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Vapor−Liquid Equilibrium of Binary Mixtures Containing Methanol + Propyl Acetate, Methanol + Isopropyl Acetate, Vinyl Acetate + Propyl Acetate, and Vinyl Acetate + Isopropyl Acetate at 101.3 kPa

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Isobaric vapor−liquid equilibria were determined at 101.3 kPa for the binary mixtures containing methanol + propyl acetate, methanol + isopropyl acetate, vinyl acetate + propyl acetate, and vinyl acetate + isopropyl acetate. The thermodynamic consistency of the experimental data was checked by means of a modified Dechema test and was satisfactory. The activity coefficients were correlated with the Margules, van Laar, Wilson, and NRTL models and the Wilson model with two suffix equations and the Wilson model with three suffix equations. The ASOG model was also used for prediction. The methanol (1) + propyl acetate (2) and methanol (1) + isopropyl acetate (2) systems show azeotropes at $x_1 = 0.922$ and $x_1 = 0.890$, respectively. Densities, excess molar volumes, refractive indices, and changes of refractive index on mixing of these mixtures were measured at 298.15 K and fitted to Redlich−Kister polynomials.

Introduction

The 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 with 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 by (Resa et al.[1]). Its 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 part of a continuing program of research, we have identified a selection of possible solvents. In previous works, we chose butanol (Resa et al.[1]), 3-methyl-1-butanol (Resa et al.[2]), butyl acetate, and isobutyl acetate (Resa et al.[3]) as entrainers for the extractive distillation to separate the azeotropic mixture. In this paper we have selected propyl acetate and isoproyl acetate as entrainers, and we have measured the vapor−liquid equilibria at 101.3 kPa of methanol + propyl acetate, methanol + isoproyl acetate, vinyl acetate + propyl acetate, and vinyl acetate + isopropyl acetate. VLE data of the mixture methanol + propyl acetate were previously reported by Grishunin et al.,[4] and a comparison with the experimental data obtained for this work has been carried out. Data for the other studied systems were not found in the literature.

Experimental Section

Methanol (99.8 mol %) was supplied by Panreac, and isopropyl acetate (>99.5 mol %) from Fluka; both were used without further purification. Propyl acetate (99 mol %) from Aldrich and vinyl acetate (>99 mol %) from Fluka were purified by distillation in a laboratory column of 100 plates; the purity of the materials was checked by gas liquid chromatography and was higher than 99.7 mol %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 3 Å from Fluka) before use. Densities, refractive indexes, and normal boiling points of the pure substances are given in Table 1 and compared with the literature values of Riddick et al.[5]

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

	ρ/kg·m^{-3}		n_D		T_b/K	
	obs	lit.[a]	obs	lit.[a]	obs	lit.[a]
methanol	786.56	786.37	1.326 34	1.32652	337.9	337.696
vinyl acetate	925.59	not available	1.392 53	1.3934	346.0	345.7
propyl acetate	881.99	883.03	1.392 53	1.3828	374.4	374.686
isopropyl acetate	866.18	870.2	1.374 57	1.375	361.9	361.751

[a] Riddick et al.[4]

The still used to measure VLE data was a dynamic recirculating one 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 four systems were determined by densimetry and refractometry. Densities were measured using an Anton Paar vibrating tube densimeter, at T = 298.15 K, 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 the cell sensor of ±0.01 K by means a semiconductor Peltier element and was measured by a calibrated platinum resistance thermometer. Refractive indexes were measured with a Mettler RE50 refractometer, accuracy ±0.000 01, and temperature control by the Peltier effect (as for the densimeter), with a temperature precision of ±0.01 K. Prior to this, density-calibration and refractive index curves for these systems were obtained to calculate the compositions of the vapor

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Table 2. Densities and Refractive Indexes of Methanol (1) + Propyl Acetate (2), Methanol + Isopropyl Acetate (2), Vinyl Acetate (1) + Propyl Acetate (2), and Vinyl Acetate (1) + Isopropyl Acetate (2) Mixtures as a Function of the Mole Fraction (x_1) of Compound 1 at 298.15 K

x_1	ρ/kg·m^{-3}	n_D	x_1	ρ/kg·m^{-3}	n_D	x_1	ρ/kg·m^{-3}	n_D
			Methanol (1) + Propyl Acetate (2)					
0.000	881.99	1.381 68	0.379	865.67	1.372 45	0.700	839.67	1.357 41
0.057	880.05	1.380 57	0.399	864.54	1.371 79	0.754	833.06	1.353 58
0.090	878.94	1.379 92	0.456	860.93	1.369 66	0.800	826.81	1.349 91
0.128	877.53	1.379 11	0.503	857.64	1.367 93	0.841	820.40	1.346 12
0.196	874.49	1.377 56	0.552	853.86	1.365 68	0.901	809.57	1.339 98
0.231	873.26	1.376 80	0.606	849.21	1.363 12	0.947	799.96	1.334 15
0.276	871.14	1.375 61	0.651	844.94	1.360 41	1.000	786.56	1.326 34
			Methanol (1) + Isopropyl Acetate (2)					
0.000	866.18	1.374 57	0.369	853.53	1.367 19	0.701	831.48	1.353 81
0.052	864.79	1.373 84	0.404	851.87	1.366 16	0.765	824.87	1.349 75
0.118	862.90	1.372 67	0.468	848.51	1.364 17	0.794	821.55	1.347 73
0.153	861.80	1.372 10	0.485	847.51	1.363 50	0.849	814.37	1.343 33
0.203	860.14	1.371 11	0.558	842.95	1.360 72	0.894	807.47	1.339 12
0.250	858.45	1.370 12	0.594	840.39	1.359 18	0.944	798.64	1.333 70
0.309	856.17	1.368 75	0.646	836.38	1.356 80	1.000	786.56	1.326 34
			Vinyl Acetate (1) + Propyl Acetate (2)					
0.000	881.99	1.381 68	0.351	895.25	1.384 95	0.704	910.65	1.388 80
0.041	883.45	1.382 06	0.406	897.46	1.385 53	0.748	912.72	1.389 35
0.101	885.64	1.382 59	0.451	899.34	1.386 01	0.800	915.28	1.389 96
0.160	887.82	1.383 10	0.503	901.58	1.386 54	0.857	918.12	1.390 68
0.213	889.83	1.383 60	0.558	903.98	1.387 12	0.904	920.52	1.391 29
0.243	890.99	1.383 87	0.602	905.92	1.387 60	0.942	922.53	1.391 75
0.300	893.19	1.384 43	0.655	908.37	1.388 20	1.000	925.59	1.392 53
			Vinyl Acetate (1) + Isopropyl Acetate (2)					
0.000	866.18	1.374 57	0.354	884.06	1.380 04	0.702	904.69	1.386 26
0.049	868.58	1.375 33	0.405	886.85	1.380 90	0.745	907.55	1.387 08
0.093	870.69	1.375 99	0.448	889.29	1.381 66	0.797	910.98	1.388 16
0.157	873.81	1.376 96	0.501	892.32	1.382 58	0.852	914.83	1.389 33
0.201	875.98	1.377 64	0.561	895.90	1.383 58	0.901	918.31	1.390 36
0.248	878.43	1.378 34	0.586	897.40	1.383 95	0.952	922.05	1.391 50
0.307	881.50	1.379 30	0.649	901.29	1.385 27	1.000	925.59	1.392 53

Table 3. Antoine Coefficients, Eq 2

compound	A_i	B_i	C_i
methanol	7.205 19	1581.993	−33.439
vinyl acetate	7.216	1798.4	0
propyl acetate	6.143 62	1284.080	−64.364
isopropyl acetate	6.129 33	1237.232	−61.714

Table 4. Published Parameters[8] Used To Calculate Fugacity Coefficients: Critical Temperature T_c, Critical Pressure P_c, Critical Volume V_c, 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
propyl acetate	549.40	3.3600	0.345 00	0.254	0.3935
isopropyl acetate	538.00	3.5800	0.336 00	0.269	0.3550

and liquid phases. All samples were prepared by weighing with a SALTER electronic balance (model ER-182A) with an accuracy of ±0.0001 g. The estimated uncertainty in the determination of both liquid- and vapor-phase mole fractions is ±0.001. Table 2 shows the density and refractive index−composition values.

Results and Discussion

The activity coefficients γ_i of the components were calculated from

$$\gamma_i = \frac{y_i \Phi_i P}{x_i P_i^\circ} \tag{1}$$

where x_i and y_i are the liquid- and vapor-phase mole fractions in equilibrium, Φ_i is the 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

$$\log(P/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{2}$$

The constants A_i, B_i, and C_i are reported in Table 3, and their values were obtained from Riddick et al.[5]

The vapor-phase correction factor is given by

$$\Phi_i = \frac{\phi_i}{\phi_i^{\text{sat}}} \exp\left[-\frac{V_i(P - P_i^\circ)}{RT}\right] \tag{3}$$

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

$$\ln \phi_1 = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12}) \tag{4}$$

$$\ln \phi_2 = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \tag{5}$$

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 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

$$B_{12} = \frac{RT_{c_{12}}}{P_{c_{12}}}(B^\circ + \omega_{12}B^1 + aT_r^{-6} - bT_r^{-8}) \tag{6}$$

where a is the polarity parameter and b is the association parameter, T_r is the reduced temperature, and B° and B^1 are functions which depend exclusively on reduced temperature and can be represented satisfactorily by

$$B^\circ = 0.083 - 0.422/T_r^{1.6} \tag{7}$$

Table 5. Vapor−Liquid Equilibrium Data for the Methanol (1) + Propyl Acetate (2), Methanol (1) + Isopropyl Acetate (2), Vinyl Acetate (1) + Propyl Acetate (2), and Vinyl Acetate (1) + Isopropyl Acetate (2) Systems: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Boiling Temperature T, Activity Coefficients γ_1 and γ_2, and Fugacity Coefficients ϕ_1 and ϕ_2 at 101.3 kPa

x_1	y_1	T/K	γ_1	ϕ_1	γ_2	ϕ_2	x_1	y_1	T/K	γ_1	ϕ_1	γ_2	ϕ_2
Methanol (1) + Propyl Acetate (2)													
0.000	0.000	374.4					0.505	0.783	343.3	1.214	0.970	1.213	0.950
0.022	0.163	370.3	2.300	0.987	0.939	0.956	0.575	0.806	342.2	1.143	0.969	1.316	0.951
0.053	0.308	365.2	2.090	0.984	0.943	0.954	0.650	0.835	341.0	1.096	0.968	1.423	0.951
0.096	0.439	360.2	1.932	0.981	0.944	0.953	0.709	0.849	340.2	1.053	0.968	1.615	0.951
0.121	0.492	357.9	1.894	0.980	0.949	0.952	0.771	0.872	339.1	1.037	0.967	1.815	0.951
0.141	0.528	355.9	1.867	0.979	0.966	0.952	0.826	0.886	338.3	1.014	0.966	2.194	0.952
0.183	0.583	352.4	1.795	0.977	1.014	0.951	0.881	0.919	337.7	1.011	0.965	2.334	0.953
0.260	0.662	347.9	1.686	0.974	1.066	0.950	0.922	0.924	337.6	0.973	0.965	3.354	0.953
0.323	0.698	345.8	1.542	0.972	1.124	0.950	0.964	0.960	337.7	0.963	0.965	3.812	0.954
0.442	0.757	344.2	1.297	0.971	1.165	0.950	1.000	1.000	337.9				
Methanol (1) + Propyl Acetate (2) (Grishunin et al.[4])													
0.076	0.340	362.3					0.594	0.839	341.3				
0.283	0.685	348.7					0.701	0.872	339.9				
0.385	0.768	345.2					0.805	0.899	338.9				
0.485	0.809	343.0					0.906	0.936	338.1				
Methanol (1) + Isopropyl Acetate (2)													
0.000	0.000	361.9					0.539	0.716	339.6	1.196	0.968	1.250	0.950
0.065	0.257	354.7	2.061	0.980	0.956	0.956	0.602	0.748	338.9	1.148	0.967	1.318	0.950
0.077	0.290	353.7	2.033	0.980	0.957	0.956	0.665	0.779	338.3	1.109	0.967	1.404	0.950
0.121	0.381	350.3	1.915	0.977	0.981	0.955	0.726	0.802	337.8	1.065	0.966	1.567	0.950
0.144	0.417	349.1	1.837	0.976	0.989	0.954	0.787	0.829	337.4	1.031	0.966	1.767	0.950
0.206	0.496	346.2	1.697	0.974	1.018	0.953	0.845	0.862	337.2	1.005	0.965	1.974	0.950
0.270	0.557	344.3	1.589	0.972	1.040	0.952	0.890	0.890	337.1	0.990	0.965	2.226	0.950
0.317	0.590	343.1	1.469	0.971	1.074	0.952	0.940	0.930	337.3	0.972	0.965	2.578	0.950
0.354	0.615	342.5	1.402	0.971	1.089	0.951	0.978	0.970	337.6	0.963	0.965	2.980	0.950
0.410	0.652	341.3	1.344	0.970	1.125	0.951	1.000	1.000	337.9				
0.475	0.683	340.3	1.261	0.969	1.194	0.950							
Vinyl Acetate (1) + Propyl Acetate (2)													
0.000	0.000	374.4					0.518	0.732	356.6	0.926	0.968	0.947	0.950
0.029	0.054	373.1	0.732	0.974	0.970	0.957	0.553	0.761	355.7	0.932	0.967	0.943	0.950
0.066	0.130	371.7	0.808	0.973	0.968	0.956	0.587	0.787	354.8	0.935	0.967	0.939	0.949
0.122	0.235	369.6	0.842	0.972	0.968	0.956	0.626	0.815	353.8	0.938	0.967	0.932	0.949
0.162	0.307	368.0	0.869	0.972	0.967	0.955	0.667	0.842	352.8	0.940	0.966	0.927	0.949
0.192	0.357	366.8	0.885	0.971	0.967	0.954	0.713	0.871	351.8	0.941	0.966	0.910	0.948
0.219	0.399	366.0	0.889	0.971	0.959	0.954	0.827	0.932	349.4	0.941	0.965	0.868	0.947
0.287	0.493	363.7	0.900	0.970	0.956	0.953	0.891	0.961	348.1	0.942	0.965	0.828	0.947
0.368	0.590	361.0	0.915	0.969	0.954	0.952	0.930	0.977	347.3	0.943	0.964	0.783	0.946
0.424	0.648	359.3	0.921	0.969	0.952	0.951	1.000	1.000	345.7				
0.488	0.706	357.5	0.924	0.968	0.951	0.951							
Vinyl Acetate (1) + Isopropyl Acetate (2)													
0.000	0.000	361.9					0.477	0.610	353.4	0.968	0.967	0.980	0.956
0.038	0.060	361.2	0.929	0.969	0.996	0.959	0.527	0.657	352.6	0.969	0.966	0.979	0.956
0.053	0.084	360.9	0.941	0.969	0.995	0.959	0.596	0.719	351.6	0.970	0.966	0.972	0.955
0.100	0.156	360.0	0.953	0.969	0.993	0.959	0.670	0.779	350.5	0.970	0.965	0.971	0.955
0.120	0.185	359.6	0.954	0.969	0.993	0.958	0.713	0.812	349.9	0.970	0.965	0.970	0.955
0.171	0.257	358.6	0.961	0.968	0.993	0.958	0.779	0.861	349.0	0.971	0.965	0.960	0.954
0.197	0.292	358.1	0.962	0.968	0.992	0.958	0.854	0.912	348.0	0.971	0.965	0.953	0.954
0.229	0.334	357.6	0.963	0.968	0.989	0.958	0.881	0.930	347.6	0.972	0.964	0.943	0.954
0.278	0.394	356.7	0.963	0.968	0.989	0.957	0.911	0.949	347.2	0.973	0.964	0.931	0.953
0.312	0.434	356.1	0.964	0.968	0.989	0.957	0.941	0.968	346.8	0.974	0.964	0.894	0.953
0.367	0.496	355.2	0.965	0.967	0.986	0.957	1.000	1.000	345.7				
0.439	0.572	354.0	0.967	0.967	0.983	0.956							

$$B^1 = 0.139 - 0.172/T_r^{4.2} \tag{8}$$

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

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{9}$$

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

$$T_{c_{12}} = (1 - k_{ij})(T_{c1}T_{c2})^{0.5} \tag{10}$$

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, $k_{ij} = 0.08$.

Also,

$$P_{c_{12}} = \frac{Z_{c_{12}}RT_{c_{12}}}{V_{c_{12}}} \tag{11}$$

where $Z_{c_{12}}$ is calculated by

$$Z_{c_{12}} = \frac{Z_{c1} + Z_{c2}}{2} \tag{12}$$

Z_{c1} and Z_{c2} are the critical compressibility factors, and $V_{c_{12}}$ is defined by the expression

$$V_{c_{12}} = \left(\frac{{V_{c1}}^{1/3} + {V_{c2}}^{1/3}}{2}\right)^3 \tag{13}$$

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 (Daubert and Danner[10]), and are presented in Table 4.

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

$$\phi_1^{sat} = \exp\frac{B_{11}P_1^{sat}}{RT} \tag{14}$$

$$\phi_2^{sat} = \exp\frac{B_{22}P_2^{sat}}{RT} \tag{15}$$

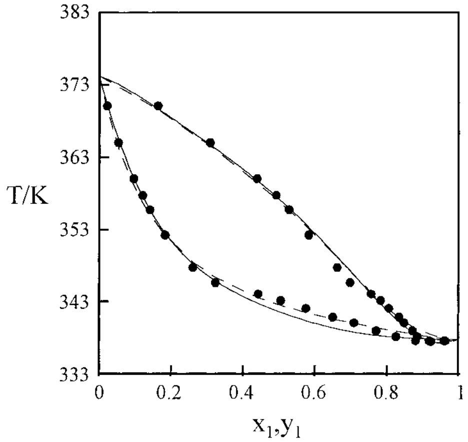

Figure 1. $T-x_1-y_1$ diagram for methanol (1) + propyl acetate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

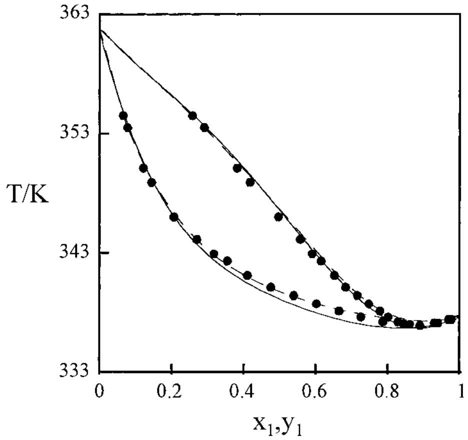

Figure 2. $T-x_1-y_1$ diagram for methanol (1) + isopropyl acetate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

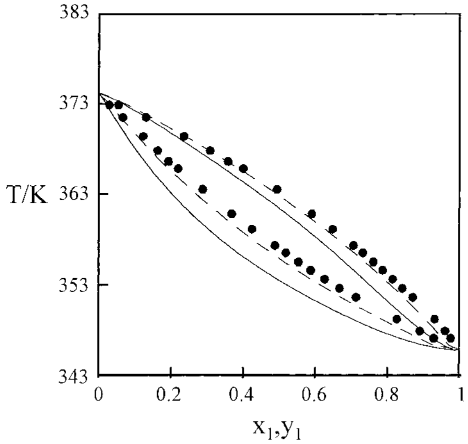

Figure 3. $T-x_1-y_1$ diagram for vinyl acetate (1) + propyl acetate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

The vapor–liquid equilibrium data for the four systems have been obtained at 101.3 kPa and are presented in Table 5 with an accuracy in the mole fractions of ±0.001. The $T-x_1-y_1$ diagrams are shown in Figures 1–4.

The activity coefficients were correlated with the Margules,[11] van Laar,[12] Wilson,[13] NRTL (Renon and Prausnitz[14]), and UNIQUAC (Abrams and Prausnitz[15]) equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[16]

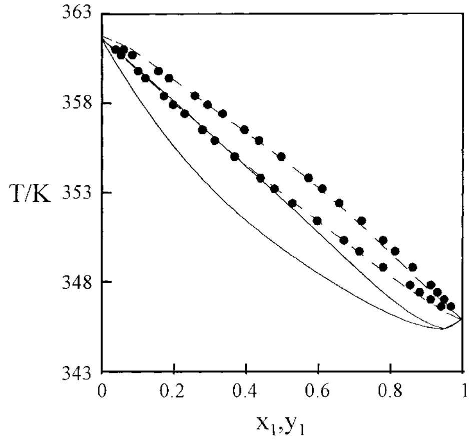

Figure 4. $T-x_1-y_1$ diagram for vinyl acetate (1) + isopropyl acetate (2) at 101.3 kPa: (●) experimental data; (- - -) Wilson correlation; (—) ASOG prediction.

Table 6. Correlation Parameters for Activity Coefficients, and Average Deviation for Studied Systems

equation	A_{12}	A_{21}	ΔT/K	Δy_1
Methanol (1) + Propyl Acetate (2)				
Margules[a]	0.8805	1.0791	0.46	0.0058
van Laar[a]	0.8829	1.0943	0.46	0.0059
Wilson[b] 2	4186.75	−821.35	0.43	0.0057
Wilson[b] 3 (C = 0.4818)	6694.00	2641.42	0.50	0.0052
NRTL[c] (α_{12} = 0.91)	2401.75	1765.95	0.52	0.0044
UNIQUAC[d]	−938.74	4914.54	0.41	0.0066
Methanol (1) + Isopropyl Acetate (2)				
Margules[a]	0.8076	1.0702	0.18	0.0054
van Laar[a]	0.8147	1.0986	0.17	0.0051
Wilson[b] 2	3841.44	−616.05	0.17	0.0046
Wilson[b] 3 (C = −2.75)	178.21	655.51	0.25	0.0076
NRTL[c] (α_{12} = 1.03)	2525.75	1767.46	0.10	0.0014
UNIQUAC[d]	−1027.46	5319.32	0.17	0.0047
Vinyl Acetate (1) + Propyl Acetate (2)				
Margules[a]	0.0200	0.0305	0.08	0.0082
van Laar[a]	148.79	0.0118	0.09	0.0087
Wilson[b] 2	−257.61	539.71	0.08	0.0080
Wilson[b] 3 (C = 0.98)	−279.11	546.41	0.08	0.0080
NRTL[c] (α_{12} = 0.32)	1720.41	−1383.91	0.08	0.0078
UNIQUAC[d]	1655.52	−1256.88	0.10	0.0060
Vinyl Acetate (1) + Isopropyl Acetate (2)				
Margules[a]	0.0044	−0.0364	0.05	0.0074
van Laar[a]	−0.0061	893.23	0.02	0.0075
Wilson[b] 2	216.07	−228.16	0.07	0.0070
Wilson[b] 3 (C = 0.97)	202.63	−213.92	0.07	0.0070
NRTL[c] (α_{12} = 0.30)	776.37	−763.68	0.07	0.0069
UNIQUAC[d]	804.59	−652.30	0.12	0.0069

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

Estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression[17] of the objective function Q_i, with the activity coefficients obtained from the consistency test as experimental values,

$$Q_i = \sum \left(\frac{\gamma_{\text{exptl}} - \gamma_{\text{calcd}}}{\gamma_{\text{exptl}}} \right)^2 \tag{16}$$

where γ_{exptl} are the activity coefficients calculated from experimental data and γ_{calcd} are the coefficients calculated with the y and T values of the correlations. The parameters along with the average deviation in T (ΔT) and the average deviation in y (Δy) are listed in Table 6. Also, the ASOG[18] method was used to obtain predictions in Figures 1–4.

Table 7. Results of the Thermodynamic Consistency Test

system	Δy	A	B	D
methanol (1) + propyl acetate (2)[a]	0.0130	0.8406	1.2328	0.3822
methanol (1) + propyl acetate (2)	0.0048	1.0079	1.2087	0.5369
methanol (1) + isopropyl acetate (2)	0.0018	0.9729	1.1924	0.5999
vinyl acetate (1) + propyl acetate (2)	0.0083	0.0548	0.0610	0.1387
vinyl acetate (1) + isopropyl acetate (2)	0.0071	−0.0244	−0.0729	−0.1604

[a] Grishunin et al.[4]

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'Connell,[20] and activity coefficients are calculated using the four-suffix Margules equation,

$$\bar{g}^{E}/RT = x_1x_2[Ax_2 + Bx_1 - Dx_1x_2] \qquad (17)$$

with the corresponding activity coefficients

$$\ln \gamma_1 = x_2^2[A + 2(B - A - D)x_1 + 3Dx_1^2] \qquad (18)$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B - D)x_2 + 3Dx_2^2] \qquad (19)$$

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

$$F = P - \left(\frac{x_1\gamma_1^{*}f_1^{\circ}}{\phi_1} + \frac{x_2\gamma_2^{*}f_2^{\circ}}{\phi_2}\right) \qquad (20)$$

Here the asterisk (∗) denotes a calculated or predicted value. An experimental value has no asterisk; f_1° and f_2° are the standard state fugacities. The errors in the prediction of y_1 were calculated. Predicted γ_1^{*} values were obtained using the equation

$$y_1^{*} = \frac{x_1\gamma_1^{*}f_1^{\circ}}{\phi_1P^{*}} \qquad (21)$$

An average deviation was calculated from

$$\text{average deviation} = \frac{\sum_{i=1}^{n}|\Delta y|}{n} \qquad (22)$$

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 four systems included in this work have passed this consistency test. In Table 7, we show these results and the values of A, B, and D of eqs 17−19.

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 8 shows the values of this constant.

Table 8. Results of the Margules Constants Test

system	Margules constant
methanol (1) + propyl acetate (2)	1.0642
methanol (1) + isopropyl acetate (2)	1.0156
vinyl acetate (1) + propyl acetate (2)	0.0129
vinyl acetate (1) + isopropyl acetate (2)	−0.0236

Table 9. Adjustable Parameters a_k ($cm^3 \cdot mol^{-1}$) and Standard Deviation σ ($cm^3 \cdot mol^{-1}$) for the Excess Volumes

system	a_0	a_1	a_2	$10^{-3}\sigma$
methanol + propyl acetate	−0.2495	0.0193	0.0414	1.6
metanol + isopropyl acetate	−0.3405	0.0354	0.0560	0.8
vinyl acetate + propyl acetate	−0.0134	−0.0204	−0.0463	0.4
vinyl acetate + isopropyl acetate	0.0574	−0.0360	−0.1101	2.0

Table 10. Adjustable Parameters a_k and Standard Deviation σ for the Changes of Refractive Index on Mixing

system	a_0	a_1	a_2	$10^{-5}\sigma$
methanol + propyl acetate	0.0558	−0.0292	0.0136	14.4
metanol + isopropyl acetate	0.0502	−0.0261	0.0132	9.4
vinyl acetate + propyl acetate	−0.0024	0.0002	0	2.9
vinyl acetate + isopropyl acetate	−0.0040	0.0008	0.0005	3.5

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

$$V^{E} = x_1M_1(1/\rho - 1/\rho_1) + x_2M_2(1/\rho - 1/\rho_2) \qquad (23)$$

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 molar fractions.

The changes of refractive index were calculated by the equation

$$\Delta n_{D} = n_{D} - (x_1n_{D1} + x_2n_{D2}) \qquad (24)$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of the pure compounds.

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

$$(V^{E} \text{ or } \Delta n_{D}) = x_1x_2\sum_{k\geq 0}a_k(x_1 - x_2)^k \qquad (25)$$

where a_k are the adjustable parameters obtained by the least-squares method and k is the degree of the polynomial expansion. Tables 9 and 10 summarize the values of the parameters together with the standard deviations σ. The coefficients a_k were used to calculate the solid curves; see Figures 5 and 6.

Binary systems formed by methanol show an azeotrope and nonideal behavior, and the ASOG method prediction is in good agreement with experimental data. For the binary systems with vinyl acetate the ASOG prediction method is not adequate, as shown in Figures 3 and 4. The data of Grishunin et al.[4] are not consistent. Due to the presence of the azeotrope, propyl acetate and isopropyl acetate are not feasible as entrainers for the rupture of an azeotropic mixture formed by methanol and vinyl acetate. The values of excess molar volumes are very close to zero, especially for the vinyl acetate + propyl acetate system;

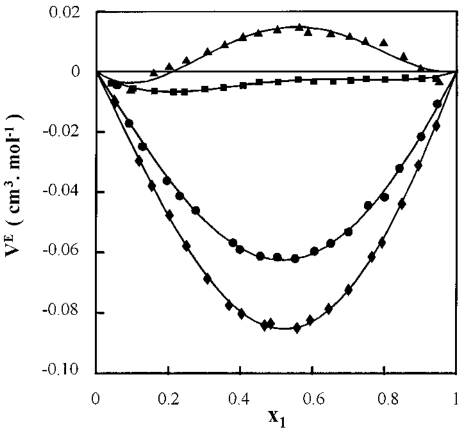

Figure 5. Excess molar volumes of mixtures of methanol (1) + propyl acetate (2), ●; methanol (1) + isopropyl acetate (2), ◆; vinyl acetate (1) + propyl acetate (2), ■; and vinyl acetate (1) + isopropyl acetate (2), ▲, at 298.15 K.

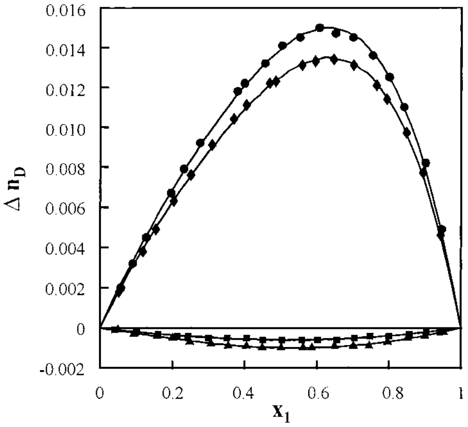

Figure 6. Changes of refractive index on mixing of methanol (1) + propyl acetate (2), ●; methanol (1) + isopropyl acetate (2), ◆; vinyl acetate (1) + propyl acetate (2), ■; and vinyl acetate (1) + isopropyl acetate (2), ▲, at 298.15 K.

similar behavior is observed for the changes of refractive index on mixing.

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