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Vapor−Liquid Equilibrium and Mixing Properties of Methanol + Diethyl Carbonate and Vinyl Acetate + Diethyl Carbonate Systems

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Different mixing properties (speed of sound, density, and refractive index on mixing) of the binary mixtures methanol + diethyl carbonate and vinyl acetate + diethyl carbonate have been measured at 298.15 K and atmospheric pressure. Corresponding derived properties have been calculated by experimental data. Values of the physical properties were fitted to Redlich−Kister polynomials. The isobaric vapor−liquid equilibrium (VLE) experimental data at 101.3 kPa were satisfactorily tested for thermodynamic consistency by means of a modified Dechema test. Activity coefficients were correlated with Margulles, Van Laar, UNIQUAC, NRTL, and Wilson equations. The ASOG group contribution method was used for prediction.

Introduction

Our earlier thermodynamic or phase equilibria studies of binary azeotropic mixtures and potential separation agents 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] have been extended to organic carbonates with the azeotropic mixture methanol + vinyl acetate to gauge their potential capability for a modified distillation process. In this article, we report new experimental data of the different mixing properties (speed of sound, density, and refractive index on mixing) of the mixtures (methanol or vinyl acetate + diethyl carbonate) that have been measured at $T = 298.15$ K and atmospheric pressure. Parameters of analytical expressions that represent the composition dependence of the derived properties were reported.

Experimental data collections of vapor−liquid equilibria for binary higher-order complexity are scarce because of the time spent to do experiments to obtain a complete description of the mixture. As an extension of our earlier work concerning phase equilibria, in this work we present consistent vapor−liquid equilibrium data of the abovementioned mixtures at $P = 101.3$ kPa. Vapor−liquid equilibria (VLE) data are usually obtained from experimental measurements but can also be estimated from available predictive VLE models of group contribution methods such ASOG. This method requires complete and fully updated experimental data to fit the group interaction parameters and reproduce the behavior of systems at other operating conditions. In this case, the ASOG group contribution method adequately predicts the nonideality of the diethyl carbonate. No bibliographic data is available in the open literature for these systems. Current correlations related to activity coefficients with composition are presented.

Experimental Section

Materials. Methanol (99.8 mol %) supplied by Panreac and diethyl carbonate (99.5 mol %) from Fluka were used without further purification. Vinyl acetate (≥99 mol %) was purified by distillation in a laboratory column of 100 plates; the purity of the material was checked by gas−liquid chromatography and was higher than 99.6 mol %. All products were degassed using ultrasound and dried on molecular sieves (pore diameter 3 Å from Fluka) before use. Densities, refractive indices, speeds of sound, and normal boiling points of the pure substances are given in Table 1 and compared with literature values of Riddick et al.[9]

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 100 Ω digital platinum resistance thermometer with an accuracy of ±0.01 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 ±0.00001 $g\cdot cm^{-3}$ 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 with a calibrated platinum resistance thermometer. Refractive indices were measured with a Mettler RE50 refractometer with an accuracy of ±0.00001, 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 $m\cdot s^{-1}$, 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 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 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,

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Table 1. Physical Properties of Pure Compounds[a]

	ρ/kg·m^{-3}		n_D		u/m·s^{-1}		T_b/K	
	obsd	lit[b]	obsd	lit[b]	obsd	lit[b]	obsd	lit[b]
methanol	786.56	786.37	1.32634	1.32652	1101.8	not available	337.9	337.696
vinyl acetate	925.59	not available	1.39253	1.3934	1115.6	not available	346.0	345.7
diethyl carbonate	969.00	969.26	1.38221	1.38287	1176.1	not available	399.6	400.0

[a] Densities ρ, refractive indices n_D, speeds of sound u at 298.15 K, and normal boiling points T_b. [b] Riddick et al.[9]

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

	ρ	$V^E \times 10^6$			u	δu		ρ	$V^E \times 10^6$			u	δu
x_1	kg·m^{-3}	m^3·mol^{-1}	n_D	δn_D	m·s^{-1}	m·s^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	n_D	δn_D	m·s^{-1}	m·s^{-1}
Methanol (1) + Diethyl Carbonate (2)													
0.063	964.93	0.010	1.38098	0.002	1174.8	3.4	0.543	917.68	−0.049	1.36700	0.015	1150.2	14.4
0.098	962.48	0.012	1.38026	0.004	1174.1	5.3	0.592	910.04	−0.053	1.36457	0.015	1146.9	14.7
0.159	958.15	0.001	1.37901	0.006	1171.5	7.2	0.655	898.92	−0.058	1.36118	0.016	1142.2	14.7
0.192	955.62	−0.003	1.37825	0.007	1169.9	8.0	0.690	892.00	−0.058	1.35900	0.015	1139.5	14.6
0.251	950.70	−0.009	1.37690	0.009	1167.0	9.5	0.750	878.54	−0.053	1.35486	0.015	1134.1	13.6
0.302	946.14	−0.019	1.37563	0.010	1164.3	10.6	0.800	865.37	−0.050	1.35090	0.013	1129.2	12.5
0.371	939.23	−0.026	1.37345	0.012	1160.6	12.0	0.848	850.75	−0.039	1.34641	0.012	1123.8	10.7
0.415	934.40	−0.034	1.37205	0.013	1158.1	12.8	0.897	833.80	−0.034	1.34105	0.009	1117.8	8.3
0.453	929.92	−0.037	1.37050	0.014	1155.9	13.4	0.948	812.41	−0.019	1.33440	0.005	1110.4	4.7
0.490	925.16	−0.045	1.36915	0.014	1153.8	14.1							
Vinyl Acetate (1) + Diethyl Carbonate (2)													
0.043	967.68	−0.014	1.38260	−0.00005	1174.2	0.70	0.556	948.60	−0.090	1.38757	−0.00038	1146.4	3.93
0.105	965.65	−0.028	1.38320	−0.00010	1171.2	1.47	0.598	946.73	−0.087	1.38804	−0.00034	1143.7	3.76
0.170	963.45	−0.040	1.38373	−0.00024	1167.9	2.11	0.650	944.30	−0.084	1.38859	−0.00033	1140.4	3.65
0.193	962.74	−0.053	1.38396	−0.00024	1166.9	2.47	0.697	942.05	−0.078	1.38917	−0.00024	1137.2	3.30
0.254	960.55	−0.060	1.38458	−0.00025	1163.6	2.87	0.744	939.73	−0.071	1.38968	−0.00021	1134.1	3.03
0.299	958.92	−0.067	1.38500	−0.00029	1161.2	3.18	0.803	936.72	−0.059	1.39031	−0.00019	1130.1	2.57
0.353	956.87	−0.075	1.38550	−0.00036	1158.2	3.47	0.850	934.22	−0.048	1.39087	−0.00011	1126.7	2.01
0.407	954.79	−0.081	1.38602	−0.00039	1155.2	3.72	0.901	931.44	−0.041	1.39143	−0.00008	1123.1	1.52
0.458	952.74	−0.086	1.38655	−0.00039	1152.3	3.91	0.946	928.87	−0.026	1.39197	0.00000	1119.8	0.93
0.507	950.71	−0.088	1.38706	−0.00038	1149.3	3.86							

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 + diethyl carbonate and vinyl acetate + diethyl carbonate.

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

$$V^E = x_1 M_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (1)$$

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 in refractive index δn_D at 298.15 K from the linear additive value of the mole fraction is 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 mole fraction x_1 of the most volatile compound of each binary system is given in Figure 2.

In the same way, the changes in the speed of sound on 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.

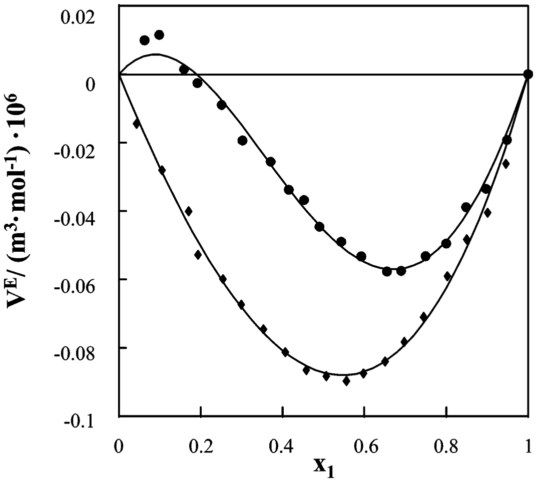

Figure 1. Excess molar volumes of mixtures of ●, methanol (1) + diethyl carbonate (2) and ◆, vinyl acetate (1) + diethyl carbonate (2) and −, Redlich−Kister fit curves at 298.15 K.

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

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

were a_k are the adjustable parameters obtained by a least-squares fitting method and k is the degree of the polynomial expansion. Table 3 lists the parameters with their

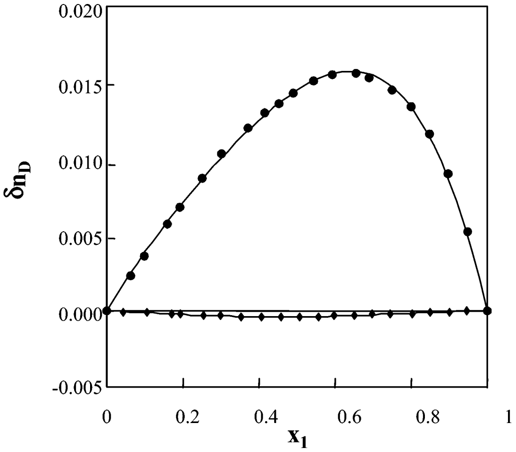

Figure 2. Change in refractive index on mixing for methanol ●, (1) + diethyl carbonate (2) ◆, and vinyl acetate (1) + diethyl carbonate (2) and –, Redlich–Kister fit curves at 298.15 K.

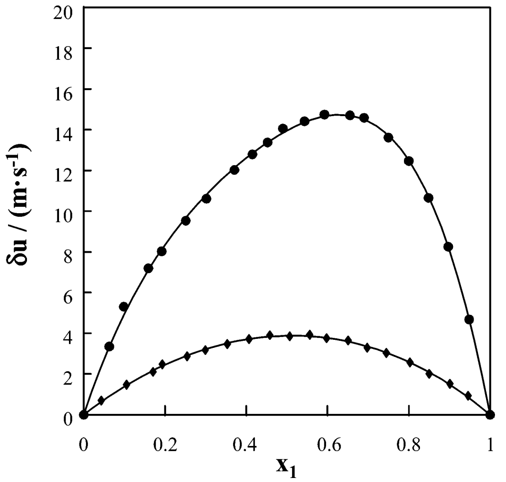

Figure 3. Change in the speed of sound on mixing for ●, methanol (1) + diethyl carbonate (2) and ◆, vinyl acetate (1) + diethyl carbonate (2) and –, Redlich–Kister fit curves at 298.15 K.

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

	$V^E \times 10^6$/m^3·mol^{-1}	δn_D	δu/m·s^{-1}
	Methanol (1) + Diethyl Carbonate (2)		
a_0	−0.182	0.058	55.8
a_1	0.248	−0.033	−21.6
a_2	−0.072	0.017	25.9
σ	0.002	0.000	0.1
	Vinyl Acetate (1) + Diethyl Carbonate (2)		
a_0	−0.349	−0.002	15.5
a_1	0.064	−0.000	−0.7
a_2	−0.009	0.001	0.7
σ	0.002	0.000	0.1

standard deviations σ. The coefficients a_k were used to calculate the solid curves (Figures 1 to 3). The standard deviations σ are defined as follows

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

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

Table 4. Vapor–Liquid Equilibrium Data for the Methanol (1) + Diethyl Carbonate (2) and Vinyl Acetate (1) + Diethyl Carbonate Systems[a]

x_1	y_1	T/K	γ_1	γ_2	ϕ_1	ϕ_2	ϕ_1^s	ϕ_2^s
		Methanol (1) + Diethyl Carbonate (2)						
0.000	0.000	399.6						
0.026	0.439	379.2	3.969	1.048	0.988	0.951	0.940	0.973
0.040	0.536	374.0	3.696	1.052	0.987	0.949	0.946	0.976
0.065	0.624	368.5	3.161	1.068	0.988	0.950	0.940	0.973
0.097	0.679	364.9	2.586	1.074	0.985	0.947	0.952	0.979
0.165	0.742	360.5	1.924	1.100	0.984	0.945	0.956	0.981
0.233	0.782	356.1	1.670	1.196	0.983	0.944	0.960	0.983
0.316	0.816	353.1	1.427	1.271	0.982	0.941	0.964	0.985
0.398	0.846	350.0	1.312	1.367	0.981	0.940	0.966	0.986
0.438	0.859	348.8	1.264	1.405	0.980	0.939	0.969	0.987
0.497	0.878	347.4	1.198	1.438	0.980	0.938	0.969	0.988
0.547	0.893	345.8	1.175	1.494	0.980	0.938	0.971	0.988
0.626	0.907	343.8	1.123	1.706	0.979	0.936	0.973	0.990
0.696	0.922	342.4	1.082	1.866	0.978	0.935	0.974	0.990
0.762	0.935	341.2	1.049	2.088	0.978	0.934	0.975	0.990
0.806	0.945	340.6	1.026	2.223	0.978	0.934	0.975	0.991
0.847	0.954	340.1	1.005	2.408	0.978	0.934	0.976	0.991
0.887	0.965	339.3	1.001	2.566	0.978	0.934	0.976	0.991
0.943	0.979	338.6	0.981	3.145	0.977	0.933	0.977	0.991
0.964	0.986	338.3	0.978	3.363	0.977	0.933	0.977	0.991
1.000	1.000	337.9						
		Vinyl Acetate (1) + Diethyl Carbonate (2)						
0.000	0.000	399.6						
0.048	0.140	395.5	0.622	0.966	0.980	0.956	0.901	0.961
0.135	0.360	389.4	0.668	0.960	0.978	0.954	0.910	0.966
0.213	0.520	383.6	0.717	0.957	0.976	0.952	0.919	0.970
0.301	0.653	377.6	0.755	0.954	0.974	0.950	0.927	0.974
0.353	0.715	374.3	0.776	0.949	0.973	0.949	0.932	0.976
0.377	0.741	372.7	0.789	0.947	0.973	0.948	0.934	0.977
0.402	0.769	370.7	0.815	0.944	0.972	0.947	0.937	0.978
0.450	0.811	367.9	0.835	0.929	0.971	0.946	0.940	0.980
0.476	0.834	365.9	0.863	0.920	0.970	0.945	0.942	0.981
0.497	0.850	364.4	0.882	0.915	0.970	0.944	0.944	0.981
0.524	0.866	363.1	0.888	0.907	0.970	0.944	0.946	0.982
0.560	0.887	361.1	0.905	0.891	0.969	0.943	0.948	0.983
0.594	0.907	359.0	0.933	0.860	0.968	0.942	0.950	0.984
0.662	0.934	356.0	0.949	0.822	0.967	0.940	0.953	0.985
0.737	0.956	353.0	0.962	0.791	0.966	0.938	0.956	0.986
0.817	0.974	350.0	0.977	0.756	0.965	0.936	0.959	0.987
0.850	0.980	349.2	0.970	0.733	0.965	0.936	0.960	0.988
0.885	0.986	348.1	0.973	0.699	0.965	0.935	0.961	0.988
0.953	0.995	347.2	0.940	0.633	0.964	0.935	0.962	0.988
1.000	1.000	346.1	–	–	–	–	–	–

[a] 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.

VLE Data. Vapor–liquid equilibrium data points (T, x_1, y_1) for the methanol (1) + diethyl carbonate (2) and vinyl acetate (1) + diethyl carbonate (2) binary systems at 101.3 kPa are presented in Table 4. The T–x_1–y_1 phase diagrams are shown in Figures4 and 5.

The activity coefficients γ_i of the components were calculated from

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

where x_i and y_i are the liquid and vapor mole fractions in 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

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

and the constants A_i, B_i, and C_i are reported in Table 5.

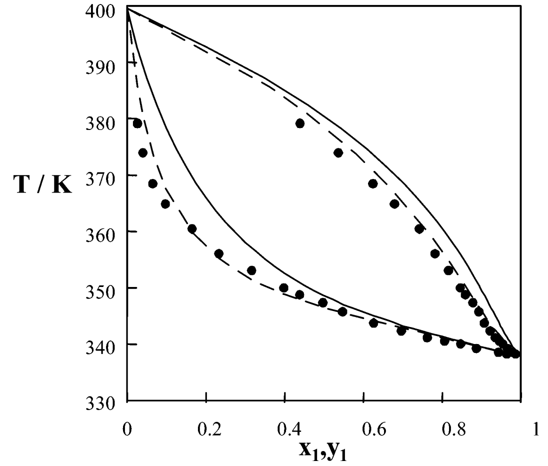

Figure 4. T–x_1–y_1 diagram for methanol (1) + diethyl carbonate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; ––, ASOG prediction.

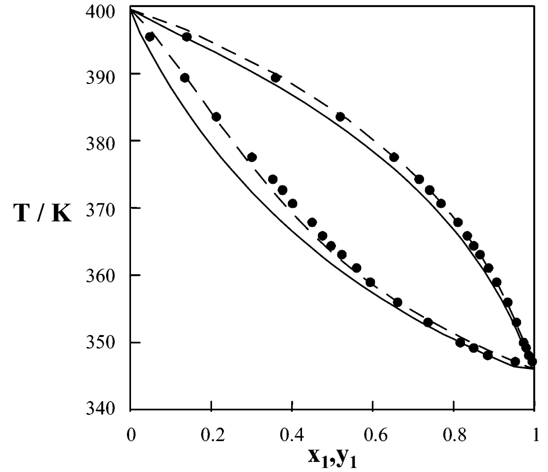

Figure 5. T–x_1–y_1 diagram for vinyl acetate (1) + diethyl carbonate (2) at 101.3 kPa: ●, experimental data; - - -, Wilson correlation; ––, ASOG prediction.

Table 5. Antoine Coefficients from Equation 7

compound	A_i	B_i	C_i
methanol	7.20519	1581.993	−33.439
vinyl acetate	7.216	1798.4	0
diethyl carbonate	7.3894	2148.1	0

The values of the Antoine constants for methanol, vinyl acetate, and diethyl carbonate were obtained from Riddck et al.[9]

The vapor-phase correction factor is given by

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

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 from 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, T is the experimental temperature, y_1 and y_2 are the vapor 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.

Table 6. Published Parameters Used for the Calculation of Fugacity Coefficients[a]

	T_c/K	P_c/Pa	V_c/m^3·kmol^{-1}	Z_c	ω
methanol	512.58	8.0959 × 6	0.11780	0.224	0.5656
vinyl acetate	524.00	4.2500 × 6	0.27000	0.263	0.3384
diethyl carbonate	576.00	3.39003 × 6	0.34600	0.252	0.4848

[a] Critical temperature T_c, critical pressure P_c, critical volume V_c, critical compression factor Z_c, and acentric factor ω of pure compounds.

Pitzer's correlation for the second virial coefficient was extended to mixtures by Reid et al.[10] to calculate B_{12} with the Tsonopoulos[11] modification for polar molecules to calculate B_{12} by

$$B_{12} = \frac{RT_{c12}}{P_{c12}}(B^{\text{o}} + \omega_{12}B^1 + aT_r^{-6} - bT_r^{-8}) \tag{11}$$

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

$$B^{\text{o}} = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{12}$$

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

The mixing rules proposed by Prausnitz[12] 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

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

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;[13] for the alcohol + acetate mixtures, $k_{ij} = 0.08$.

Also,

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

where Z_{c12} is calculated from

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

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

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

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[14] and are presented in Table 6.

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) + Diethyl Carbonate (2)				
Margules[a]	1.0654	0.9717	1.50	0.021
van Laar[a]	1.0972	0.9616	1.50	0.019
Wilson[b]	5836.02	−2094.15	1.50	0.019
NRTL[c] ($\alpha_{12} = 1.0$)	2775.26	4770.71	0.10	0.001
UNIQUAC[d]	−862.03	5003.80	2.30	0.034
Vinyl Acetate (1) + Diethyl Carbonate (2)				
Margules[a]	−0.4895	−0.0.0331	0.60	0.006
van Laar[a]	−0.4365	−0.1586	0.70	0.006
Wilson[b]	2323.52	−2570.11	0.80	0.007
NRTL[c] ($\alpha_{12} = 5.02$)	−620.91	189.98	0.70	0.006
UNIQUAC[d]	4975.94	−2690.21	0.40	0.004

[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}).

Table 8. Results of the Thermodynamic Consistency Test

system	average deviation	A	B	D
methanol (1) + diethyl carbonate (2)	0.005	1.5716	1.3040	1.5626
vinyl acetate (1) + diethyl carbonate (2)	0.007	−0.0377	0.2635	1.4280

Table 9. Results of the Margules Constant Test

system	Margules constant
methanol (1) + diethyl carbonate (2)	1.2762
vinyl acetate (1) + diethyl carbonate (2)	−0.2620

The fugacity coefficients at saturation ϕ_1^s and ϕ_2^s were calculated by the expressions

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

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

The activity coefficients were correlated with the Margules,[15] van Laar,[16] Wilson,[17] NRTL,[18] and UNIQUAC[19] equations. To determine the constants of each model, we have used the method "VLE calc" suggested by Gess et al.[20] The estimation of the parameters for the equation was based on the iterative solution, using the maximum likelihood regression of the objective function Q_i,[21] with the activity coefficients obtained from the consistency test as experimental values

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

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 7. Also, the ASOG[22] 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[23] where the fugacity coefficients are calculated by the method of Hayden and O'Connell[24] and activity coefficients are calculated by using the four-suffix Margules equation

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

with the corresponding activity coefficients

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

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

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

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

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

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

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 of A, B, and D of eqs 23 to 25.

We also carried out the Margules constant test using the program of Gess et al.[20] The Margules constant can be used to indicate the ideality of a system. Systems that yield a Margules constant whose absolute value is less than 0.60 can be considered ideal, whereas those that 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.

Conclusions

New vapor−liquid equilibria data not previously reported in the literature have been measured. The binary system formed by methanol + diethyl carbonate shows nonideal behavior; the ASOG method prediction is not adequate (Figure 4), and the best correlation of data is the NRTL equation. The system vinyl acetate + diethyl carbonate presents nonideal behavior too, and theASOG method prediction is better than that of the other system, although is not adequate. UNIQUAC shows the best correlation. The values of excess molar volumes are negative and small in both systems. Otherwise, changes in refractive index are clearly different for each system; the value for vinyl acetate + diethyl carbonate is close to zero, and that for methanol + vinyl acetate is positive and high. Changes in the speed of sound values are positive in both systems and clearly larger for the methanol + diethyl carbonate systems.

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