Vapor−Liquid Equilibrium for Propylene Glycol + 2-(2-Hexyloxyethoxy)ethanol and 1-Methyl-2-pyrrolidone + 1-Methoxypropan-2-ol[†]

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The saturation pressures of propylene glycol at (393 to 423) K, 2-(2-hexyloxyetoxy)ethanol at (402 to 423) K, 1-methyl-2-pyrrolidone at (352 to 378) K, and 1-methoxypropan-2-ol at (347 to 378) K were measured by an ebulliometric method. The vapor−liquid equilibrium (*P*, *T*, *x*, *y*) was measured by an ebulliometric method for the system propylene glycol + 2-(2-hexyloxyethoxy)ethanol at (403.15, 413.15, and 423.15) K and for the system 1-methyl-2-pyrrolidone + 1-methoxypropan-2-ol at (353.15, 363.15, and 373.15) K. The experimental vapor pressures were correlated with Antoine and association + equation of state (AEOS) equations, while the VLE was correlated with the AEOS equation of state for all the temperature intervals and with equations representing activity coefficients at specific particular isotherms.

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 paper we report part of the experimental measurements that have been made under Projects 805-(B)/96 and 805(B)/97. Vapor−liquid equilibrium (VLE) data for the investigated systems 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 conceptn, such as ASOG[1] or UNIFAC.[2]

Experimental Section

Chemicals. Propylene glycol (CA Registry No. 57-55-6) was purchased from Fluka (puriss, >99.5 mol %, water content < 0.1%) was distilled at subambient pressure on a 40 theoretical plate column. The purity of collected fractions was checked by gas liquid chromatography (GLC) with a flame ionization detector (FID) on the nitroterephthalic acid modified poly(ethylene glycol) (FFAP), 30 m long capillary column, and those fractions of purity better than 99.8 mol % were collected and used for measurements. The water content, detected as above with a thermal conductivity detector (TCD), was lower than 0.01 mol %. The GLC results were based on calibration with appropriate mixtures, prepared by weighing, and the calibration curves were fitted to the polynomial with the accuracy 0.02 mol %. 2-(2-Hexyloxyethoxy)ethanol (CA Registry No. 112-59-4) was purchased from Aldrich (pure, >98 mol %) and distilled as above at subambient pressures. Fractions of purity better than 99.5 mol % (GLC and FFAP column) were collected and used for measurements. The water content established as above was <0.02 mol %. 1-Methyl-2-pyrrolidone (NMP) (CA Registry No. 872-50-4) was purchased from Chemipan Warsaw in glass ampules sealed under vacuum with a guaranteed purity of better than 99.9 mol % and was used without further purification. The water content in samples of pure substance withdrawn from the ebulliometer was lower than 0.01 mol % (as checked by means of the gas chromatograph with a TCD detector). 1-Methoxypropan-*2*-ol (propylene glycol monomethyl ether) (CA Registry No. 107-98-2) was purchased from Fluka (purum, >99 mol %). The compound was freshly distilled at subambient pressures with a 40 theoretical plate column. The purity of fractions was checked by GLC (with an FID detector) on a FFAP, 30 m long capillary column, and those of purity better than 99.8 mol % were collected and used for measurements. The water content detected as above was <0.01 mol %.

Vapor Pressure. When processing VLE data, the most crucial data are the saturation pressures of the pure components. An internally consistent compilation of vapor pressure data that includes all investigated substances was reported (DIPPR Project 801) by Daubert and Danner.[3] Experimental vapor pressure data were reported for NMP by Gierycz et al.[4] and by Kneisl and Zondlo.[5] For propylene glycol and 1-methoxypropan-*2*-ol only low quality data are available.[6] For 2-(2-hexyloxyethoxy)ethanol there are no literature data available. Experimental data on the vapor pressures of all compounds in this study were measured with the same apparatus which was used for the VLE measurements; the modified Świętosławski's ebulliometer[7] was used with the previously described[8] experimental procedure. The estimated accuracy of the pressure measurement was ±10 Pa, and that of temperature was ±10 mK. Temperatures were reported on the ITS-90 scale. The vapor pressures obtained are given in Table 1. The comparison of our NMP vapor pressure with literature data is given in Figure 1.

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

[†] 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.

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Table 1. Vapor Pressure *p* as a Function of Temperature *T* of Pure Components

propylene glycol		2-(2-hexyloxyethoxy)ethanol		NMP		1-methoxypropan-2-ol	
T/K	*p*/kPa	*T*/K	*p*/kPa	*T*/K	*p*/kPa	*T*/K	*p*/kPa
393.22	8.198	402.96	1.1106	352.27	1.2852	347.62	19.2451
393.25	8.207	403.01	1.1172	352.48	1.2972	352.64	23.7434
398.09	10.226	408.02	1.4346	359.26	1.8225	357.89	29.3549
403.14	12.766	413.2	1.8345	363.36	2.2172	362.93	35.7237
408.30	15.893	418.17	2.2931	368.27	2.7771	368.03	43.2911
413.10	19.364	422.87	2.8251	373.09	3.4437	373.22	52.3037
418.16	23.675	423.15	2.8584	377.86	4.2290	378.01	61.8896
423.26	28.814						

Table 2. Vapor−Liquid Equilibria in the Systems Propylene Glycol (1) + 2-(2-Hexyloxyethoxy)ethanol (2) and NMP (1) + 1-Methoxypropan-2-ol (2)

Propylene Glycol (1) + 2-(2-Hexyloxyethoxy)ethanol (2)

T/K = 403.15			*T*/K = 413.15			*T*/K = 423.15		
x_1	y_1	*p*/kPa	x_1	y_1	*p*/kPa	x_1	y_1	*p*/kPa
0.0000	0.0000	1.1239	0.0000	0.0000	1.8305	0.0000	0.0000	2.8584
0.0234	0.0037	1.2746	0.0233	0.0041	2.0625	0.0233	0.0039	3.2211
0.0623	0.0093	1.5905	0.0560	0.0084	2.5958	0.0559	0.0086	4.0837
0.0926	0.0122	2.4985	0.0923	0.0123	3.8690	0.0930	0.0131	5.8702
0.1613	0.0189	4.0223	0.1453	0.0184	6.0742	0.1432	0.0184	8.9579
0.2570	0.0265	5.5995	0.2577	0.0300	8.6606	0.2586	0.0294	12.9949
0.3813	0.0418	7.2674	0.3662	0.0408	11.1737	0.3650	0.0394	16.7720
0.4847	0.0480	8.7219	0.4766	0.0513	13.2002	0.4755	0.0551	19.4424
0.6057	0.0670	9.6819	0.6020	0.0708	14.8588	0.5578	0.0700	22.0195
0.7348	0.0861	10.7391	0.7240	0.0953	16.3133	0.7209	0.1008	24.0767
0.8378	0.1149	11.5111	0.8365	0.1341	17.6505	0.8352	0.1498	26.1259
0.9240	0.2028	12.0097	0.9261	0.2245	18.2532	0.9195	0.2420	27.0218
0.9723	0.4552	12.2590	0.9704	0.3944	18.6985	0.9653	0.3811	27.6511
0.9881	0.7257	12.5630	0.9866	0.7206	19.0971	0.9868	0.7012	28.2497
1.0000	1.0000	12.7709	1.0000	1.0000	19.3944	1.0000	1.0000	28.6910

NMP (1) + 1-Methoxypropan-2-ol (2)

T/K = 353.15			*T*/K = 363.15			*T*/K = 373.15		
x_1	y_1	*p*/kPa	x_1	y_1	*p*/kPa	x_1	y_1	*p*/kPa
0.0000	0.0000	24.248	0.0000	0.0000	36.028	0.0000	0.0000	52.161
0.0231	0.0002	23.727	0.0215	0.0002	35.235	0.0239	0.0002	50.989
0.0568	0.0005	22.775	0.0562	0.0005	33.854	0.0560	0.0005	49.017
0.1077	0.0008	21.576	0.1079	0.0007	32.093	0.1090	0.0010	46.412
0.1623	0.0022	20.173	0.1651	0.0022	30.029	0.1614	0.0023	43.479
0.2349	0.0044	18.376	0.2296	0.0046	27.333	0.2281	0.0048	39.604
0.3302	0.0094	15.658	0.3221	0.0090	23.569	0.3195	0.0104	34.321
0.4280	0.0151	13.035	0.4119	0.0155	19.957	0.4067	0.0177	29.278
0.5280	0.0257	10.342	0.5226	0.0259	15.635	0.5127	0.0240	23.619
0.5792	0.0324	8.994	0.5804	0.0312	13.537	0.5754	0.0324	20.179
0.6477	0.0493	7.374	0.6474	0.0491	11.286	0.6438	0.0517	16.750
0.7344	0.0940	5.553	0.7382	0.0961	8.480	0.7371	0.0926	12.623
0.8245	0.1797	3.894	0.8211	0.1627	6.138	0.8185	0.1626	9.337
0.9103	0.3776	2.544	0.9093	0.3879	3.989	0.9102	0.3736	6.096
0.9562	0.6173	1.879	0.9543	0.5761	3.080	0.9492	0.5477	4.897
0.9727	0.7246	1.665	0.9719	0.7174	2.692	0.9722	0.7217	4.194
1.0000	1.0000	1.344	1.0000	1.0000	2.193	1.0000	1.0000	3.456

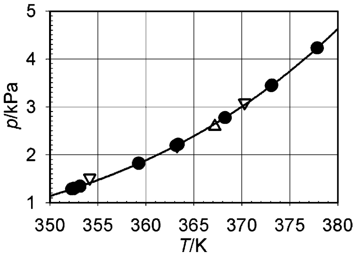

Figure 1. Vapor pressure of NMP: ●, this work; ▽, Gierycz et al.;[4] △, Kneisl and Zondlo;[5] solid line, correlation with the Antoine equation for the whole available range of temperature.

The procedure and apparatus used were described earlier.[8] The results obtained are given in Table 2.

Analytical Method. The sample composition was determined by the GLC method with an uncertainty of 0.1 mol % for the liquid phase and 0.5 mol % for the vapor phase. 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 with NMP, a HP-17 (50% phenyl and 50% methyl siloxane), 10 m long capillary column and, for mixtures with propylene glycol, a Reoplex, 2 m long packed column were used.

Correlation

Vapor Pressure. The vapor pressure data were correlated with the Antoine equation. The details were described earlier.[9]

The correlation results are summarized in Table 3. A comparison of correlation results with literature data is given in Figure 1 for NMP.

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

Table 3. Correlation of Pure Component Vapor Pressures with the Antoine and AEOS Equations

temp range/K =	propylene glycol 393−423	2-(2-hexyloxyethoxy)ethanol 402−423	NMP 352−378	1-methoxypropan-2-ol 347−378
Parameters of the Antoine Equation (T/K, p/kPa)				
A =	6.700349	6.571846	5.664526	6.453613
B =	1668.621	1966.962	1384.407	1443.384
C =	104.867	101.479	103.085	68.399
RMSD(p)/Pa =	2.29	4.94	1.32	5.22
Enthalpy of Vaporization/kJ·mol^{-1}				
at T/K = 298.15				
calculated =	76.00	86.54	61.91	46.42
literature =	71.2 ± 0.1[a] 66.68[b] 64.43 ± 2.4[c]	78.49[b]	55.21[b] 54.88 ± 0.13[d]	43.84[b] 43.99[c]
at normal boiling point T/K =	460.30	532.25	481.46	392.91
calculated =	52.07	54.31	41.40	38.77
literature =	54.52[b] 58.2[c]	59.73b	44.28[b] 44.54 ± 0.53[d]	39.55[b]
Parameters of the AEOS Equation of State				
T'_c/K =	608.83	649.98	586.37	617.82
p'_c/MPa =	5.47	1.75	3.62	7.21
ω'_H =	0.490	0.819	0.409	0.370
$-\Delta H°$/kJ·mol^{-1} =	20.93	9.60	21.31	
$-\Delta S°$/J·mol^{-1}·K^{-1} =	82.00	54.91	79.39	
$-\Delta C_p°$/J·mol^{-1}·K^{-1} =	9.803	14.027	−58.40	
RMSD(p)/Pa =	4.16	4.53	1.84	5.52

[a] Reference 10. [b] Reference 3. [c] Reference 11. [d] Reference 12.

$$\mathrm{RMSD}(p)/\mathrm{Pa} = \sqrt{\frac{\sum_{i=1}^{n}(p_i^{\mathrm{exp}} - p_i^{\mathrm{calc}})^2}{n}} \qquad (1)$$

where m is the number of adjustable parameters, 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 calculation of the enthalpy 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 and estimated data, taking into account that they were calculated at 298.15 K and at normal boiling point while the vapor pressures were measured for temperatures differing even more than 100 K.

The investigated mixtures contain associating compounds. To properly represent such mixtures, a special treatment is necessary. In previous work[13] 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 in a mixture. The detailed formulas have been discussed by Antosik and al.[8,9] and Chylinski at al.[14]

The values of parameters obtained by fitting the equation to vapor pressure data are given in Table 3. 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 $\Delta C_p°$ are also given in Table 3).

Comparisons of correlations of vapor pressure by the Antoine equation and the AEOS equation are shown in Figures 2−5. It is clear from these figures that there is no significant difference between the correlation abilities of these equations. In all cases the distribution of deviations is random.

Table 4. Binary Parameters of the AEOS Equation and RMSD(y_1) and RMSD(p)

T/K	10^6K_{12}	θ_{12}	RMSD(y_1)	RMSD(p)/Pa
Propylene Glycol (1) + 2-(2-Hexyloxyethoxy)ethanol (2): Correlation				
403.15	8.461919	−0.121 056	0.0649	281.50
413.15	4.704637	−0.132 884	0.0726	464.78
423.15	0.631892	−0.157 580	0.0636	826.95
Propylene Glycol (1) + 2-(2-Hexyloxyethoxy)ethanol (2): Prediction				
403.15	7.9652	−0.118 838	0.0602	289.68
413.15	4.0452	−0.137 098	0.0722	492.01
423.15	0.1252	−0.155 358	0.0574	868.80
403−423	eq 3	eq 4	0.0633	550.2
NMP (1) + 1-Metoxypropan-2-ol (2): Correlation				
353.15		−0.133 730	0.0495	375.79
363.15		−0.135 153	0.0611	580.77
373.15		−0.136 573	0.0703	888.01
NMP (1) + 1-Methoxypropan-2-ol (2): Prediction				
353.15		−0.133 677	0.0495	376.08
363.15		−0.135 097	0.0611	581.41
373.15		−0.136 517	0.0703	888.98
353−373		eq 5	0.0603	615.5

The mixture propylene glycol + 2-(2-hexyloxyethoxy)ethanol consists of two associating compounds while the binary NMP + 1-methoxypropan-2-ol contains only one associating compound. It was concluded that the continuous linear association Mecke−Kempter model with the following equation for the chemical term represents the self- as well as cross-association,

$$z^{(\mathrm{ch})} = \sum_{i=1}^{2}(2x_{A_i}/(1 + \sqrt{1 + 4RT(\sum_{j=1}^{2}K_{ij}x_{A_j})/V})) \qquad (2)$$

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

Table 5. Results of Correlation by Various Equations

	parameters							RMSD(p)
equation	1	2	3	4	5	6	RMSD(y)	Pa
			Propylene Glycol (1) + 2-(2-Hexyloxyethoxy)ethanol (2)					
			T/K = 403.15					
Redlich−Kister	0.695 48						0.0723	230.2
	0.626 84	0.265 81					0.0946	69.4
	0.660 66	0.223 31	0.320 93				0.0745	129.9
	0.621 30	0.225 17	0.089 39	0.121 57			0.0927	28.0
	0.629 44	0.210 33	0.095 82	0.129 79	0.044 75		0.0898	34.0
	0.615 33	0.250 03	0.093 63	−0.036 27	−0.040 71	0.245 27	0.0955	15.6
Wilson	−781.94	−9 051.47					0.1355	792.5
UNIQUAC[a]	−2 484.69	4 415.68					0.0901	37.9
NRTL	5 351.92	1 018.89	−2.454 7				0.0888	35.5
SSF	0.700 01	0.500 01					0.1119	1038.0
	0.650 96	0.564 30	0.097 43	0.097 17			0.0722	782.1
	0.565 34	0.561 09	0.161 12	0.094 52	0.764 94	0.969 22	0.0635	929.7
			T/K = 413.15					
Redlich−Kister	0.661 32						0.0856	330.4
	0.591 69	0.257 47					0.1079	103.4
	0.601 16	0.255 46	0.251 73				0.0948	151.1
	0.579 81	0.224 28	0.069 32	0.128 90			0.1083	51.9
	0.602 17	0.193 90	0.071 13	0.110 35	0.134 96		0.0997	57.0
	0.618 56	0.186 04	0.054 70	0.083 77	0.200 20	−0.100 20	0.0934	82.9
Wilson	−3 207.86	−11 345.04					0.1266	571.2
UNIQUAC[a]	−2 776.33	4 704.82					0.1033	58.2
NRTL	5 048.45	1 076.28	−2.772 2				0.1018	53.9
SSF	0.275 93	0.929 22					0.1178	854.0
	0.436 40	1.351 15	0.193 75	0.992 35			0.1023	56.6
	−0.093 21	−1.264 95	0.576 49	1.318 37	0.147 55	0.930 63	0.1018	57.4
			T/K = 423.15					
Redlich−Kister	0.604 32						0.0872	498.7
	0.534 01	0.235 95					0.1080	255.9
	0.568 74	0.151 28	0.132 28				0.0935	236.1
	0.522 34	0.173 26	0.115 78	0.220 57			0.1075	141.9
	0.488 90	0.198 80	0.175 49	0.311 12	−0.227 24		0.1183	146.1
	0.516 35	0.165 74	0.180 33	0.329 55	−0.140 79	−0.144 63	0.1092	129.9
Wilson	−5 767.14	−11 250.51					0.1075	203.8
UNIQUAC[a]	−3 906.40	6 036.63					0.1054	193.2
NRTL	2 808.87	13 009.88	1.517 2				0.1014	172.4
SSF	0.249 49	0.860 98					0.1147	1221.8
	0.535 87	1.286 76	−0.073 70	0.189 35			0.1103	194.0
	0.324 47	1.580 34	0.127 11	0.083 25	0.298 44	0.874 19	0.1202	152.5
			NMP (1) + 1-Methoxy-2-propanol (2)					
			T/K = 353.15					
Redlich−Kister	−0.569 30						0.0483	86.3
	−0.608 26	−0.068 68					0.0535	53.9
	−0.595 07	−0.040 66	0.054 00				0.0505	41.0
	−0.592 24	−0.042 48	0.066 41	0.028 75			0.0498	39.5
	−0.596 93	−0.042 61	0.091 66	−0.003 37	−0.083 64		0.0505	34.8
	−0.595 86	−0.038 74	0.087 80	−0.027 90	−0.068 57		0.0504	34.5
Wilson	7 055.69	−330.73					0.0536	58.9
UNIQUAC[b]	−1 284.77	−1 476.25					0.0535	57.3
NRTL	55 430.7	−44 293.3	0.091 4				0.0514	43.5
SSF	−0.609 07	1.056 87					0.0534	56.4
	−1 482 656.0	1.273 92	1 482 655.5	−1.273 92			0.0696	817.5
	−1 209 438.6	0.811 37	1 209 438.1	−0.811 37	−0.049 86	0.390 16	0.0500	31.4
			T/K = 363.15					
Redlich−Kister	−0.548 29						0.0607	79.3
	−0.562 89	−0.026 55					0.0627	68.6
	−0.554 73	−0.007 16	0.038 45				0.0606	57.3
	−0.559 40	−0.003 71	0.017 98	−0.048 21			0.0618	50.5
	−0.560 64	−0.003 82	0.024 03	−0.055 86	−0.020 09		0.0621	50.1
	−0.558 81	0.003 39	0.017 29	−0.100 62	0.005 62	0.077 97	0.0619	48.2
Wilson	5 644.13	981.93					0.0628	71.0
UNIQUAC[b]	−1 284.77	−1 476.25					0.0535	57.3
NRTL	1 371.36	−6 980.36	0.360 4				0.0554	156.0
SSF	−0.562 75	1.023 24					0.0626	69.1
	−311.53	1.159 04	310.98	1.159 33			0.0609	62.0
	−312.53	1.159 18	311.98	1.159 50	0.007 60	0.469 46	0.0604	59.5
			T/K = 373.15					
Redlich−Kister	−0.522 49						0.0704	74.5
	−0.528 77	−0.011 55					0.0713	70.1
	−0.527 42	−0.008 15	0.006 92				0.0709	69.4
	−0.527 60	−0.007 99	0.006 06	−0.002 06			0.0710	69.4
	−0.527 48	−0.008 00	0.005 33	−0.001 22	0.002 30		0.0710	69.4
	−0.528 17	−0.010 79	0.008 24	0.016 90	−0.008 21	−0.03139	0.0710	68.9
Wilson	5 128.43	1 327.80					0.0714	70.8
UNIQUAC[b]	546.48	−3 054.24					0.0713	70.2
NRTL	80 991.66	−72 937.56	0.032 7				0.0710	69.4
SSF	−0.528 82	1.010 98					0.0713	70.1
	−22.963	1.077 73	22.438	−1.079 44			0.0709	69.4
	−23.439	1.096 04	22.916	1.098 16	−0.002 55	0.173 98	0.0708	68.2

[a] $q_1 = 4.0160$; $q_2 = 6.7640$; $r_1 = 4.0224$; $r_2 = 8.0035$. [b] $q_1 = 3.2$; $q_2 = 3.904$; $r_1 = 3.981$; $r_2 = 4.1674$.

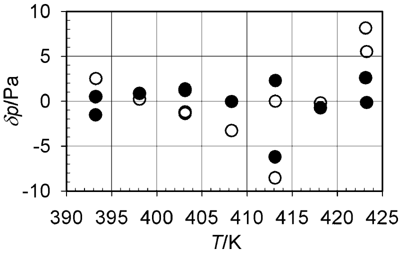

Figure 2. Deviations $dP = P_{calc} - P_{exp}$ of the experimental vapor pressure of propylene glycol from the Antoine correlation (●) and the AEOS equation (○).

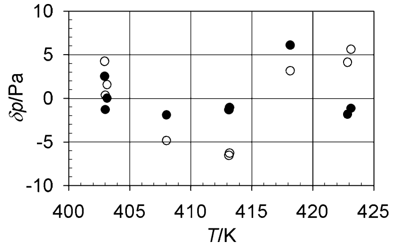

Figure 3. Deviations $dP = P_{calc} - P_{exp}$ of the experimental vapor pressure of 2-(2-hexyloxyethoxy)ethanol from the Antoine correlation (●) and the AEOS equation (○).

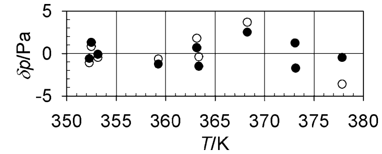

Figure 4. Deviations $dP = P_{calc} - P_{exp}$ of the experimental vapor pressure of NMP from the Antoine correlation (●) and the AEOS equation (○).

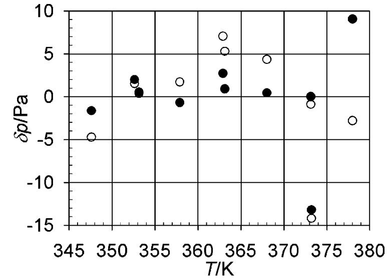

Figure 5. Deviations $dP = P_{calc} - P_{exp}$ of the experimental vapor pressure of 1-methoxypropan-*2*-ol from the Antoine correlation (●) and the AEOS equation (○).

The parameters of the AEOS equation of state obtained from pure component data (Table 3) were used without change for mixture calculations. The binary parameters *a*, *b*, and *c* of the Yu et al.[15] equation (z^{ph} term) were calculated using the classical mixing rules.

These mixing rules contain only one binary adjustable parameter θ_{12}. The propylene glycol + 2-(2-hexyloxyethoxy)ethanol consists of two polar compounds. In this case, better results were obtained with the cross-association constant K_{12} of eq 2 calculated from binary data. For the system NMP + 1-methoxypropan-2-ol, containing one associating component (NMP), a calculation of the θ_{12} parameter was sufficient. The correlation results are summarized in Table 4.

For the system propylene glycol + 2-(2-hexyloxyethoxy)ethanol, the temperature dependence of the parameters K_{12} and θ_{12} has been calculated for the temperature range (403 to 423) K by linear regression from isothermal VLE data reported in this paper

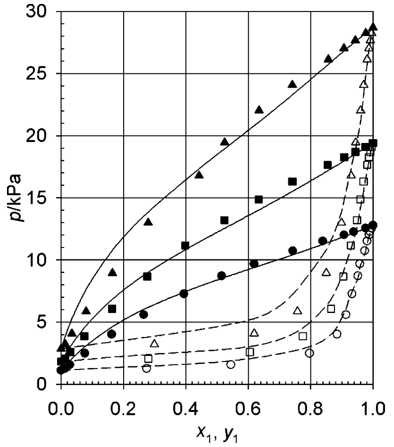

Figure 6. VLE for propylene glycol + 2-(2-hexyloxyethoxy)ethanol: ● and ○, 403.15 K; ■ and □, 413.15 K; ▲ and △, 423.15 K; the lines represent a prediction with the AEOS equation of state; solid symbols represent experimental bubble points; hollow symbols represent experimental dew points.

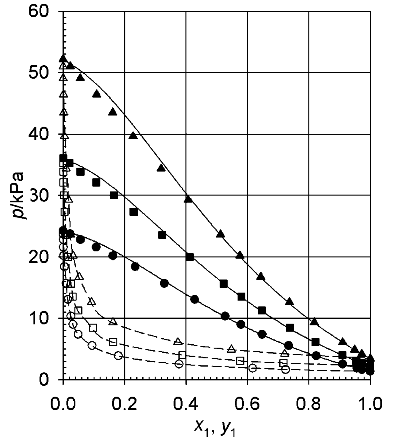

Figure 7. VLE for NMP + 1-methoxypropan-2-ol: ● and ○ 353.15 K; ■ and □, 363.15 K; ▲ and △, 373.15 K; the lines represent a prediction with the AEOS equation of state; solid symbols represent experimental bubble points; hollow symbols represent experimental dew points.

$$K_{12} = (1.66 \times 10^{-4}) - (3.92 \times 10^{-7})T \tag{3}$$

$$\theta_{12} = 0.617\,314 - (1.826 \times 10^{-3})T \tag{4}$$

For the system NMP + 1-methoxypropan-2-ol, θ_{12} has been calculated for the temperature range (353 to 373) K

$$\theta_{12} = -0.083\,53 - (1.42 \times 10^{-4})T \tag{5}$$

The RMSDs for *p* and y_1 obtained with this prediction are given in Table 5.

The results of calculation by the AEOS equation with eqs 3−5 used for K_{12} and θ_{12} given in Table 4 and in Figures 6 and 7 are very satisfactory. A comparison of the correlation results for single isotherms with those predicted for the same isotherms using eqs 3−5 leads to the conclusion that the correlated results are similar to those predicted with the temperature dependent K_{12} and θ_{12} parameters.

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 coefficient models. The exact form of these equations is given by Malanowski and Anderko.[16]

The necessary fugacity coefficients (ϕ_i) of component i in the vapor phase were calculated by the method described earlier.[9] Second virial coefficients β_i as functions of T were calculated from the Daubert and Danner[3] data. The results obtained are summarized in Table 5.

A comparison of all RMSD values in Table 5 leads to the conclusion that the results predicted by the AEOS equation of state with temperature dependent θ_{12} and the K_{12} parameters are of similar or better accuracy to that for those correlated with equations for activity coefficients at one temperature only.

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Literature Cited

(1) Kojima, K.; Tochigi, T. *Prediction of Vapour-Liquid Equilibria by the ASOG Method*; Elsevier: Amsterdam, 1979.
(2) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapour-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(3) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*, Core Edition and Supplements 1−8; Taylor & Francis: London, 1998.
(4) Gierycz, P.; Rogalski, M.; Malanowski, S. Vapor-liquid equilibria in binary systems formed by *N*-methylpyrrolidone with hydrocarbons and hydroxyl derivatives. *Fluid Phase Equilib.* **1985**, *22*, 107−122.
(5) Kneisl, P.; Zondlo, J. W. Vapor Pressure, Liquid Density, and the Latent Heat of Vaporization as Functions of Temperature for Four Dipolar Aprotic Solvents. *J. Chem. Eng. Data* **1987**, *32*, 11−13.
(6) Stephenson, R. M.; Malanowski, S. *Handbook of the Thermodynamics of Organic Compounds*; Elsevier: New York, 1987.
(7) Rogalski, M.; Malanowski, S. Ebulliometers Modified for the Accurate Determination of Vapour-Liquid Equilibrium. *Fluid Phase Equilib.* **1980**, *5*, 97−112.
(8) 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.
(9) Antosik, M.; Gałka, M.; Malanowski, S. K. Vapor-Liquid Equilibrium for Acetonitrile + Propanenitrile and 1-Pentanamine + 1-Methoxy-2-propanol. *J. Chem. Eng. Data*, in press.
(10) Knauth, P.; Sabbah, R. Energetics of inter- and intramolecular bonds in alkanediols. IV. The thermochemical study of 1,2-alkanediols at 298.15 K. *Thermochim. Acta* **1990**, *164*, 145−152.
(11) Gardner, P. J.; Hussain, K. S. The standard enthalpies of formation of some aliphatic diols. *J. Chem. Thermodyn.* **1972**, *4*, 819−827.
(12) Steele, W. V.; Chirico, R. D.; Nguyen, A.; Hossenlopp, I. A.; Smith, N. K. Determination of ideal gas enthalpies of formation for key compounds. *AIChE Symp. Ser.* **1990**, *86*, 138−154.
(13) 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.
(14) 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.
(15) 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.
(16) Malanowski, S.; Anderko, A. *Modelling Phase Equilibria. Thermodynamical Background and Practical Tools*; J. Wiley & Sons: New York, 1992.

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