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Density, Refractive Index, Speed of Sound, and Vapor−Liquid Equilibria for Binary Mixtures of Methanol + Ethyl Propionate and Vinyl Acetate + Ethyl Propionate

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Densities, refractive indices, and speeds of sound at 298.15 K, and isobaric vapor−liquid equilibria data at 101.3 kPa were reported for binary mixtures containing methanol + ethyl propionate and vinyl acetate + ethyl propionate. Excess molar volumes, refractive index deviations, and changes of speed of sound on mixing were calculated from the measured results and fitted to Redlich−Kister polynomials. VLE experimental data were tested for thermodynamic consistency by means of a modified Dechema test and were demonstrated to be consistent. The activity coefficients were correlated with the Margules, van Laar, UNIQUAC, NRTL, and Wilson equations with two suffixes and the Wilson model with three suffix equations. The ASOG model also was used for prediction. The methanol (1) + ethyl propionate (2) system shows an azeotrope at $x_1 = 0.984$.

Introduction

Polymerization of vinyl acetate in a methanol solution takes place by an incomplete reaction. The mixture contains mainly methanol and unreacted monomers of vinyl acetate. This process is only economical if the main compounds of the mixture, methanol and vinyl acetate, can be recovered at a high purity and recycled. The methanol + vinyl acetate system shows a minimum boiling point azeotrope at $T = 332.2$ K at the methanol mole fraction $x = 0.58$, as reported in a previous work.[1] A separation by simple distillation is impossible. Extractive distillation would be an attractive method for carrying out the separation of vinyl acetate from methanol if adequate entrainers could be found.

As a part of a continuing program of research, we have identified a selection of possible solvents. In previous works, we chose butanol,[1] 3-methyl-1-butanol,[2] butyl acetate and isobutyl acetate,[3] and pentyl acetate and isopentyl acetate[4] as entrainers for the extractive distillation to separate the azeotropic mixture. In this paper, we have selected ethyl propionate as an entrainer, and we have measured the vapor−liquid equilibria at 101.3 kPa of methanol + ethyl propionate and vinyl acetate + ethyl propionate systems. Experimental measurements of density, refractive index, speed of sound, and vapor−liquid equilibrium data for the binary mixtures of methanol + ethyl propionate and vinyl acetate + ethyl propionate have not been found in the literature.

Experimental Section

Materials. Methanol (99.8 mol %) was supplied by Panreac and was used without further purification. Vinyl acetate (≥99 mol %) and ethyl propionate (99 mol %) from Fluka were purified by distillation in a laboratory column of 100 plates; the purities of the materials were checked by gas liquid chromatography and were higher than 99.6 mol %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 3 Å from Fluka) before use. The densities, refractive indices, speeds of sound, and normal boiling points of the pure substances are given in Table 1 and compared with the literature values of Riddick et al.[5]

Apparatus and Procedure. The still used to measure VLE data was a dynamic recirculating apparatus described by Resa et al.[3] The equilibrium temperature was measured with a digital platinum 100 resistance thermometer with an accuracy of ±0.1 K. For the pressure measurement, a digital manometer regulator (Divatronic DT1 model), manufactured by Leybold, with an accuracy of ±0.1 kPa was used. Both vapor- and liquid-phase compositions for the two systems were determined by densimetry, refractometry, and speed of sound. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating tube densimeter with an accuracy of $\pm 0.000\,01$ g·cm^{-3}, that had been calibrated at atmospheric pressure with twice distilled water and dry air. The temperature of the densimeter was maintained at 298.15 K with a precision of ±0.01 K by means a semiconductor Peltier element and measured by a calibrated platinum resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an accuracy of ±0.000 01, and temperature was controlled as it was for the densimeter, with a temperature precision of ±0.01 K. Speeds of sound were measured with an Anton Paar DSA 48 sound analyzer with an accuracy of ±0.1 m·s^{-1}, and temperature was controlled with a Peltier cooler to a precision of ±0.1 K. Prior to measurements, density calibration, refractive index, and speed of sound curves for these systems were obtained to calculate the compositions of the vapor and liquid phases. The binary mixtures were prepared by directly weighing the constituent components with an electronic balance (Salter model ER-182A) with an accuracy of ±0.0001 g. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions. The estimated uncertainty in the determination of both liquid- and vapor-phase mole fractions is ±0.001.

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Table 1. Physical Properties of Pure Compounds: Densities, ρ, Refractive Indices, n_D, and Speeds of Sound, u, at 298.15 K, and Normal Boiling Points, T_b

	ρ/(g·cm^{-3})		n_D		u/(m·s^{-1})		T_b/K	
	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]
methanol	0.786 56	0.786 37	1.326 34	1.326 52	1101.8	not available	337.9	337.696
vinyl acetate	0.925 59	not available	1.392 53	1.393 4	1115.6	not available	346.0	345.7
ethyl propionate	0.884 16	0.884 0	1.381 37	1.381 4	1156.9	not available	371.7	372.25

[a] Riddick et al.[5]

Table 2. Densities, Refractive Indices, Speed Sounds, for Methanol (1) + Ethyl Propionate (2) and Vinyl Acetate (1) + Ethyl Propionate (2) at 298.15 K with Excess Molar Volume, V^E, Refractive Index Deviation, δn_D, and Speeds of Sound Deviation, δu

x_1	ρ g·cm^{-3}	V^E cm^3·mol^{-1}	n_D	δn_D	u m·s^{-1}	δu m·s^{-1}
Methanol (1) + Ethyl Propionate (2)						
0.034	0.882 98	−0.001	1.380 66	0.0012	1156.6	1.6
0.096	0.880 70	−0.006	1.379 47	0.0034	1155.5	3.9
0.152	0.878 54	−0.022	1.378 32	0.0053	1154.0	5.5
0.209	0.876 08	−0.028	1.377 01	0.0072	1152.1	6.7
0.268	0.873 37	−0.039	1.375 51	0.0089	1150.1	7.9
0.286	0.872 44	−0.040	1.374 65	0.0090	1149.4	8.3
0.326	0.870 33	−0.042	1.373 47	0.0101	1147.8	8.9
0.410	0.865 46	−0.051	1.371 00	0.0122	1144.4	10.1
0.448	0.862 99	−0.054	1.369 60	0.0129	1142.7	10.5
0.508	0.858 67	−0.053	1.367 27	0.0139	1139.9	11.0
0.544	0.855 82	−0.050	1.365 61	0.0142	1138.0	11.1
0.597	0.851 31	−0.052	1.363 04	0.0145	1135.3	11.3
0.639	0.847 27	−0.049	1.360 80	0.0146	1132.9	11.2
0.702	0.840 41	−0.038	1.356 94	0.0142	1129.0	10.8
0.759	0.833 26	−0.034	1.353 90	0.0141	1124.9	9.8
0.802	0.827 20	−0.032	1.349 36	0.0122	1121.6	8.9
0.858	0.818 22	−0.025	1.344 39	0.0102	1116.8	7.1
0.894	0.811 48	−0.019	1.340 52	0.0084	1113.4	5.7
0.951	0.799 21	−0.008	1.333 48	0.0045	1107.5	3.0
Vinyl Acetate (1) + Ethyl Propionate (2)						
0.048	0.885 73	0.004 90	1.381 83	−0.0001	1155.3	0.4
0.109	0.887 85	0.002 37	1.382 41	−0.0003	1153.1	0.7
0.153	0.889 45	−0.003 20	1.382 81	−0.0004	1151.4	0.8
0.214	0.891 66	−0.007 14	1.383 37	−0.0006	1149.2	1.1
0.261	0.893 42	−0.008 98	1.383 84	−0.0007	1147.4	1.3
0.298	0.894 83	−0.012 52	1.384 21	−0.0008	1146.0	1.4
0.358	0.897 11	−0.014 50	1.384 86	−0.0008	1143.6	1.5
0.397	0.898 63	−0.014 70	1.385 27	−0.0009	1142.1	1.6
0.450	0.900 73	−0.015 14	1.385 82	−0.0010	1140.0	1.7
0.497	0.902 65	−0.015 74	1.386 35	−0.0010	1138.1	1.7
0.554	0.905 00	−0.016 32	1.387 02	−0.0010	1135.7	1.7
0.608	0.907 30	−0.016 94	1.387 63	−0.0011	1133.4	1.6
0.646	0.908 96	−0.015 52	1.388 06	−0.0011	1131.7	1.5
0.707	0.911 63	−0.014 33	1.388 76	−0.0011	1129.1	1.4
0.745	0.913 35	−0.013 85	1.389 24	−0.0011	1127.4	1.3
0.806	0.916 17	−0.012 08	1.390 01	−0.0011	1124.7	1.1
0.854	0.918 42	−0.010 83	1.390 62	−0.0010	1122.5	0.9
0.898	0.920 54	−0.009 08	1.391 25	−0.0009	1120.5	0.7
0.954	0.923 31	−0.007 40	1.392 05	−0.0008	1117.8	0.3

Results and Discussion

Density, Refractive Index, and Speed of Sound. Table 2 lists the measured density, ρ, refractive index, n_D, and speed of sound, u, data at 298.15 K with the corresponding excess molar volume, V^E, refractive index deviation, δn_D, and speed of sound deviation, δu, for the binary mixtures of methanol + ethyl propionate and vinyl acetate + ethyl propionate.

The excess molar volumes of binary mixtures were calculated from density measurements by applying the equation

$$V^E = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \qquad (1)$$

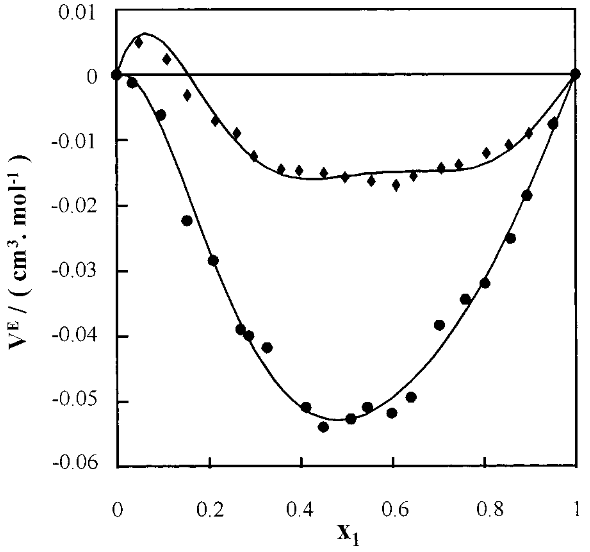

Figure 1. Excess molar volumes of mixtures of methanol (1) + ethyl propionate (2) (●) and vinyl acetate (1) + ethyl propionate (2) (◆). Redlich−Kister fit curves (—) at 298.15 K.

where ρ is the density of the mixture, ρ_1 and ρ_2 are the densities of the pure substances, M_1 and M_2 are the molar masses, and x_1 and x_2 are the mole fractions. The uncertainty in the calculation of V^E from density measurements was estimated to be ±0.001 cm^3·mol^{-1}. Figure 1 illustrates the excess molar volumes of the two binary systems at 298.15 K.

The changes of refractive index δn_D at 298.15 K from the linear additive value of the mole fraction are obtained by

$$\delta n_D = n_D - (x_1n_{D1} + x_2n_{D2}) \qquad (2)$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of the pure compounds. The plot of δn_D versus the mole fraction x_1 of the most volatile compound of each binary system is given in Figure 2.

In the same way, the changes of speed of sound on mixing were calculated by the equation

$$\delta u = u - (x_1u_1 + x_2u_2) \qquad (3)$$

where u is the speed of sound of the mixture and u_1 and u_2 are the speeds of sound of the pure compounds. The plot of δu versus the mole fraction x_1 of the more volatile compound of each binary system is given in Figure 3.

Excess molar volumes and changes of refractive index and speeds of sound on mixing of the binary systems were fitted to Redlich−Kister polynomials of the form

$$(V^E \text{ or } \delta_D \text{ or } \delta u) = x_1x_2\sum_{k\geq 0}a_k(x_1 - x_2)^k \qquad (4)$$

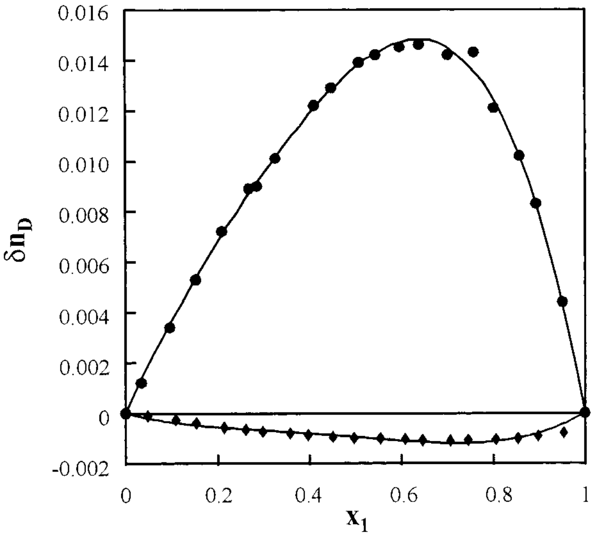

Figure 2. Change of refractive indices on mixing of methanol (1) + ethyl propionate (2) (●) and vinyl acetate (1) + ethyl propionate (2) (◆). Redlich–Kister fit curves (—) at 298.15 K.

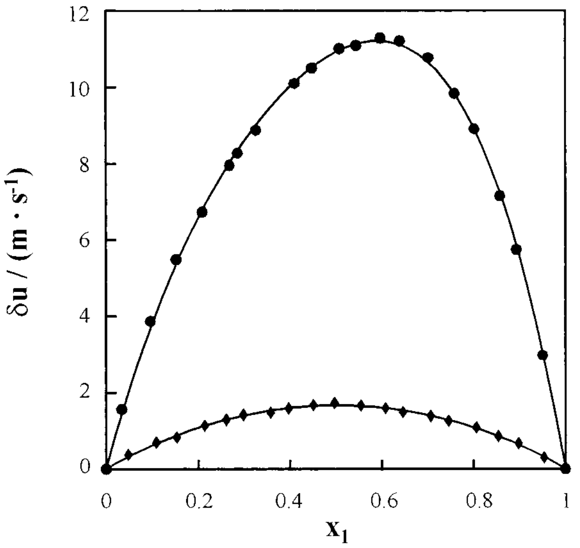

Figure 3. Change of speeds of sound on mixing of methanol (1) + ethyl propionate (2) (●) and vinyl acetate (1) + ethyl propionate (2) (◆). Redlich–Kister fit curves (—) at 298.15 K.

where a_k are the adjustable parameters obtained by a least-squares fit method, and k is the degree of the polynomial expansion. Table 3 lists the parameters with their standard deviations, σ. The coefficients a_k were used to calculate the solid curves; see Figures 1–3. The standard deviations, σ, are defined as follows

$$\sigma = \sqrt{\frac{\sum (Z_{\mathrm{cal}} - Z_{\mathrm{exp}})_i^2}{N - m}} \tag{5}$$

where N is the number of experimental data points, m is the number of equation parameters, and Z is the considered property (V^E or δn_D or δu).

VLE Data. Vapor–liquid equilibrium data (T, x_1, y_1) for the methanol (1) + ethyl propionate (2) and vinyl acetate (1) + ethyl propionate (2) binary systems at 101.3 kPa are presented in Table 4. The T–x_1–y_1 phase diagrams are shown in Figures 4 and 5.

Table 3. Adjustable Parameters, a_k, with the Standard Deviations, σ, for Excess Molar Volumes, V^E, Refractive Index Deviations, δn_D, and Speeds of Sound Deviations, δu

	V^E (cm^3·mol^{-1})	δn_D	δu (m·s^{-1})
	Methanol (1) + Ethyl Propionate (2)		
a_0	−0.2111	0.0547	43.7
a_1	−0.0209	−0.0295	−12.4
a_2	0.0484	0.0153	13.5
a_3	0.1253		
a_4	0.0910		
σ	0.0019	0.0002	0.09
	Vinyl Acetate (1) + Ethyl Propionate (2)		
a_0	−0.0623	−0.0038	6.7
a_1	−0.0173	0.0029	−0.1
a_2	−0.0538	−0.0041	0.4
a_3	0.1771		
a_4	0.1846		
σ	0.0020	0.0001	0.03

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^\circ} \tag{6}$$

$$\log(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) + C_i} \tag{7}$$

where x_i and y_i are the liquid- and vapor-phase mole fractions at equilibrium, Φ_i is a vapor-phase correction factor, P is the total pressure, and P_i° is the vapor pressure of pure component i. These vapor pressures were calculated from the Antoine equation
The constants A_i, B_i, and C_i are reported in Table 5, and their values were obtained from Riddick et al.[5]

The vapor-phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{\mathrm{sat}}} \exp\left[-\frac{V_i(P - P_i^\circ)}{RT}\right] \tag{8}$$

where ϕ_i is the fugacity coefficient of component i in the mixture, ϕ_i^{sat} is the fugacity coefficient at saturation, and V_i is the molar volume of component i in the liquid phase.

The fugacity coefficients for ϕ_1 and ϕ_2 were calculated by the expressions

$$\ln \phi_1 = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12}) \tag{9}$$

$$\ln \phi_2 = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \tag{10}$$

where P is the total pressure and T is the experimental temperature, y_1 and y_2 are the vapor-phase mole fractions of compounds 1 and 2, B_{11} and B_{22} are the second virial coefficients of pure compounds 1 and 2, and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, in which B_{12} is the second cross virial coefficient.

Pitzer's correlation for the second virial coefficient was extended to mixtures by Reid et al.[6] to calculate B_{12} with the Tsonopoulos[7] modification for polar molecules by

$$B_{12} = \frac{RT_{\mathrm{c12}}}{P_{\mathrm{c12}}}(B^\circ + \omega_{12}B^1 + aT_{\mathrm{r}}^{-6} - bT_{\mathrm{r}}^{-8}) \tag{11}$$

where a is the polarity parameter and b is the association parameter, T_{r} is the reduced temperature, and B° and B^1

Table 4. Vapor−Liquid Equilibrium Data for the Methanol (1) + Ethyl Propionate (2) and Vinyl Acetate (1) + Ethyl Propionate Systems: Liquid-Phase Mole Fraction, x_1, Vapor-Phase Mole Fraction, y_1, Boiling Temperature, T, Activity Coefficients, γ_1 and γ_2, Fugacity Coefficients, ϕ_1 and ϕ_2, and Fugacity Coefficients at Saturation, ϕ_1^s and ϕ_2^s, at 101.3 kPa

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
Methanol (1) + Ethyl Propionate (2)								
0.000	0.000	371.7			0.988	0.957	0.949	0.958
0.040	0.248	365.0	2.391	0.975	0.986	0.955	0.955	0.964
0.063	0.343	361.9	2.319	0.962	0.984	0.954	0.958	0.966
0.120	0.499	355.8	2.168	0.954	0.983	0.951	0.964	0.970
0.138	0.527	353.9	2.124	0.980	0.982	0.950	0.965	0.972
0.169	0.573	351.7	2.035	0.989	0.981	0.949	0.967	0.973
0.229	0.641	348.3	1.894	1.009	0.980	0.948	0.970	0.975
0.298	0.701	345.7	1.748	1.013	0.979	0.947	0.971	0.977
0.397	0.745	343.4	1.517	1.093	0.979	0.946	0.973	0.978
0.475	0.775	341.8	1.400	1.175	0.978	0.945	0.974	0.979
0.563	0.801	340.8	1.267	1.296	0.978	0.945	0.975	0.980
0.638	0.821	340.0	1.181	1.450	0.978	0.944	0.976	0.980
0.702	0.841	339.4	1.125	1.601	0.978	0.944	0.976	0.981
0.760	0.861	338.9	1.084	1.771	0.978	0.944	0.976	0.981
0.807	0.879	338.6	1.054	1.939	0.977	0.944	0.977	0.981
0.861	0.903	338.3	1.027	2.184	0.977	0.944	0.977	0.981
0.910	0.930	338.1	1.008	2.453	0.977	0.944	0.977	0.981
0.956	0.959	338.0	0.993	2.951	0.977	0.944	0.977	0.981
0.984	0.984	337.9	0.994	3.180	0.977	0.944	0.977	0.981
1.000	1.000	337.9			0.977	0.944	0.977	0.981
Vinyl Acetate (1) + Ethyl Propionate (2)								
0.000	0.000	371.7			0.973	0.957	0.935	0.958
0.033	0.061	370.6	0.844	1.019	0.973	0.957	0.937	0.959
0.069	0.133	369.4	0.911	1.013	0.972	0.956	0.938	0.960
0.138	0.256	367.2	0.934	1.004	0.972	0.956	0.941	0.962
0.174	0.315	366.0	0.944	1.000	0.971	0.955	0.942	0.963
0.244	0.418	364.0	0.947	0.989	0.970	0.954	0.945	0.964
0.280	0.466	362.9	0.951	0.986	0.970	0.954	0.946	0.965
0.323	0.521	361.6	0.959	0.981	0.969	0.953	0.947	0.966
0.379	0.587	360.0	0.966	0.971	0.969	0.953	0.949	0.967
0.454	0.663	357.9	0.972	0.965	0.968	0.952	0.951	0.969
0.547	0.746	355.6	0.974	0.946	0.967	0.951	0.954	0.971
0.597	0.785	354.4	0.975	0.937	0.967	0.950	0.955	0.971
0.645	0.819	353.3	0.976	0.929	0.966	0.950	0.956	0.972
0.707	0.860	351.9	0.977	0.913	0.966	0.949	0.957	0.973
0.742	0.881	351.1	0.979	0.906	0.966	0.949	0.958	0.974
0.819	0.923	349.4	0.982	0.887	0.965	0.948	0.959	0.975
0.862	0.944	348.6	0.979	0.870	0.965	0.948	0.960	0.975
0.906	0.964	347.8	0.978	0.845	0.964	0.947	0.961	0.976
0.958	0.985	346.9	0.972	0.813	0.964	0.947	0.962	0.976
1.000	1.000	346.0			0.964	0.947	0.963	0.977

are functions which depend exclusively on reduced temperature, which can be represented satisfactorily by

$$B^{\circ} = 0.083 - 0.422/T_r^{1.6} \tag{12}$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \tag{13}$$

The mixing rules proposed by Prausnitz[8] for the calculation of ω_{12}, T_{c12}, and P_{c12} are

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{14}$$

where ω_1 and ω_2 are the acentric factors of compounds 1 and 2, and

$$T_{c12} = (1 - k_{ij})(T_{c1}T_{c2})^{0.5} \tag{15}$$

where T_{c1} and T_{c2} are the critical temperatures of compounds 1 and 2, and k_{ij} is the binary interaction constant proposed by Lee and Chen;[9] for the alcohol + acetate mixtures, $k_{ij} = 0.08$.

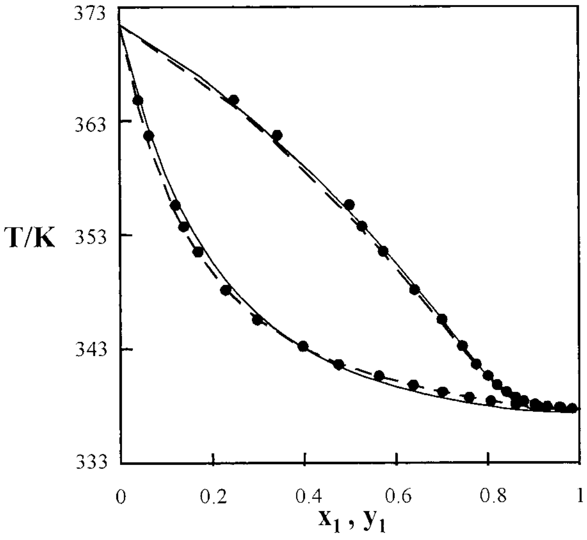

Figure 4. $T-x_1-y_1$ diagram for methanol (1) + ethyl propionate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

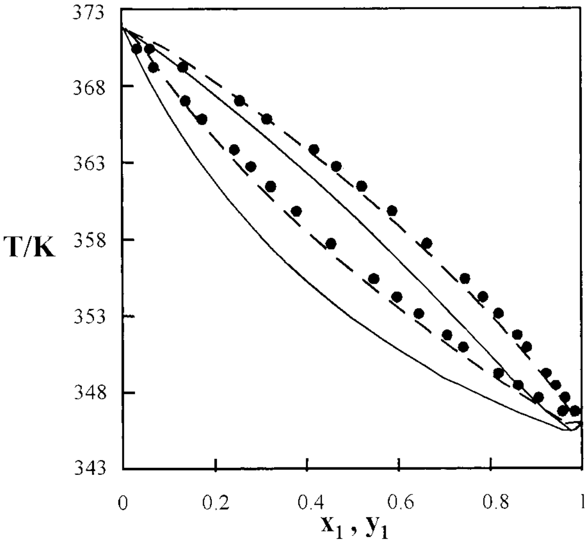

Figure 5. $T-x_1-y_1$ diagram for vinyl acetate (1) + ethyl propionate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

Table 5. Antoine Coefficients for Eq 7

compound	A_i	B_i	C_i
methanol	7.205 19	1581.993	−33.439
vinyl acetate	7.216	1798.4	0
ethyl propionate	6.134 869	1268.942	−64.849

Also,

$$P_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \tag{16}$$

where Z_{c12} is calculated by

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} \tag{17}$$

Z_{c1} and Z_{c2} are the critical compressibility factors, and V_{c12} is defined by the expression

$$V_{c12} = \left(\frac{V_{c1}^{1/3} + V_{c2}^{1/3}}{2}\right)^3 \tag{18}$$

Table 6. Published Parameters[10] Used for the Calculation of Fugacity Coefficients: Critical Temperature, T_c, Critical Pressure, Pc, Critical Volume, Vc, Critical Compression Factor, Z_c, and Acentric Factor, ω, of Pure Compounds

	T_c/K	$10^{-6}P_c$/Pa	V_c/m^3·kmol^{-1}	Z_c	ω
methanol	512.58	8.0959	0.117 80	0.224	0.5656
vinyl acetate	524.00	4.2500	0.270 00	0.263	0.3384
ethyl propionate	546.00	3.3620	0.345 00	0.256	0.3944

Table 7. Correlation Parameters for Activity Coefficients, and Average Deviations for the Studied Systems

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Methanol (1) + Ethyl Propionate (2)				
Margules[a]	0.9258	1.1905	0.13	0.0075
van Laar[a]	0.9491	1.1984	0.14	0.0073
Wilson[b] 2	4275.92	−582.79	0.14	0.0088
Wilson[b] 3 ($C = 1.56$)	3588.79	−1630.74	0.11	0.0094
NRTL[c] ($\alpha_{12} = 0.08$)	4898.38	−1485.42	0.12	0.0086
UNIQUAC[d]	−863.77	5014.74	0.14	0.0087
Vinyl Acetate (1) + Ethyl Propionate (2)				
Margules[a]	0.0358	−0.0389	0.11	0.0082
van Laar[a]	24.78	0.0057	0.14	0.0072
Wilson[b] 2	3655.21	−2623.54	0.10	0.0084
Wilson[b] 3 ($C = 0.65$)	4129.69	−2763.68	0.13	0.0078
NRTL[c] ($\alpha_{12} = 0.30$)	686.91	−657.95	0.13	0.0066
UNIQUAC[d]	1607.10	−1253.30	0.18	0.0056

[a] Margules and van Laar constants (dimensionless). [b] Wilson interaction parameters (J·mol^{-1}). [c] NRTL interaction parameters (J·mol^{-1}). [d] UNIQUAC interaction parameters (J·mol^{-1}).

where V_{c1} and V_{c2} are the critical volumes of compounds 1 and 2. Values of P_c, V_c, T_c, Z_c, and ω have been obtained from the literature[10] and are presented in Table 6.

The fugacity coefficients at saturation ϕ_1^{sat} and ϕ_2^{sat} were calculated by the expressions

$$\phi_1^{\text{sat}} = \exp \frac{B_{11}P_1^{\text{sat}}}{RT} \tag{19}$$

$$\phi_2^{\text{sat}} = \exp \frac{B_{22}P_2^{\text{sat}}}{RT} \tag{20}$$

The activity coefficients were correlated with the Margules,[11] van Laar,[12] Wilson,[13] NRTL,[14] and UNIQUAC[15] equations. To determine the constants of each model, we have used the method “VLE calc” suggested by Gess et al.[16] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function Q_i,[17] with the activity coefficients obtained from the consistency test as experimental values,

$$Q_i = \sum\left(\frac{\gamma_{\text{exp}} - \gamma_{\text{cal}}}{\gamma_{\text{exp}}}\right)^2 \tag{21}$$

where γ_{exp} are the activity coefficients calculated from experimental data and γ_{cal} are the coefficients calculated with the correlations. The parameters, the average deviation in T (ΔT), and the average deviation in y (Δy) are listed in Table 7. Also, the ASOG[18] method was used to obtain the predictions in Figures 4 and 5.

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test[19] where the fugacity coefficients are calculated by the method of Hayden and O’Connel,[20] and activity coefficients are calculated by using the four-suffix Margules equation,

Table 8. Results of the Thermodynamic Consistency Test

system	avg dev	A	B	D
methanol (1) + ethyl propionate (2)	0.0079	0.8723	1.142	−0.2237
vinyl acetate (1) + ethyl propionate (2)	0.0093	0.1024	0.0043	0.2305

Table 9. Results of the Margules Constant Test

system	Margules constant
methanol (1) + ethyl propionate (2)	1.0589
vinyl acetate (1) + ethyl propionate (2)	−0.0351

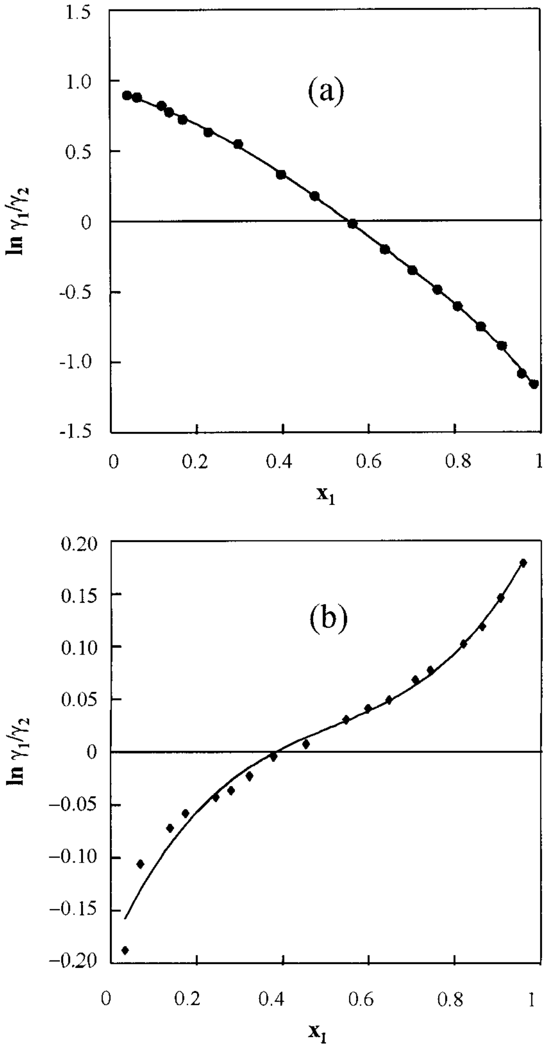

Figure 6. Herington test. ln γ_1/γ_2 versus x_1 for (a) methanol (1) + ethyl propionate (2) (●) and (b) vinyl acetate (1) + ethyl propionate (2) (◆).

$$\bar{g}^{E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \tag{22}$$

with the corresponding activity coefficients,

$$\ln \gamma_1 = x_2^2[A + 2(B - A - D)x_1 + 3Dx_1^2] \tag{23}$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B - D)x_2 + 3Dx_2^2] \tag{24}$$

The parameters A, B, and D were estimated using the error-in-variables regression maximum likelihood technique. The constraint equation for the regression was

$$F = P - \left(\frac{x_1\gamma_1{}^*f_1{}^\circ}{\phi_1} + \frac{x_2\gamma_2{}^*f_2{}^\circ}{\phi_2}\right) \tag{25}$$

Here the asterisk (*) denotes a calculated or predicted value. An experimental value has no asterisk; $f_1{}^\circ$ and $f_2{}^\circ$ are the standard state fugacities. The errors in the prediction of y_1 were calculated. Predicted $y_1{}^*$ values were obtained using the equation

$$y_1{}^* = \frac{x_1\gamma_1{}^*f_1{}^\circ}{\phi_1P^*} \tag{26}$$

An average deviation was calculated from

$$\text{average deviation} = \frac{\sum_{i=1}^{n}|\Delta y|}{n} \tag{27}$$

Here $\Delta y = y_1 - y_1{}^*$ and n = number of experimental data points. To pass the consistency test, a system must have an average deviation less than 0.01. The two systems included in this work have passed this consistency test. In Table 8, we show these results and the values for A, B, and D of eqs 22−24.

We also carried out the Margules constant test using the program of Gess et al.[16] The Margules constant can be used to indicate the ideality of a system. Systems which yield a Margules constant whose absolute value is less than 0.60 can be considered ideal, while those which yield an absolute value greater than 0.60 can be considered nonideal. This criterion for classification, however, is not rigorous. Table 9 shows the values of this constant.

Another useful thermodynamic consistency is that of Herington.[21] It is rather old, but it is based on fundamental principles and has been used with modifications. In Figure 6, the plot of ln γ_1/γ_2 versus x_1 for binary systems is shown. Both systems satisfy this test.

Conclusions

The binary system formed by methanol + ethyl propionate shows an azeotrope and nonideal behavior; the ASOG method prediction is in good agreement with experimental data. For the binary system vinyl acetate + ethyl propionate, the behavior is close to ideality and the ASOG prediction method is not adequate, as shown in Figure 5. The values of excess molar volumes are very close to zero, especially for the vinyl acetate + ethyl propionate system; similar behavior is observed for the changes of refractive index and speeds of sound on mixing.

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