equilibrium (VLE) data are for acetonitrile + propanenitrile.[1] Those were taken as a function of pressure (P) and temperature (T) for constant composition samples, and due to lack of auxiliary information, they are hard to analyze and to compare with our results. Data for 1-pentanamine + 1-methoxy-2-propanol have not been reported in the literature, and results cannot be predicted with sufficient accuracy either by using pure component property data or by using a semiempirical method, for example, one based on a group contribution concept such as ASOG[2] or UNIFAC.[3]

Experimental Section

Chemicals. Acetonitrile (CAS Registry No. 75-05-8) was supplied by ROTH (99.9 wt %, with the content of water less than 0.02%). The purity was checked by gas liquid chromatography (GLC) with a flame ionization detector (FID) after an appropriate calibration procedure. A HP 5890 Series II gas chromatograph and HP 17 column (10 m, 0.53 mm) were used. Propanenitrile (CAS Registry No. 107-12-0) was supplied by Fluka (99+%). 99.6 wt % was found by the same GLC procedure. This substance was purified by fractional distillation in a 40 theoretical plate laboratory column. The final result was 99.9 wt % (checking by GLC) with a content of water less than 0.03 wt %. 1-Pentanamine (CAS Registry No. 110-58-7) was supplied by ACROS Organics (99 wt %). The purity was checked by the same GLC gas chromatograph and HP 17 column (10 m, 0.53 mm). The water content was 2.5%. This substance was purified by fractional distillation in the same column. The result was 99.88 wt % and a water content less than 0.05 wt %. 1-Methoxy-2-propanol (CAS Registry No. 107-98-2) was supplied by Fluka (purum >99%). The compound was freshly distilled at subambient pressure on a 40 theoretical plate column. The purities of the fractions were checked by GLC (with an FID detector) on a nitroterephthalic acid modified poly(ethylene glycol) (FFAP) 30 m long capillary column, and fractions of purity better than 99.8 mol % were collected and used for vapor pressure and VLE measurements. The water content detected as above was lower than 0.01 mol %.

Vapor Pressure. When processing VLE data, the most crucial data are the saturation pressures of the pure components. In the literature there are numerous data for acetonitrile. The best known are those reported by Putnam et al.,[4] Van Ness and Kochar,[5] Francesconi and Comelli,[6] Meyer et al.,[7] and Dojčanský and Heinrich.[8] There are also numerous others of lower quality. For propanenitrile there are data by Hall and Baldt[9] and by Dreisbach and Shrader.[10] There are significant discrepancies in these data. For 1-pentanamine and 1-methoxy-2-propanol there are no experimental data available in the literature. The internally consistent compilation of vapor pressure data for all investigated substances was published within DIPPR Project 801 by Daubert and Danner.[11] A comparison of various data for nitriles is shown in Figures 1 and 2. Since there are discrepancies between experimental data, the vapor pressures of all pure compounds were measured in this work. The same arrangement as for VLE measurements was used. The modified Świętosławski's ebulliometer[12] and the previously described[13] experimental procedure were used. The estimated accuracy of the pressure measurement was ±10 Pa, and that of temperature was ±10 mK. The ITS-90 scale was used to report temperature. The results obtained are given in Table 1.

Vapor−Liquid Equilibrium. The vapor−liquid equilibrium measurements were made with sampling both the liquid phase and vapor condensate in the ebulliometer. The

---

[†] This contribution will be part of a special print edition containing papers reporting experimental results from the various projects of the Design Institute for Physical Properties of the American Institute of Chemical Engineers.

* To whom correspondence should be addressed. E-mail: SKM@ichf.edu.pl.

10.1021/je025660t CCC: $27.50

Table 1. Vapor Pressures of Pure Components

acetonitrile		propanenitrile		*n*-pentylamine		1-methoxy-2-propanol	
T/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa	*T*/K	*P*/kPa
302.25	14.154	309.38	10.589	322.61	13.077	331.47	9.246
307.09	17.522	311.56	11.551	328.37	16.866	333.15	10.012
311.49	21.132	313.15	12.549	333.14	20.650	339.12	13.105
313.15	22.649	315.89	14.138	338.07	25.251	343.15	15.793
316.27	25.724	318.35	15.71	340.66	27.986	347.71	19.245
318.18	27.780	320.51	17.218	343.16	30.853	351.56	22.636
320.65	30.642	323.15	19.219	345.56	33.811	353.15	24.168
323.16	33.802	325.74	21.351	348.11	37.219	355.59	26.693
326.16	37.898	328.27	23.637	353.15	44.754	358.15	29.575
328.50	41.379	330.82	26.114	358.15	53.383	360.78	32.79
331.15	45.622	333.15	28.574	363.14	63.269	363.01	35.739
333.15	49.063	335.82	31.636	370.62	80.723	368.23	43.48
335.84	54.009	338.22	34.612	377.93	101.327	373.31	52.31
338.15	58.579	343.08	41.331				
343.18	69.620	348.09	49.316				
348.25	82.372	353.15	58.603				
353.10	96.336						

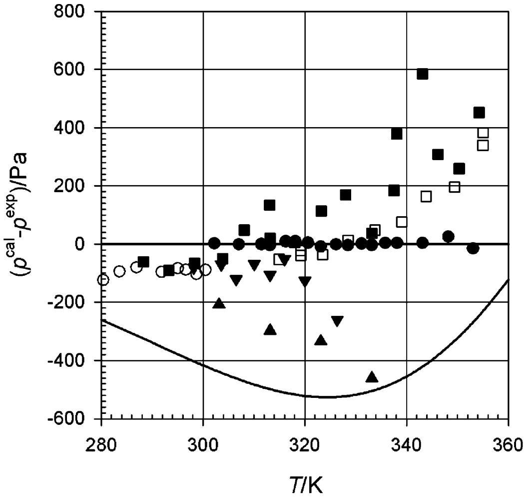

Figure 1. Deviation of acetonitrile saturation pressure data from correlation with the Antoine equation: ●, this work; ○, Putnam et al.;[4] ▲, Van Ness and Kochar;[5] ▼, Francesconi and Comelli;[6] □, Meyer et al.;[7] ■, Dojčanský and Heinrich;[8] —, calculated with the Antoine correlation of Daubert and Danner.[11]

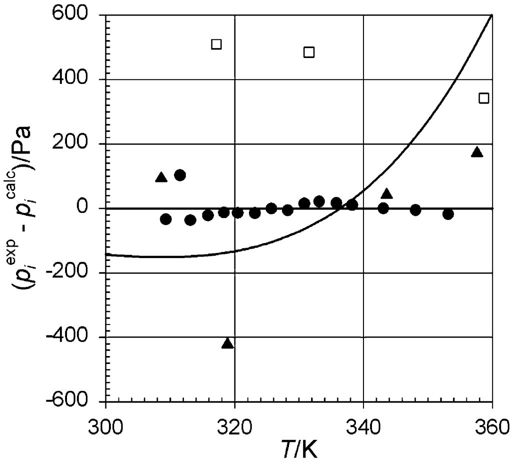

Figure 2. Deviation of propanenitrile saturation pressure data from correlation with the Antoine equation: ●, this work; □, Hall and Baldt;[9] ▲, Dreisbach and Shrader;[10] —, calculated with Antoine correlation of Daubert and Danner.[11]

procedure and apparatus used were described earlier.[13] The results obtained are given in Table 2.

Analytical Method. The sample composition was determined by the GLC method. An internal standard was used in the calibration procedure. A HP 5890 Series II gas chromatograph equipped with an HP 3396 integrator and an FID detector was used. For mixtures containing nitriles HP-17 and for mixtures with 1-pentanamine FFAP, above-mentioned, capillary columns were used.

Correlation

Vapor Pressure. The vapor pressure data were correlated by means of the Antoine equation,

$$\log(P/\text{kPa}) = A - \frac{B}{T/\text{K} - C} \tag{1}$$

where *P* is pressure, *T* is temperature, and *A*, *B*, and *C* are adjustable parameters.

The correlation results are summarized in Table 3. The comparison of correlation results with literature data is given in Figures 1 and 2.

The root-mean-square deviations of pressure (RMSD(*P*/Pa)) are calculated by

$$\text{RMSD}(P/\text{Pa}) = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\text{exp}} - p_i^{\text{calc}})^2}{n - m}} \tag{2}$$

where *m* is the number of adjustable parameters, *n* is the number of experimental points, p_i^{exp} is the pressure measured at point number *i*, and p_i^{calc} is the pressure calculated from eq 1 at point number *i*. The best evidence of the accuracy of the vapor pressure determination is the calculation of the heat of vaporization from the measured vapor pressure and comparison with those obtained by other methods. This is also presented in Table 3. The calculated values exhibit small deviations from published calorimetric data.

The *n*-pentylamine + 1-methoxy-2-propanol mixture contains associating compounds. To properly represent such mixtures, a special treatment is necessary. In previous work[14] it has been found that the AEOS (association + equation of state) equation of state is most suitable for representation of phase equilibria in the systems formed by associating or even chemically reacting compounds. In the AEOS model, the thermodynamic properties of an associated mixture are viewed as a result of chemical equilibrium between associated species and physical interactions between all, associated or inert, species existing

Table 2. Vapor−Liquid Equilibrium Experimental Data

Acetonitrile (1) + Propanenitrile (2)

T/K = 313.15			T/K = 323.15			T/K = 333.15		
x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.000	0.000	12.662	0.000	0.000	19.220	0.000	0.000	28.575
0.032	0.059	12.886	0.032	0.057	19.720	0.032	0.056	29.292
0.070	0.124	13.314	0.069	0.125	20.324	0.069	0.125	30.131
0.112	0.193	13.748	0.112	0.191	20.960	0.111	0.189	31.047
0.172	0.282	14.408	0.172	0.279	21.908	0.171	0.277	32.360
0.243	0.378	15.171	0.244	0.377	23.022	0.245	0.374	33.936
0.319	0.468	15.961	0.320	0.465	24.158	0.321	0.462	35.502
0.390	0.545	16.711	0.391	0.542	25.223	0.393	0.541	37.046
0.462	0.614	17.445	0.462	0.611	26.275	0.463	0.608	38.505
0.524	0.669	18.059	0.525	0.668	27.168	0.526	0.666	39.778
0.602	0.734	18.840	0.602	0.732	28.276	0.602	0.729	41.317
0.679	0.793	19.585	0.680	0.792	29.367	0.681	0.790	42.854
0.740	0.837	20.168	0.739	0.834	30.194	0.740	0.833	44.034
0.824	0.893	20.980	0.825	0.892	31.380	0.826	0.891	45.687
0.913	0.948	21.806	0.914	0.949	32.595	0.914	0.948	47.393
0.930	0.959	21.988	0.959	0.976	33.200	0.959	0.975	48.248
0.959	0.976	22.246	0.983	0.990	33.531	0.983	0.990	48.675
0.983	0.990	22.483	1.000	1.000	33.800	1.000	1.000	49.064
1.000	1.000	22.650						

n-Pentanamine (1) + 1-Methoxy-2-propanol (2)

T/K = 333.15			T/K = 343.15			T/K = 353.15		
x_1	y_1	P/kPa	x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.000	0.000	10.013	0.000	0.000	15.793	0.000	0.000	24.169
0.039	0.040	10.003	0.040	0.041	15.843	0.040	0.044	24.307
0.082	0.085	10.018	0.084	0.093	15.885	0.085	0.096	24.402
0.130	0.143	10.054	0.130	0.149	15.983	0.130	0.153	24.597
0.187	0.220	10.152	0.187	0.226	16.191	0.187	0.232	25.011
0.242	0.306	10.362	0.242	0.310	16.516	0.242	0.314	25.462
0.310	0.418	10.728	0.310	0.422	17.103	0.312	0.422	26.307
0.369	0.519	11.178	0.370	0.519	17.761	0.370	0.511	27.212
0.423	0.600	11.672	0.427	0.596	18.509	0.429	0.601	28.290
0.483	0.684	12.343	0.489	0.687	19.485	0.488	0.676	29.607
0.559	0.768	13.338	0.565	0.775	20.910	0.570	0.767	31.547
0.628	0.837	14.393	0.635	0.839	22.341	0.636	0.830	33.447
0.721	0.904	15.873	0.726	0.904	24.322	0.726	0.893	36.054
0.812	0.952	17.468	0.813	0.946	26.400	0.813	0.940	38.782
0.887	0.976	18.745	0.888	0.971	28.172	0.888	0.968	41.175
0.955	0.990	19.896	0.955	0.989	29.754	0.955	0.988	43.284
1.000	1.000	20.650	1.000	1.000	30.853	1.000	1.000	44.755

Estimated Uncertainties of Measurements

$\delta x_1 = \pm 0.001$	$\delta y_1 = \pm 0.002$	$\delta P/\text{Pa} = \pm 30$	$\delta T/\text{mK} = \pm 10$

Table 3. Correlation of Pure Component Vapor Pressure with Antoine Equation

compound	acetonitrile	propanenitrile	*n*-pentanamine	1-methoxy-2-propanol
temp range/K	302−354	309−354	322−378	331−373
A	6.378 961 6	6.166 440	6.022 286	6.503 081
B	1403.063	1330.287	1225.889	1472.144
C	33.877	50.719	72.723	65.612
RMSD(P/Pa)	8.36	31.16	8.35	8.61
$\Delta H_{\text{vap}}(298.15)/\text{kJ·mol}^{-1}$				
calculated	32.98	35.86	40.86	46.22
literature	33.06[11]	36.36[11]	39.62[11]	43.84[11]
$\Delta H_{\text{vap}}(T/\text{K})/\text{kJ·mol}^{-1}$	33.225[4]	36.116[16]		
$\Delta H_{\text{vap}}(\text{bp})/\text{kJ·mol}^{-1}$	354.71	370.44	377.93	392.95
calculated	29.84	30.01	34.31	38.87
literature	30.30[11]	32.85[11]	34.62[11]	39.55[11]
	29.75[15]	31.81[15]	34.01[15]	

in a mixture. The detailed formulas have been discussed by Antosik et al.[13] and Chylinski at al.[17]

The use of the AEOS equation leads to the split of the compressibility factor into two parts

$$z = \frac{pV}{RT} = z^{(\text{ph})} + z^{(\text{ch})} - 1 \tag{3}$$

where $z^{(\text{ph})}$ and $z^{(\text{ch})}$ are the physical and chemical contributions to the compressibility factor, respectively. The $z^{(\text{ph})}$ contribution is equivalent to the equation of state for nonreacting monomeric species. In this work it was calculated from the cubic equation of state of Yu et al.[18]

$$z^{(\text{ph})} = \frac{\nu}{\nu - b} - \frac{a(T)\nu}{RT[\nu(\nu + c) + b(3\nu + c)]} \tag{4}$$

where $a(T)$, b, and c are generalized functions of the critical temperature T_c, critical pressure P_c, and acentric factor ω of a pure component.

Table 4. Correlation of Pure Component Vapor Pressure with AEOS Equation of State

compound	T_c'/K	P_c'/MPa	ω'	$-\Delta H°$/kJ·mol^{-1}	$-\Delta S°$/J·mol^{-1}·K^{-1}	$-\Delta C_p$/J·mol^{-1}·K^{-1}	RMSD(P)/Pa
1-pentanamine	565.46	40.28	0.0763	19.189	91.34	28.84	3.96
1-methoxy-2-propanol	545.50	64.52	0.0543	24.083	92.32	1.33	6.10

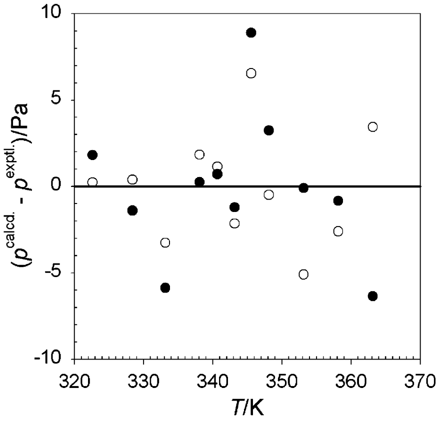

Figure 3. Deviation of *n*-pentanamine saturation pressure data (this work) from correlation with the AEOS (●) and Antoine (○) equations.

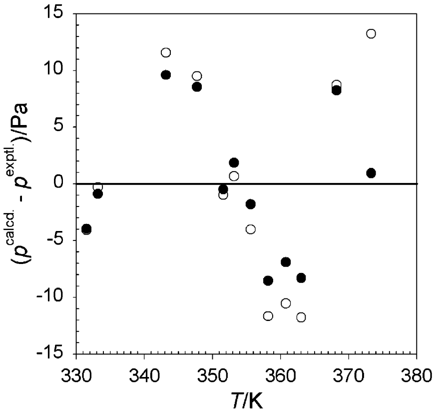

Figure 4. Deviation of 1-methoxy-2-propanol saturation pressure data (this work) from correlation with the AEOS (●) and Antoine (○) equations.

The $z^{(\text{ch})}$ contribution is equal to the reciprocal mean association number (K) and depends on the association model applied. In this work, the linear Mecke–Kempter-type association model has been used. It well represents compounds such as alcohols, phenols, ketones, amines, pyridine bases, and others.[19] For pure compounds this model leads to the equation

$$z^{(\text{ch})} = \frac{2}{1 + \sqrt{1 + 4RTK/V}} \tag{5}$$

The complete equation of state for an associating compound, eq 3, has five characteristic parameters: the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of association; the critical temperature (T'_c); the critical pressure (P'_c); and the acentric factor (ω') of a hypothetical monomeric compound with nonspecific interactions identical to those in the associating substance but incapable of forming associates. Description of the procedure was given earlier.[17] The values of parameters obtained by fitting the equation to vapor pressure data are given in Table 4. The temperature dependence of the association constant can be expressed by assuming that $\Delta H°$ and $\Delta S°$ of association are linearly dependent on temperature (the appropriate values of C_p are given in Table 4),

$$\ln K_{ij} = \frac{-\Delta H°(T_0) + \Delta C_p° T_0}{RT} + \frac{1}{R}[\Delta S°(T_0) - \Delta C_p° - \Delta C_p° \ln T_0] + \frac{\Delta C_p°}{R} \ln T \tag{6}$$

The results of correlation of pure component vapor pressures by means of the AEOS equation are given in Table 4. A comparison of correlations of vapor pressure by the Antoine and AEOS equations is shown in Figures 3 and 4. It is clear from these figures that there is no significant difference between the correlation ability of both equations. In both cases the distribution of deviations is random.

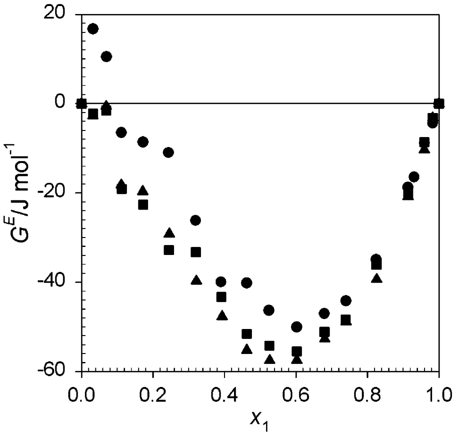

Figure 5. Experimental excess Gibbs energy of the system acetonitrile + propanenitrile: ●, T/K = 313.15; ■, T/K = 323.15; ▲, T/K = 333.15.

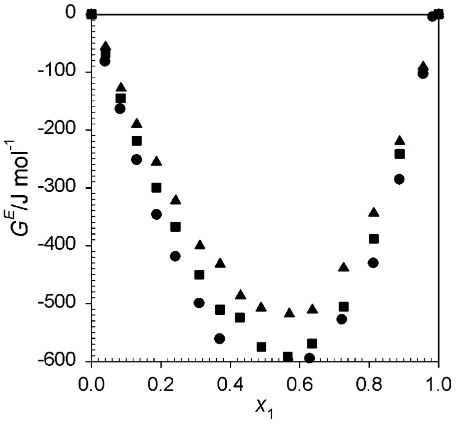

Figure 6. Experimental excess Gibbs energy of the system *n*-pentanamine + 1-methoxy-2-propanol; ●, T/K = 333.15; ■, T/K = 343.15; ▲, T/K = 353.15.

Vapor–Liquid Equilibrium. The results of $PTxy$ measurements, which are equilibrium pressure as a function of liquid and vapor phases compositions at constant temperature, exhibit negative deviations from ideal behavior. This can be seen in Figures 5 and 6, which represent the excess Gibbs energy of mixtures as a function

Table 5. Results of Correlations by Various Equations

		acetonitrile + propanenitrile		n-pentanamine + 1-methoxy-2-propanol	
equation	no. of parameters	RMSD(y)	RMSD(P/Pa)	RMSD(y)	RMSD(P/Pa)
		T/K = 313.15		T/K = 333.15	
ideal mixture		0.00453	48.5		
Redlich−Kister	1	0.00536	27.1	0.00905	18.0
Redlich−Kister	2	0.00522	16.7	0.00820	8.9
Redlich−Kister	3	0.00501	9.2	0.00841	6.3
Redlich−Kister	4	0.00497	8.3	0.00836	5.0
Redlich−Kister	5	0.00490	5.9	0.00834	5.0
Redlich−Kister	6	0.00488	5.3	0.00830	4.5
Wilson	2	0.00543	17.7	0.00815	10.8
UNIQUAC	3	0.00548	17.8	0.00820	9.2
NRTL	3	0.00478	7.5	0.00820	6.0
SSF	2	0.00471	8.2	0.00782	12.3
SSF	4	0.00480	3.7	0.00829	4.9
SSF	6	0.00480	3.7	0.00822	5.1
AEOS	2			0.00810	34.8
		T/K = 323.15		T/K = 343.15	
ideal mixture		0.00564	95.3		
Redlich−Kister	1	0.00631	29.0	0.01146	17.9
Redlich−Kister	2	0.00663	10.3	0.01104	13.2
Redlich−Kister	3	0.00657	6.9	0.01109	12.9
Redlich−Kister	4	0.00659	5.9	0.01100	8.3
Redlich−Kister	5	0.00658	5.6	0.01101	8.2
Redlich−Kister	6	0.00660	4.5	0.01097	7.1
Wilson	2	0.00646	14.7	0.01101	14.0
UNIQUAC	3	0.00667	10.9	0.01104	13.3
NRTL	3	0.00665	10.7	0.01103	10.2
SSF	2	0.00662	5.6	0.01104	13.3
SSF	4	0.00661	4.0	0.01101	10.2
SSF	6	0.00660	4.0	0.01096	5.7
AEOS	2			0.00940	89.0
		T/K = 333.15		T/K = 353.15	
ideal mixture		0.00652	136.9		
Redlich−Kister	1	0.00761	80.4	0.01261	24.3
Redlich−Kister	2	0.00814	11.6	0.01229	19.9
Redlich−Kister	3	0.00812	10.8	0.01241	16.7
Redlich−Kister	4	0.00814	7.8	0.01234	12.3
Redlich−Kister	5	0.00814	7.7	0.01235	12.3
Redlich−Kister	6	0.00814	7.7	0.01233	11.7
Wilson	2	0.00792	21.2	0.01227	21.2
UNIQUAC	3	0.00817	12.3	0.01229	20.1
NRTL	3	0.00809	9.4	0.01229	13.5
SSF	2	0.00812	10.0	0.01229	20.0
SSF	4	0.00811	7.1	0.01232	13.3
SSF	6	0.00815	6.5	0.01232	13.2
AEOS	2			0.01020	179.8
				T/K = 330−355	
AEOS prediction	3			0.01159	174.7

of liquid composition. The necessary fugacity coefficients (ϕ_i) of the component i in the vapor phase were calculated from

$$\phi_i = \exp\left[\frac{(\nu_i^{\mathrm{L}} - \beta_i)(P - P_i^{\circ}) - P_i^{\circ}(1 - y_i)^2(\beta_1 + \beta_2)/2}{RT}\right] \tag{7}$$

while the second virial coefficients β_i as functions of T were calculated from the Daubert and Danner[11] formula

$$\beta/\mathrm{m}^3\cdot\mathrm{kmol}^{-1} = A + \frac{B}{T} + \frac{C}{T^3} + \frac{D}{T^8} + \frac{E}{T^9} \tag{8}$$

where A, B, C, D, and E are the parameters recommended by Daubert and Danner.

The $PTxy$ data were reduced to activity coefficients. The equations of Redlich−Kister with one to six adjustable parameters, Wilson, UNIQUAC, NRTL with adjustable α, and SSF with two, four, and six adjustable parameters were used as activity coefficients models. The exact form of these equations is given by Malanowski and Anderko.[19] The results obtained are summarized in Table 5.

A reasonable VLE fit, within experimental accuracy, was obtained for both systems with a SSF (sum of symmetric functions) equation with two adjustable parameters

$$\ln \gamma_1 = \sum_{j=1}^{m} x_2^2 A_j \frac{a_j + x_1(a_i - 1/a_j)}{(x_1/a_j + x_2 a_j)^3} \tag{9}$$

$$\ln \gamma_2 = \sum_{j=1}^{m} x_1^2 A_j \frac{a_j + x_1(a_i - 1/a_j)}{(x_1/a_j + x_2 a_j)^3} \tag{10}$$

where A_j and a_j are adjustable parameters.

The mixture acetonitrile + propionitrile is almost ideal. The G^{E} value for the equimolar mixture is less than −60 J·mol^{-1} (Figure 5), and the vapor composition calculated for the ideal mixture is very close to experimental values. To obtain a good representation with a Redlich−Kister

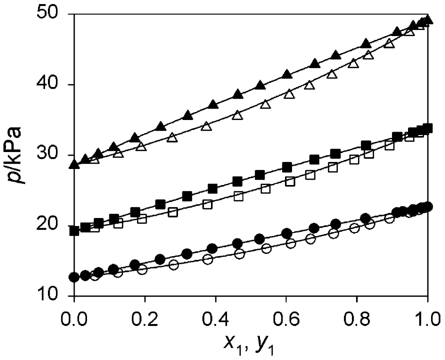

Figure 7. Vapor−liquid equilibrium in the system acetonitrile + propanenitrile: ●, T/K = 313.15; ■, T/K = 323.15; ▲, T/K = 333.15; solid symbols, bubble points; hollow symbols, dew points; solid line, correlation with SSF equation.

equation, four adjustable parameters are necessary for both systems.

$$\ln \gamma_1 = x_1^2\left(A_1 + \sum_{j=2}^{m} A_j(x_1 - x_2)^{j-2}((2j + 1)x_1 - x_2)\right) \quad (11)$$

$$\ln \gamma_2 = x_1^2\left(A_1 + \sum_{j=2}^{m} A_j(x_1 - x_2)^{j-2}(x_1 - (2j + 1)x_2)\right) \quad (12)$$

All other equations lead to less precise results.

The mixture n-pentylamine + 1-methoxy-2-propanol contains two associating compounds. The continuous linear association Mecke−Kempter model with the following equation for the chemical term represents the self- as well as cross-association,

$$z^{(\mathrm{ch})} = \sum_{i=1}^{2}\left(2x_{A_i}/\left(1 + \sqrt{1 + 4RT\left(\sum_{j=1}^{2} K_{ji}x_{A_j}\right)/V}\right)\right) \quad (13)$$

where K_{ij} is either the self-association constant (for $i = j$) or the cross-association constant (for $i \neq j$).

The parameters of the AEOS equation of state obtained from pure component data (Table 3) were used unchanged for mixture calculations. The binary parameters a, b, and c of the Yu et al.[18] equation ($z^{(\mathrm{ph})}$ term) were calculated using the classical mixing rules,

$$a = \sum_{i=1}^{2}\sum_{i=1}^{2} x_i x_j (1 - \theta_{ij})\sqrt{a_i a_j} \quad (14)$$

$$b = \sum_{i=1}^{2} x_i b_i \quad (15)$$

$$c = \sum_{i=1}^{2} x_i c_i \quad (16)$$

These mixing rules contain only one binary adjustable parameter θ_{12}. The mixture consists of two polar compounds, and better results were obtained with the cross-association constant K_{12} calculated from binary data. The correlation results are summarized in Table 5 and in Figures 7 and 8.

For the system n-pentanamine + 1-methoxy-2-propanol the temperature dependence of the parameter K_{12} has been calculated for the temperature range (330 to 355) K by linear regression from isothermal data reported in Table 2.

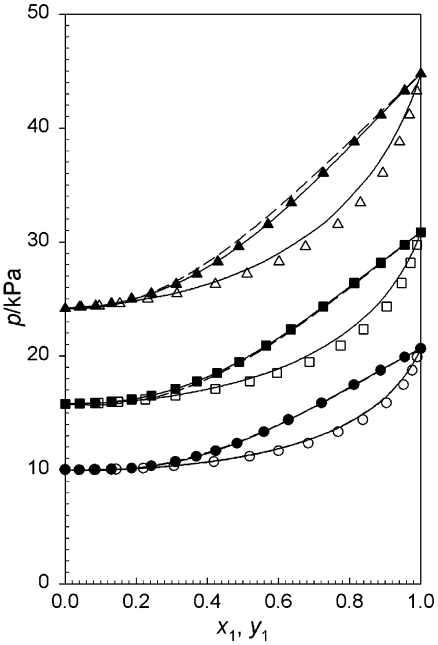

Figure 8. Vapor−liquid equilibrium in the system n-pentanamine + 1-methoxy-2-propanol: ●, T/K = 333.15; ■, T/K = 343.15; ▲, T/K = 353.15; solid symbols, bubble points; hollow symbols, dew points; solid line, correlation with SSF equation; dotted line, prediction with AEOS equation.

Table 6. Azeotropic Parameters in the System *n*-Pentanamine + 1-Methoxy-2-propanol

T_{az}/K	P_{az}/kPa	$x_1 = y_1$
333.15	10.002	0.038
343.15	15.773	0.015
353.15	azeotropic	

$$K_{12} = (4.8045 \times 10^{-4}) - (1.26995 \times 10^{-6})T \quad (17)$$

The parameter θ_{12} has been found to be independent of temperature. The RMSD values for P and y_1 obtained with this prediction are given in Table 5. The results of prediction by the AEOS equation with eq 17 used for K_{12} and θ_{12} = −0.0656 are very satisfactory. A comparison of all results leads to the conclusion that the correlated results are similar to those predicted with θ_{12} and the temperature dependent K_{12} parameters.

Azeotropes. The almost tangent negative azeotrope was observed at two lower temperatures for the system n-pentanamine + 1-methoxy-2-propanol. The azeotropic parameters determined by the ebulliometric method[20] are given in Table 6.

Literature Cited

(1) Vilcu, R.; Langshaw, V.; Genuse, Z. Isothermal Liquid−Vapor Equilibrium in the Acetonitrile-Propionitrile System. *Rev. Roum. Chim.* **1987**, *32*, 1025−1031.

(2) Kojima, K.; Tochigi, T. *Prediction of Vapour-Liquid Equilibria by the ASOG Method*; Elsevier: Amsterdam, 1979.

(3) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.

(4) Putnam, W. E.; McEachern, D. M.; Kilpatrick, J. E., Entropy and related thermodynamic properties of acetonitrile (methyl cyanide). *J. Chem. Phys.* **1965**, *42*, 749−755.

(5) Van Ness, H. C.; Kochar, N. K. Vapor-Liquid Equilibria: Acetone−Acetonitrile. *J. Chem. Eng. Data* **1967**, *12*, 38−39.

(6) Francesconi, R.; Comelli, F. Excess Thermodynamic Properties for the Binary System 1,4-Dioxane−Acetonitrile at 40° C. *J. Chem. Eng. Data* **1988**, *33*, 80−83.

(7) Meyer, E. F.; Renner, T. A.; Stec, K. S. Cohesive Energies in Polar Organic Liquids. II. The *n*-Alkyl Nitriles and the 1-Chloroalkanes. *J. Phys. Chem.* **1971**, *75*, 642−648.

(8) Dojčanský, J.; Heinrich, J. Saturated vapour pressure of acetonitrile. *Chem. Zvesti* **1974**, *28*, 157−159.

(9) Hall, H. K.; Baldt, J. H. Thermochemistry of Strained-Ring Bridgehead Nitriles and Esters. *J. Am. Chem. Soc.* **1971**, *93*, 140−145.

(10) Dreisbach, R. R.; Shrader, S. A. Vapor Pressure−Temperature Data on Some Organic Compounds. *Ind. Eng. Chem.* **1949**, *41*, 2879−2880.

(11) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*, Core Edition and Supplements 1−8; Taylor & Francis: London, 1998.

(12) Rogalski, M.; Malanowski, S. Ebulliometers Modified for the Accurate Determination of Vapour-Liquid Equilibrium. *Fluid Phase Equilib.* **1980**, *5*, 97−112.

(13) Antosik, M.; Fraś, Z.; Malanowski, S. K. Vapor-Liquid Equilibrium in 2-Ethoxyethanol + Methanol at 313.15 to 333.15 K. *J. Chem. Eng. Data* **1999**, *44*, 368−372.

(14) Anderko, A.; Malanowski, S. K. Calculation of solid−liquid, liquid−liquid and vapor-liquid equilibria by means of an equation of state incorporating association. *Fluid Phase Equilib.* **1989**, *48*, 223−241.

(15) Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, U.K., 1985.

(16) Weber, L. A.; Kilpatrick, J. E. Entropy and related thermodynamic properties of propionitrile. *J. Chem. Phys.* **1962**, *36*, 829−834.

(17) Chyliński, K.; Fraś, Z.; Malanowski, S. K. Vapor−Liquid Equilibrium in Phenol + 2-Ethoxyethanol at 363.15 to 383.15 K. *J. Chem. Eng. Data* **2001**, *46*, 29−33.

(18) Yu, J. M.; Lu, B. C.-Y.; Iwai, Y. Simultaneous calculation of VLE and saturated liquid and vapor volumes by means of a 3P1T cubic EOS. *Fluid Phase Equilib.* **1987**, *37*, 207−222.

(19) Malanowski, S.; Anderko, A. *Modelling Phase Equilibria. Thermodynamical Background and Practical Tools*; J. Wiley & Sons: New York, 1992. Świętosławski, W. *Azeotropy and Polyazeotropy*; Pergamon Press: Oxford, 1963.

(20) Świętosławski, W. *Azeotropy and Polyazeotropy*; Pergamon Press: Oxford, 1963.

Received for review December 19, 2002. Accepted May 1, 2003. The authors thank the Steering Committee of Project 805 of the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers for selection of the systems and for financial support.

JE025660T