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Vapor−Liquid Equilibrium in 2-Ethoxyethanol + Valeraldehyde and + Propyl Ether at 313.15 to 333.15 K

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The vapor−liquid equilibrium (*P*, *T*, *x*, *y*) was measured at 313.15, 323.15, and 333.15 K by the ebulliometric method for the binary systems formed by 2-ethoxyethanol with valeraldehyde and with propyl ether. The experimental results were correlated with equations representing liquid-phase activity coefficients.

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)/94 (system with valeraldehyde) and 805(B)/95 (system with propyl ether). 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, based on a group contribution concept such as ASOG[1] or UNIFAC.[2]

Experimental Section

Chemicals. 2-Ethoxyethanol (CA registry no. 110-80-5) was described previously (Antosik et al.[3]). Valeraldehyde (CA registry no. 110-62-3) was purchased from Aldrich-Chemie GmbH & Co. KG as 97% pure. A purity of 98 wt % of pure compound was found by gas chromatography (GC). It is likely that during distillation some polycondensation took place. That is why in the next step this substance was distilled with an inhibitor (hydroquinone). Moreover, this distillation was carried out under an argon atmosphere. From a GC analysis we found the resulting purity to be approximately 99.8%, by using a 60 m SPB-1 capillary column. The water content was determined by GC analysis with a TC detector and a glass 2.5 m by 3 mm column filled with Chromosorb 101 (60/80 Mesh) and is <0.03 wt %. Propyl ether (CA registry no. 111-43-3) was purchased from Aldrich-Chemie GmbH & Co. KG, with a purity of 99+%; 99.3 wt % was found by a GC method. The substance was purified by fractional distillation over lithium aluminum hydride. The final purity was 99.7 wt % (checking by GC) with a content of water < 0.03 wt %.

Vapor Pressure Measurements. In the processing of VLE data the most crucial data are the saturation pressures of pure components. The vapor pressure data of pure compounds were measured in this work. An arrangement for VLE measurements was used. A modified Świętosławski's ebulliometer (Rogalski and Malanowski[4]) and the previously described (Antosik et al.[3]) experimental procedure were used. The estimated accuracy of the pressure measurement was ±10 Pa, and that of temperature was ±10 mK. The ITS-90 was used for temperature determination. The results are given in Table 1.

Table 1. Vapor Pressure of Pure Components

propyl ether		valeraldehyde	
T/K	*P*°/kPa	*T*/K	*P*°/kPa
308.29	13.371	307.24	7.629
308.30	13.376	313.13	10.066
311.55	15.456	315.20	11.046
313.15	16.571	317.93	12.492
316.60	19.209	320.46	13.975
318.75	21.016	322.49	15.244
323.14	25.173	326.03	17.720
326.13	28.346	328.84	19.896
328.84	31.503	332.99	23.526
331.75	35.185	337.67	28.260
333.16	37.092	343.05	34.600
338.80	45.614		

VLE Measurements. The vapor−liquid equilibrium measurements were made with the ebulliometer set up to sample the liquid phase and vapor condensate. The procedure and apparatuses used were described earlier by Antosik et al.[3] The results are given in Table 2.

Analytical Method. The sample composition was determined by gas chromatography with a flame ionization detector. An internal standard was used in the calibration procedure. A HP 5890 Series II gas chromatograph equipped with an HP 3396 integrator and a 2 m Reoplex packed column was used.

Measurements

Vapor Pressure. The experimental data and correlations recommended by DIPPR (Daubert and Danner[5]) are available for all components. There are discrepancies between these data. Data for 2-ethoxyethanol have been discussed earlier (Antosik et al.[3]). For propyl ether the most reliable measurements were reported by Ambrose et al.[6] Earlier measurements were reported by Cidlinsky and Polak[7] and by Meyer and Hotz.[8] The discrepancies between various authors are within 0.5%. For valeraldehyde discrepancies are much larger. The old data by Stage et al.[9] differ from DIPPR[5] recommendations based on TRC[10] correlations by up to 100%. The measurements by Kassmann and Knapp[11] are 2 to 3% higher than the DIPPR recommendations. This situation justified the necessity for

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Table 2. Vapor−Liquid Equilibrium

x_1	y_1	P/kPa	$y_{1,calcd} - y_1$	$P_{calcd} - P$/Pa	x_1	y_1	P/kPa	$y_{1,calcd} - y_1$	$P_{calcd} - P$/Pa
2-Ethoxyethanol (1) + Propyl Ether (2): Correlation with the SSF Equation									
T/K = 313.15									
0.0000	0.0000	16.571		0.0	0.8513	0.1500	7.869	0.04909	7.9
0.0405	0.0174	16.301	0.00130	−11.8	0.9131	0.2283	5.798	0.05230	57.7
0.0910	0.0295	15.907	0.00423	21.8	0.9460	0.3148	4.433	0.05945	74.6
0.1924	0.0441	15.183	0.01040	19.3	0.9650	0.4283	3.570	0.04448	54.3
0.2974	0.0540	14.496	0.01637	−30.4	0.9770	0.5545	2.958	0.01812	64.6
0.4097	0.0660	13.699	0.01845	−11.8	0.9872	0.7003	2.393	0.00296	90.0
0.5245	0.0721	12.814	0.02641	10.0	0.9948	0.8555	2.033	0.00332	30.0
0.6568	0.0936	11.460	0.02588	54.7	0.9963	0.9081	1.943	0.01819	35.8
0.7322	0.1025	10.443	0.03568	8.7	0.9985	0.9596	1.839	0.00751	14.3
0.8008	0.1249	9.149	0.04059	−8.0	1.0000	1.0000	1.767		0.0
T/K = 323.15									
0.0000	0.0000	25.173		0.0	0.8516	0.1514	12.044	0.07796	54.9
0.0400	0.0180	24.813	0.00219	−65.0	0.9096	0.2213	9.431	0.08735	−54.2
0.0909	0.0301	24.215	0.00836	−17.1	0.9426	0.3205	7.349	0.07883	80.5
0.1841	0.0459	23.190	0.01516	39.6	0.9661	0.4481	5.761	0.07103	60.7
0.2979	0.0603	22.066	0.02021	15.9	0.9810	0.6150	4.620	0.03705	71.5
0.4138	0.0734	20.877	0.02402	−19.1	0.9872	0.7123	4.144	0.02100	49.4
0.5299	0.0799	19.469	0.03506	−18.9	0.9962	0.9013	3.418	0.00027	20.6
0.6401	0.0959	17.725	0.03989	37.1	0.9983	0.9576	3.249	0.00462	8.5
0.7304	0.1001	15.909	0.06079	−8.0	1.0000	1.0000	3.109		0.0
0.7950	0.1255	14.108	0.06353	15.0					
T/K = 333.15									
0.0000	0.0000	37.092		0.0	0.8573	0.1662	17.717	0.10209	−42.7
0.0395	0.0180	36.634	0.00320	−140.3	0.9072	0.2210	14.328	0.12274	−34.9
0.0895	0.0325	35.738	0.00908	−31.4	0.9414	0.3367	11.476	0.10323	−22.9
0.1778	0.0513	34.283	0.01608	55.0	0.9655	0.4660	9.057	0.09567	80.0
0.2878	0.0632	32.637	0.02726	43.2	0.9817	0.6472	7.471	0.05419	−59.3
0.4081	0.0752	30.856	0.03608	−31.7	0.9864	0.7238	6.787	0.03433	94.9
0.5361	0.0872	28.594	0.04649	−27.6	0.9947	0.8739	5.874	0.01405	42.9
0.6310	0.0998	26.455	0.05433	10.2	0.9981	0.9600	5.486	0.00353	23.0
0.7311	0.1120	23.462	0.07339	34.6	1.0000	1.0000	5.278		0.0
0.7923	0.1281	21.037	0.08729	22.2					
2-Ethoxyethanol (1) + Valeraldehyde (2): Correlation with the Redlich−Kister Equation									
T/K = 313.15									
0.0000	0.0000	10.071	0.00000	0.0	0.6697	0.2337	4.530	0.02205	−2.1
0.0601	0.0080	9.458	0.00315	85.3	0.7532	0.3213	3.768	0.02881	−10.4
0.1357	0.0216	8.857	0.00673	26.3	0.8122	0.4057	3.248	0.03665	−18.1
0.2094	0.0361	8.269	0.01097	6.2	0.8660	0.5213	2.766	0.03049	8.1
0.3085	0.0579	7.557	0.01658	−46.4	0.9060	0.6325	2.424	0.02115	32.5
0.3310	0.0633	7.367	0.01786	−26.6	0.9427	0.7518	2.208	0.01541	−27.6
0.3870	0.0795	6.917	0.01945	1.4	0.9640	0.8304	2.007	0.01399	19.6
0.4655	0.1092	6.274	0.01895	33.1	0.9915	0.9375	1.852	0.02238	−18.7
0.5255	0.1272	5.790	0.02856	23.9	1.0000	1.0000	1.775		0.0
0.5961	0.1677	5.213	0.02956	−13.1					
T/K = 323.15									
0.0000	0.0000	15.684		0.0	0.6682	0.2128	7.770	0.05544	5.6
0.0600	0.0121	14.895	0.00247	35.2	0.7503	0.3034	6.615	0.04951	0.1
0.1318	0.0252	14.027	0.00940	14.3	0.8122	0.3835	5.741	0.05837	−20.4
0.2061	0.0413	13.155	0.01560	12.6	0.8653	0.4883	4.964	0.05533	−7.1
0.3033	0.0637	12.128	0.02386	−36.0	0.9069	0.6027	4.353	0.04382	16.4
0.3864	0.0853	11.203	0.03059	−7.1	0.9416	0.7059	3.885	0.04786	6.3
0.4655	0.1126	10.304	0.03414	15.8	0.9670	0.8254	3.544	0.02326	5.0
0.5245	0.1292	9.630	0.04478	1.7	1.0000	1.0000	3.113		0.0
0.5951	0.1626	8.749	0.05143	3.7					
T/K = 333.15									
0.0000	0.0000	23.674		0.0	0.7496	0.2939	10.947	0.07138	−9.4
0.0904	0.0222	22.230	0.00700	42.8	0.8189	0.3871	9.401	0.07322	17.6
0.2040	0.0482	20.569	0.01653	−35.2	0.8641	0.4744	8.406	0.06981	−19.5
0.3144	0.0772	18.769	0.02482	26.9	0.9073	0.5865	7.362	0.06184	19.8
0.4549	0.1147	16.521	0.04368	−39.1	0.9437	0.7359	6.541	0.02529	−4.8
0.5810	0.1687	14.207	0.05581	53.9	0.9609	0.7874	6.145	0.03734	−3.7
0.6668	0.2220	12.662	0.06312	−29.3	1.0000	1.0000	5.268		−0.4

our new measurements. The comparisons are presented in Figures 1 and 2.

VLE. The results of measurements obtained for the equilibrium pressure (P/kPa), the temperature (T/K), and the mole fraction of component 1 in the liquid (x_1) and vapor (y_1) phases are listed in Table 2 and given in Figures 3 and 4. There are no literature data available for comparison.

Correlation

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

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

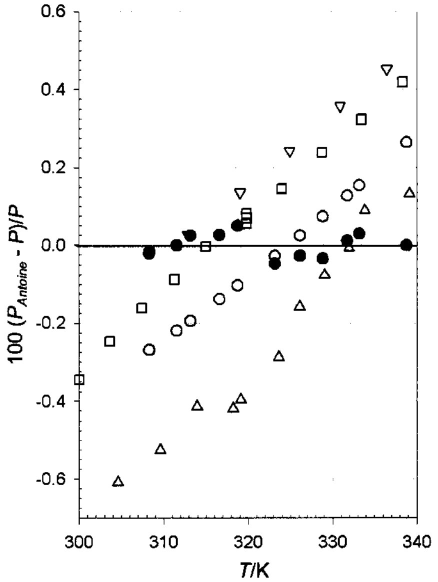

Figure 1. Deviation of measured propyl ether vapor pressure P from (●) the correlation with the Antoine equation; (○) the DIPPR recommendation (Daubert and Danner[5]); and measurements by (□) Ambrose et al.,[6] (△) Cidlinsky and Polak,[7] and (▽) Meyer and Hotz.[8]

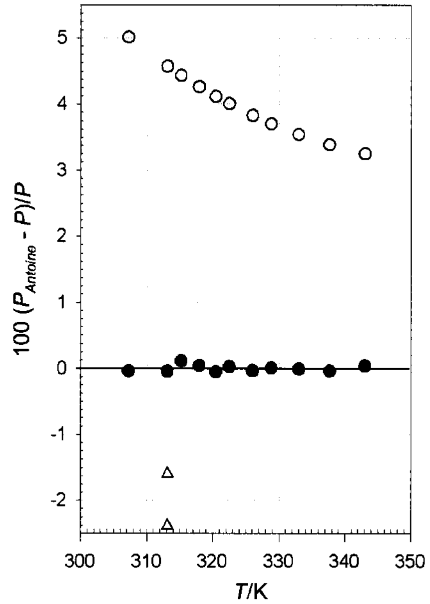

Figure 2. Deviation of measured valeraldehyde vapor pressure P from (●) the correlation with the Antoine equation; (○) the DIPPR recommendation (Daubert and Danner[5]); and measurements by (△) Kassmann and Knapp.[10]

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

The root-mean-square deviations (RMSDs) of a property (p or y_1) are calculated from the equation

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

$$\mathrm{RMSD}(p) = 100\sqrt{\frac{\sum_{i=1}^{n}((p_i^{\mathrm{calc}} - p_i^{\mathrm{exp}})/p_i^{\mathrm{exp}})^2}{n}} \tag{2}$$

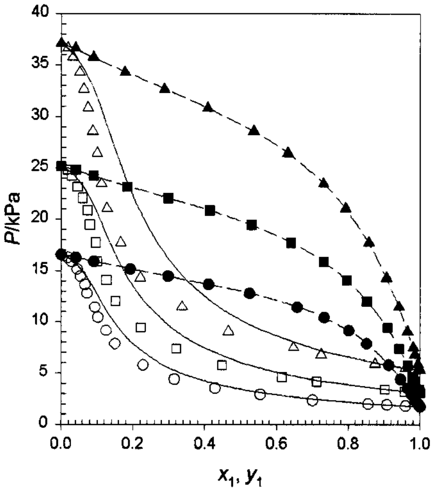

Figure 3. VLE at (●) 313.15 K, (■) 323.15 K, and (▲) 333.15 K for *2*-ethoxyethanol (1) + propyl ether (2); the lines represent the correlation with the SSF equation, solid symbols represent bubble points, and hollow symbols represent dew points.

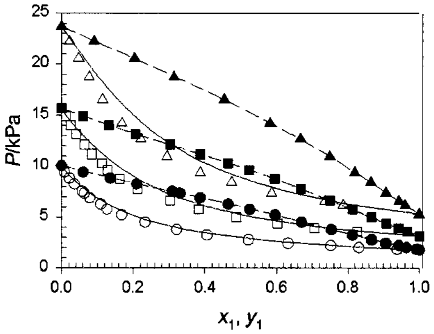

Figure 4. VLE at (●) 313.15 K, (■) 323.15 K, and (▲) 333.15 K for *2*-ethoxyethanol (1) + valeraldehyde (2); the lines represent the correlation with the Redlich−Kister equation, solid symbols represent bubble points, and hollow symbols represent dew points.

where n is the number of experimental points, p_i^{calc} is the property calculated at point number i, and p_i^{exp} is the property measured at point number i.

The correlation results are summarized in Table 3 and in Figures 1 and 2. The uncertainties of adjustable parameters have been calculated by means of a standard error propagation formula. The standard enthalpies of vaporization ($\Delta_{\mathrm{vap}}H°$) calculated for propyl ether from the vapor pressures measured in the course of this work show very small deviations from the values reported in the literature[13] and those obtained by calorimetric methods. The deviations are within the reported accuracy of calorimetric methods. For valeraldehyde, only estimated $\Delta_{\mathrm{vap}}H°$ values are available.[5] For these values, agreement is reasonable, as shown in Table 3.

VLE. The results of *PTxy* measurements, which are equilibrium pressure as a function of liquid- and vapor-phase compositions at constant temperature, were reduced to activity and fugacity coefficients. The Redlich−Kister equation with 2 to 4 adjustable parameters, the Wilson equation, the UNIQUAC equation, the NRTL equation with adjustable α, and the SSF[15] equation were used as activity coefficient models. Malanowski and Anderko[16] give the exact form of these equations. The fugacity coefficients of the components in the vapor phase were calculated from

$$\phi_i = \exp\left[\frac{(\nu_i^{\mathrm{L}} - \beta_i)(P - P_i^{\circ}) - P_i^{\circ}(1 - y_i)^2(\beta_1 + \beta_2)/2}{RT}\right] \tag{3}$$

Table 3. Correlation of Pure Components Vapor Pressure with the Antoine Equation

	propyl ether	valeraldehyde
temp range (K)	300−340	300−345
calc from data in Table 1		
A	6.064 302 32 ± 0.002 931 03	6.244 866 27 ± 0.003 856 63
B	1245.1863 ± 12.3768	1375.5194 ± 17.2399
C	56.1377 ± 1.3217	50.7370 ± 1.7197
errors		
RMSD(p)	0.029%	0.049%
RMSD(p)/Pa	19.8	20.6
	Enthalpy of Vaporization (kJ·mol^{-1}) at T/K = 298.15	
calc from Antoine eq	35.85	38.021
lit.	value (deviation)	value (deviation)
DIPPR[5] (calc)	36.689 (2.34%)	39.499 (3.89%)
Majer et al.[12] (calorimetric)	35.68 (−0.47%)	
Majer and Svoboda[13] (recommended)	35.79 ± 0.25% (−0.17%)	
Colomina et al.[14] (calc)	36.5 (1.81%)	

where virial coefficients β_i as functions of T were calculated from DIPPR data and the formula[5]

$$p/\mathrm{Pa} = \exp\left(A + \frac{B}{T} + C \ln T + DT^{E}\right) \qquad (4)$$

A, B, C, D, and E are recommended parameters.

The best VLE fit was obtained for the 2-ethoxyethanol + propyl ether mixture with an SSF equation with four adjustable parameters

$$\ln \gamma_1 = \sum_{i=1}^{2} x_2^2 A_i \frac{a_i + x_1(a_i - 1/a_i)}{(x_1/a_i + x_2 a_i)^3} \qquad (5)$$

$$\ln \gamma_2 = \sum_{i=1}^{2} x_1^2 A_i \frac{a_i + x_2(a_i - 1/a_i)}{(x_1/a_i + x_2 a_i)^3} \qquad (6)$$

and for 2-ethoxyethanol + valeraldehyde with a Redlich−Kister equation

$$\ln \gamma_1 = x_2^2[A_1 + A_2(3x_1 - x_2) + A_3(x_1 - x_2)(5x_1 - x_2)] \qquad (7)$$

$$\ln \gamma_2 = x_1^2[A_1 + A_2(x_1 - 3x_2) + A_3(x_1 - x_2)(x_1 - 5x_2)] \qquad (8)$$

where a_i and A_i are adjustable parameters.

The deviations of P and y_i obtained with these two equations are given in Table 2. Full results of the correlation are given in the Supporting Information. Introduction of association of 2-ethoxyethanol into the AEOS equation of state is contrary to previous experience[3,17] and produces worse results for mixture correlation. Some systematic deviations are observed in calculated values of y_1. These deviations are caused by the inability of the model to represent measured data.

Supporting Information Available:

Results of correlation of experimental data with various equations (24 pages PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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