Density, Refractive Index, Speed of Sound, and Vapor−Liquid Equilibria for Binary Mixtures of Methanol + Vinyl Propionate and Vinyl Acetate + Vinyl Propionate. Vapor Pressures of Vinyl 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 are reported for the binary mixtures containing methanol + vinyl propionate and vinyl acetate + vinyl propionate. Excess molar volumes, refractive index deviations, and changes of speeds of sound upon mixing were calculated from the measured data and fitted to Redlich−Kister polynomials. Vapor−liquid equilibrium (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) + vinyl propionate (2) system shows an azeotrope at $x_1 = 0.825$. Experimental vapor pressures of vinyl propionate are also included, and the Antoine constants were determined.

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 a methanol mole fraction of $x = 0.580$, 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] pentyl acetate and isopentyl acetate,[4] propyl acetate and isopropyl acetate,[5] allyl acetate,[6] ethyl propionate,[7] and ethyl butyrate[8] 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 the methanol + vinyl propionate and vinyl acetate + vinyl propionate systems. Experimental measurements of density, refractive index, speed of sound, and vapor−liquid equilibrium data for the binary mixtures of methanol + vinyl propionate and vinyl acetate + vinyl 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 vinyl 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.[9]

Apparatus and Procedure. The still used to measure vapor−liquid equilibrium (VLE) data was a dynamic recirculating apparatus described by Resa et al.[3] The equilibrium temperature was measured with a digital platinum 100 Ω 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 sound. Densities were measured at 298.15 K by using an Anton Paar DMA 58 vibrating tube densimeter with an accuracy of ±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 of 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 like 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 by 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

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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/(kg·m^{-3})		n_D		u/(m·s^{-1})		T_b/K	
	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]
methanol	786.56	786.37	1.326 34	1.32652	1101.8	not available	337.9	337.696
vinyl acetate	925.59	925.59[b]	1.392 53	1.39253[b]	1115.6	not available	346.0	345.7
vinyl propionate	909.69	not available	1.401 53	not available	1133.9	not available	368.1	364.35

[a] Riddick et al.[5] [b] Resa et al.[6]

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

	ρ	V^E			u	δu
x_1	kg·m^{-3}	(m^3·mol^{-1})·10^6	n_D	δn_D	m·s^{-1}	m·s^{-1}
		Methanol (1) + Vinyl Propionate (2)				
0.050	907.45	−0.011	1.400 22	0.0024	1132.9	0.6
0.101	905.00	−0.023	1.398 81	0.0048	1131.7	1.0
0.168	901.52	−0.042	1.396 80	0.0079	1130.2	1.7
0.198	899.81	−0.045	1.395 73	0.0091	1129.5	1.9
0.242	897.25	−0.057	1.394 16	0.0108	1128.4	2.2
0.311	892.66	−0.061	1.391 41	0.0133	1126.7	2.8
0.337	890.92	−0.070	1.390 39	0.0142	1126.0	2.9
0.390	886.94	−0.073	1.387 89	0.0157	1124.6	3.2
0.452	881.80	−0.080	1.384 74	0.0172	1122.8	3.4
0.526	874.78	−0.083	1.380 44	0.0185	1120.5	3.5
0.547	872.66	−0.083	1.379 11	0.0187	1119.8	3.4
0.597	867.20	−0.084	1.375 83	0.0192	1118.0	3.2
0.657	859.70	−0.084	1.371 15	0.0190	1115.9	3.0
0.708	852.65	−0.082	1.366 85	0.0185	1114.1	2.8
0.748	846.29	−0.077	1.362 83	0.0176	1112.6	2.6
0.800	837.26	−0.071	1.357 25	0.0159	1110.7	2.4
0.850	827.36	−0.064	1.35120	0.0136	1108.7	2.0
0.899	816.21	−0.060	1.344 44	0.0105	1106.5	1.4
0.949	803.01	−0.051	1.336 49	0.0063	1104.9	0.8
		Vinyl Acetate (1) + Vinyl Propionate (2)				
0.050	910.31	0.007	1.401 14	0.0000	1132.8	−0.2
0.102	911.01	0.009	1.400 70	0.0001	1131.8	−0.2
0.167	911.87	0.015	1.400 17	0.0001	1130.5	−0.3
0.207	912.40	0.020	1.399 86	0.0002	1129.7	−0.4
0.264	913.20	0.022	1.399 37	0.0002	1128.6	−0.5
0.297	913.66	0.025	1.399 06	0.0002	1128.0	−0.5
0.354	914.50	0.025	1.398 50	0.0002	1126.9	−0.5
0.403	915.25	0.025	1.398 17	0.0003	1126.0	−0.5
0.466	916.22	0.025	1.397 62	0.0003	1124.9	−0.5
0.504	916.80	0.026	1.397 30	0.0003	1124.2	−0.5
0.545	917.48	0.024	1.396 90	0.0003	1123.4	−0.5
0.601	918.39	0.023	1.396 40	0.0003	1122.4	−0.5
0.650	919.18	0.024	1.395 91	0.0002	1121.6	−0.4
0.696	919.96	0.022	1.395 54	0.0003	1120.8	−0.4
0.753	920.95	0.020	1.394 93	0.0002	1119.8	−0.3
0.800	921.79	0.018	1.394 56	0.0002	1119.0	−0.3
0.839	922.51	0.014	1.394 10	0.0001	1118.3	−0.2
0.901	923.67	0.009	1.393 58	0.0001	1117.2	−0.2
0.955	924.72	0.003	1.392 95	0.0000	1116.3	−0.1

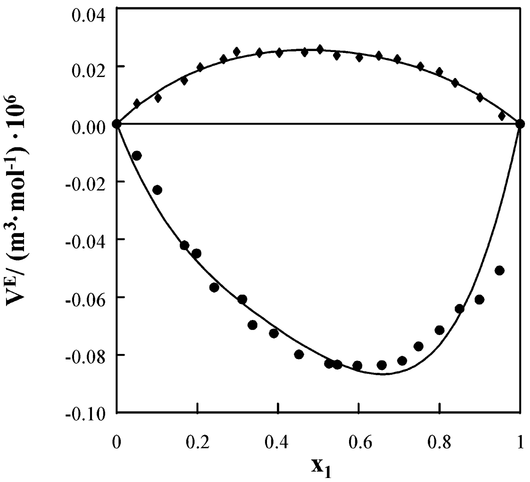

Figure 1. Excess molar volumes of mixtures of methanol (1) + vinyl propionate (2) (●) and vinyl acetate (1) + vinyl propionate (2) (◆). Redlich−Kister fit curves (—) at 298.15 K.

mixtures were prepared by directly weighing the constituent components with an electronic balance (Salter model ER-182A) that has 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.

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 sound deviation, δu, for the binary mixtures of methanol + vinyl propionate and vinyl acetate + vinyl propionate.

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

$$V^E = x_1 M_1(1/\rho - 1/\rho_1) + x_2 M_2(1/\rho - 1/\rho_2) \qquad (1)$$

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

$$\delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \qquad (2)$$

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 upon mixing were calculated by the equation

$$\delta u = u - (x_1 u_1 + x_2 u_2) \qquad (3)$$

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.

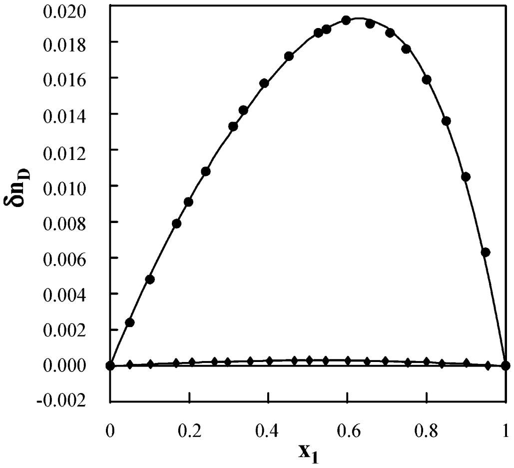

Figure 2. Change of refractive indices upon mixing of methanol (1) + vinyl propionate (2) (●) and vinyl acetate (1) + vinyl propionate (2) (◆). Redlich–Kister fit curves (—) at 298.15 K.

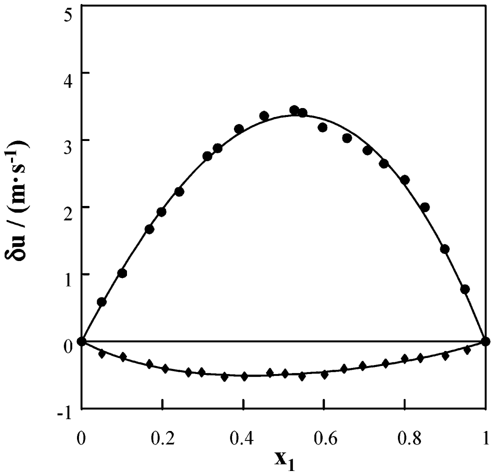

Figure 3. Change of speeds of sound upon mixing of methanol (1) + vinyl propionate (2) (●) and vinyl acetate (1) + vinyl propionate (2) (◆). Redlich–Kister fit curves (—) at 298.15 K.

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

	$V^E/(m^3\cdot mol^{-1})\cdot 10^6$	δn_D	$\delta u/(m\cdot s^{-1})$
	Methanol (1) + Vinyl Propionate (2)		
a_0	−0.3187	0.0723	13.4
a_1	0.1542	−0.0354	−1.9
a_2	−0.1951	0.0186	0.0
σ	0.0061	0.0002	0.07
	Vinyl Acetate (1) + Vinyl Propionate (2)		
a_0	0.1022	0.0012	−2.0
a_1	0.0088	−0.0001	−0.5
a_2	0.0206	−0.0003	−0.54
σ	0.0011	0.0001	0.03

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

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

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

Table 4. Experimental Vapor Pressures of Vinyl Propionate as a Funcion of Temperature

T/K	$P_{exptl}°$/kPa	$P_{calcd}°$/kPa	$P_{exptl}° - P_{calcd}°$
320.7	17.5	17.6	−0.1
325.3	21.5	21.4	0.1
329.4	25.5	25.4	0.1
333.0	29.5	29.4	0.1
336.3	33.5	33.5	0.0
339.3	37.5	37.6	−0.1
341.9	41.5	41.5	0.0
344.4	45.5	45.5	0.0
346.8	49.5	49.7	−0.2
348.9	53.5	53.6	−0.1
350.9	57.5	57.5	0.0
352.8	61.5	61.5	0.0
354.7	65.5	65.7	−0.2
356.3	69.5	69.3	0.2
358.0	73.5	73.4	0.1
359.6	77.5	77.4	0.1
361.1	81.5	81.4	0.1
362.6	85.5	85.5	0.0
364.0	89.5	89.4	0.1
365.4	93.5	93.5	0.0
366.7	97.5	97.5	0.0
368.0	101.3	101.5	−0.2

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

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

The activity coefficients, γ_i, of the components were calculated from

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

where x_i and y_i are the liquid and vapor 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

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

and the constants A_i, B_i, and C_i are reported in Table 6. The values of the Antoine constants for methanol and vinyl acetate were obtained from Riddck et al.[9] The corresponding values of vinyl propionate were determined from experimental vapor pressures using the same still used in the literature, and the calculated pressures in Table 4 were estimated by eq 7.

Table 4 shows experimental pressures as a function of temperature. The deviation that resulted was $\sigma = 0.13$, and

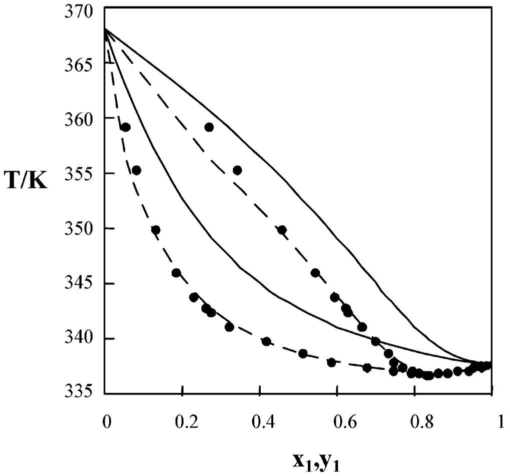

Figure 4. $T-x_1-y_1$ diagram for methanol (1) + vinyl propionate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; —, ASOG prediction.

Table 5. Vapor−Liquid Equilibrium Data for the Methanol (1) + Vinyl Propionate (2) and Vinyl Acetate (1) + Vinyl 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) + Vinyl Propionate (2)						
0.000	0.000	368.1						
0.054	0.270	359.2	2.326	1.012	0.983	0.958	0.961	0.968
0.082	0.343	355.3	2.218	1.065	0.982	0.956	0.964	0.971
0.132	0.458	349.9	2.219	1.115	0.981	0.954	0.969	0.974
0.185	0.544	346.0	2.162	1.144	0.980	0.953	0.972	0.977
0.230	0.594	343.8	2.058	1.167	0.979	0.952	0.973	0.978
0.262	0.623	342.8	1.966	1.172	0.979	0.951	0.974	0.979
0.275	0.629	342.4	1.919	1.191	0.979	0.951	0.974	0.979
0.322	0.665	341.1	1.819	1.206	0.978	0.950	0.975	0.980
0.418	0.700	339.8	1.549	1.320	0.978	0.950	0.976	0.980
0.512	0.733	338.7	1.381	1.460	0.978	0.949	0.976	0.981
0.586	0.747	337.9	1.268	1.680	0.977	0.949	0.977	0.981
0.678	0.770	337.4	1.151	2.001	0.977	0.949	0.977	0.981
0.746	0.795	337.1	1.093	2.287	0.977	0.949	0.977	0.982
0.792	0.812	336.9	1.060	1.581	0.977	0.944	0.978	0.982
0.839	0.832	336.7	1.033	3.002	0.977	0.944	0.978	0.982
0.886	0.862	336.9	1.005	3.457	0.977	0.944	0.978	0.982
0.941	0.912	337.1	0.994	4.229	0.977	0.944	0.977	0.981
0.974	0.953	337.4	0.992	5.069	0.977	0.950	0.977	0.981
0.986	0.972	337.6	0.992	5.567	0.977	0.950	0.977	0.981
1.000	1.000	337.9						
		Vinyl Acetate (1) + Vinyl Propionate (2)						
0.000	0.000	368.1						
0.058	0.068	366.9	0.595	1.021	0.971	0.961	0.941	0.962
0.085	0.100	366.1	0.612	1.040	0.971	0.961	0.942	0.963
0.110	0.132	365.4	0.637	1.053	0.971	0.960	0.943	0.963
0.150	0.203	364.2	0.744	1.050	0.970	0.960	0.944	0.964
0.220	0.318	362.3	0.841	1.039	0.970	0.959	0.947	0.966
0.295	0.450	360.1	0.969	0.994	0.969	0.958	0.949	0.967
0.328	0.495	359.3	0.962	0.982	0.969	0.958	0.950	0.968
0.359	0.536	358.5	0.975	0.971	0.968	0.958	0.951	0.969
0.405	0.586	357.4	0.977	0.971	0.968	0.957	0.952	0.969
0.502	0.679	355.2	0.979	0.963	0.967	0.956	0.954	0.971
0.530	0.705	354.7	0.978	0.953	0.967	0.956	0.955	0.971
0.594	0.758	353.3	0.981	0.948	0.966	0.956	0.956	0.972
0.779	0.885	349.8	0.977	0.932	0.965	0.954	0.959	0.974
0.828	0.915	348.9	0.978	0.913	0.965	0.954	0.960	0.975
0.868	0.940	348.2	0.981	0.861	0.965	0.954	0.960	0.975
0.910	0.965	347.4	0.986	0.757	0.964	0.953	0.962	0.976
0.971	0.991	346.4	0.981	0.626	0.964	0.953	0.962	0.976
1.000	1.000	346.1						

it was computed by using eq 8, where n is the number of experimental data points.

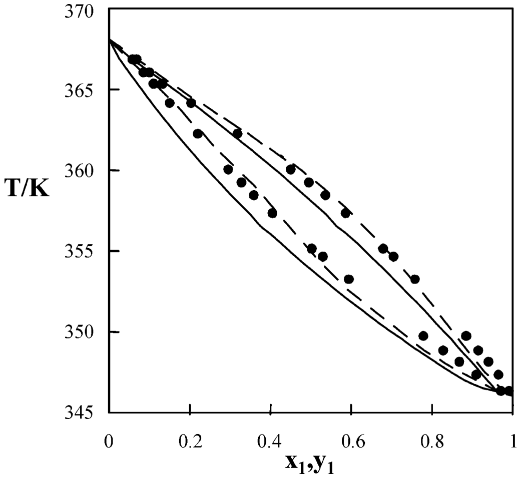

Figure 5. $T-x_1-y_1$ diagram for vinyl acetate (1) + vinyl propionate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; —, ASOG prediction.

Table 6. Antoine Coefficients for eq 7

compound	A_i	B_i	C_i
methanol[a]	7.20519	1581.993	−33.439
vinyl acetate[a]	7.216	1798.4	0
vinyl propionate[b]	6.1792	1278.2	−61.626

[a] Riddick et al.[5] [b] Calculated in this work.

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(P_{\text{exptl}}^{\circ} - P_{\text{calcd}}^{\circ})_i^2}{n}} \tag{8}$$

The vapor-phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{\text{sat}}} \exp\left[-\frac{V_i(P - P_i^{\circ})}{RT}\right] \tag{9}$$

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 activity coefficients were correlated with the Margules,[10] van Laar,[11] Wilson,[12] NRTL,[13] and UNIQUAC[14] equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[15] Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function Q_i,[16] with the activity coefficients obtained from the consistency test as experimental values

$$Q_i = \sum\left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}}\right)^2 \tag{10}$$

where γ_{exptl} are the activity coefficients calculated from experimental data and γ_{calcd} 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 8. Also, the ASOG[17] method was used to obtain predictions in Figures 4 and 5.

The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test[18] where the fugacity coefficients are calculated by the method of Hayden and O'Connell,[19] and activity coefficients are calculated by using the four-suffix Margules equation

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

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Methanol (1) + Vinyl Propionate (2)				
Margules[a]	0.9826	1.3728	0.38	0.0090
van Laar[a]	1.0290	1.3849	0.38	0.0090
Wilson[b] 2	4396.34	−157.64	0.38	0.0100
NRTL[c] (α_{12} = 0.10)	5531.40	−1601.21	0.36	0.0091
UNIQUAC[d]	−355.19	4193.56	0.55	0.0107
Vinyl Acetate (1) + Vinyl Propionate (2)				
Margules[a]	−0.7166	0.1225	0.64	0.0119
van Laar[a]	−7.6782	−0.1243	0.70	0.0140
Wilson[b] 2	2945.23	−3034.05	0.77	0.0183
NRTL[c] (α_{12} = 21.03)	−452.64	120.64	0.15	0.0104
UNIQUAC[d]	4165.77	−2505.31	0.75	0.0187

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

Table 8. Results of the Thermodynamic Consistency Test

system	avg dev	A	B	D
methanol (1) + vinyl propionate (2)	0.0081	0.8199	1.3070	−0.4542
vinyl acetate (1) + vinyl propionate (2)	0.0098	−1.1407	−0.3706	−2.1066

$$\bar{g}^{E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \qquad (11)$$

with the corresponding activity coefficients

$$\ln \gamma_1 = x_2^{\,2}[A + 2(B - A - D)x_1 + 3Dx_1^{\,2}] \qquad (12)$$

$$\ln \gamma_2 = x_1^{\,2}[B + 2(A - B - D)x_2 + 3Dx_2^{\,2}] \qquad (13)$$

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

$$F = P - \left(\frac{x_1\gamma_1{}^{*}f_1{}^{\circ}}{\phi_1} + \frac{x_2\gamma_2{}^{*}f_2{}^{\circ}}{\phi_2}\right) \qquad (14)$$

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

$$y_1{}^{*} = \frac{x_1\gamma_1{}^{*}f_1{}^{\circ}}{\phi_1P^{*}} \qquad (15)$$

An average deviation was calculated from

$$\text{average deviation} = \frac{\sum_{i=1}^{n}|\Delta y|}{n} \qquad (16)$$

Here, $\Delta y = y_1 - y_1{}^{*}$ and n is the number of experimental data points. To pass the consistency test, a system must have an average deviation of <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 11−13.

We also carried out the Margules constant test using the program of Gess et al.[15] The Margules constant can be used to indicate the ideality of a system. Systems which yield a Margules constant whose absolute value is <0.60 can be considered ideal, while those which yield an absolute value >0.60 can be considered nonideal. This criterion for classification, however, is not rigorous. Table 9 shows the values of this constant.

Table 9. Results of the Margules Constant Test

system	Margules constant
methanol (1) + vinyl propionate (2)	1.1892
vinyl acetate (1) + vinyl propionate (2)	−0.3618

Conclusions

New vapor−liquid equilibria data not previously reported in the literature have been measured. The binary system formed by methanol + vinyl propionate shows an azeotrope and nonideal behavior, and the ASOG method prediction is not adequate, as shown in Figure 4. For the binary system vinyl acetate + vinyl propionate, the behavior is close to ideality and the ASOG prediction method shows poor agreement with experimental data, as shown in Figure 5. The values of excess molar volumes are very close to zero, especially for the vinyl acetate + vinyl propionate system. In other studied properties, this last mixture shows also small deviations. The vinyl propionate is inappropriate because the methanol + vinyl propionate system shows an azeotrope.

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