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Vapor–Liquid Equilibrium Data at 298.15 K for Binary Systems Containing Methyl Acetate or Methanol with 2-Methoxyethanol or 2-Ethoxyethanol

Maria C. Martin,[†] **Maria J. Cocero,**[*,‡] **and Rafael B. Mato**[‡]

Departamento de Ingenieria Energetica y Fluidomecanica, ETSII, Universidad de Valladolid,
47011 Valladolid, Spain, and Departamento de Ingenieria Quimica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid, Spain

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Isothermal vapor–liquid equilibria were measured at 298.15 K for the systems containing methyl acetate or methanol with 2-methoxyethanol or 2-ethoxyethanol. Mixtures containing methanol show a behavior close to ideal, while those containing methyl acetate exhibit positive deviations from ideality and satisfy the Redlich–Kister thermodynamic consistency test. The liquid-phase activity coefficients were fitted by using the van Laar, Wilson, NRTL, and NRTL-m (a modified NRTL equation) equations.

Introduction

Distillation is the most widely utilized industrial separation method. However, when an azeotrope is involved, the separation of mixture components by ordinary fractional distillation is not feasible.

The present work is part of a research program whose purpose is to study the separation by modified distillation of the azeotropic mixture methyl acetate + methanol, involved in the industrial manufacturing process of poly(vinyl alcohol). With this purpose some azeotropic and extractive agents, as well as some salts, were selected for the separation study.

In previous papers some chlorinated compounds (*1*) and some polar nitrogen-containing compounds (*2*) have been studied as azeotropic and extractive agents, respectively. In the present paper 2-methoxyethanol and 2-ethoxyethanol were selected as extractive separating agents, and the isothermal vapor–liquid equilibrium (VLE) data, at 298.15 K, were measured for the four binary systems methyl acetate or methanol with 2-methoxyethanol or 2-ethoxyethanol.

Experimental Section

All chemicals were from Farmitalia Carlo Erba; 2-methoxyethanol (>99.5%) and 2-ethoxyethanol (>99%) were used without purification while methanol and methyl acetate were distilled, at 1 atm of pressure, through a column (20-mm i.d., 900 mm long) packed with 2 × 2 mm Dixon rings. The first and last portions of the distillate were discarded, and the intermediate fraction distilling at constant temperature was collected. Gas chromatography analysis failed to show any significant impurities in the used chemicals, and the density values, accurate to ±0.0001 g/mL, compared well with those reported in the literature (Table 1).

The VLE results were obtained by a saturation method which is based on the isothermal saturation of a flow of dry nitrogen passing through the liquid phase embedded in a packed column. The equilibrium temperature, T, was measured accurately to 298.15 K ± 0.05 K with a mercury thermometer previously calibrated with a Hewlett-Packard Model 2804A certified quartz thermometer. The vapor phase is condensed in a liquid air trap, and the condensate is dissolved in an adequate solvent (diethyl ether in this work). The detailed experimental technique and operation procedure have been described previously (*3*). The vaporized fraction of the liquid phase being very small, it was not necessary to make a correction for the mole fraction of the liquid phase, x, which was calculated from the weighed amounts charged to the column. The liquid mole fractions were accurate to ±0.0002. The composition of the vapor phase was determined by use of a gas chromatograph equipped with a flame ionization detector previously calibrated with synthetic mixtures. The mole fraction of the vapor phase, y, accurate to within ±0.001, was calculated from the peak ratio of the samples.

Table 1. Densities (ρ) of the Pure Components at 298.15 K

compound	$\rho/(\mathrm{g\ cm^{-3}})$ exptl	$\rho/(\mathrm{g\ cm^{-3}})$ lit. (*8*)	compound	$\rho/(\mathrm{g\ cm^{-3}})$ exptl	$\rho/(\mathrm{g\ cm^{-3}})$ lit. (*8*)
methyl acetate	0.9270	0.9273	2-methoxyethanol	0.9602	0.9602
methanol	0.7866	0.7866	2-ethoxyethanol	0.9251	0.9252

Table 2. Vapor–Liquid Equilibrium Data for the System Methanol (1) + 2-Methoxyethanol (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.103	0.607	2.97	1.038	1.006
0.207	0.777	4.59	1.018	0.994
0.285	0.837	5.79	1.006	1.017
0.399	0.896	7.60	1.010	1.013
0.496	0.928	9.20	1.019	1.012
0.603	0.955	10.99	1.029	0.958
0.696	0.968	12.51	1.027	1.011

Results

For the methanol + 2-methoxyethanol and methanol + 2-ethoxyethanol systems, all deviations from both liquid and vapor nonideality are within experimental uncertainty. On the contrary, the liquid mixtures of methyl acetate with 2-methoxyethanol or 2-ethoxyethanol exhibit positive deviations from ideality.

Tables 2–5 show the experimental x–y data for the four binary systems, together with the calculated values of the total vapor pressure, P, and the liquid-phase activity coefficients, γ_i. The vapor-phase nonidealities were calculated from the Peng–Robinson equation of state (*4*), where the binary interaction parameter, δ_{ij}, was set as zero for all the systems. All the vapor-phase fugacity coefficients were very close to unity, and therefore, data reduction was performed neglecting vapor-phase corrections.

[†] Departamento de Ingenieria Energetica y Fluidomecanica.
[‡] Departamento de Ingenieria Quimica.

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Table 3. Vapor–Liquid Equilibrium Data for the System Methanol (1) + 2-Ethoxyethanol (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.120	0.759	2.36	0.882	0.912
0.205	0.861	3.88	0.966	0.959
0.308	0.916	5.61	0.987	0.960
0.394	0.944	7.01	0.995	0.914
0.492	0.965	8.81	1.022	0.855
0.603	0.979	11.16	1.071	0.830
0.697	0.986	13.19	1.102	0.856
0.797	0.992	14.89	1.095	0.824
0.894	0.995	15.89	1.044	1.052

Table 4. Vapor–Liquid Equilibrium Data for the System Methyl Acetate (1) + 2-Methoxyethanol (2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.102	0.837	7.36	2.112	1.029
0.205	0.906	11.17	1.726	1.016
0.300	0.928	13.89	1.499	1.096
0.397	0.940	16.27	1.342	1.240
0.495	0.956	18.41	1.239	1.228
0.594	0.963	20.41	1.152	1.423
0.705	0.975	22.54	1.084	1.459
0.795	0.980	24.28	1.040	1.807
0.893	0.989	26.29	1.011	2.060

Table 5. Vapor–Liquid Equilibrium Data for the System Methyl Acetate (1) + 2-Ethoxyethanol at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.107	0.897	5.63	1.649	0.914
0.202	0.942	10.47	1.704	1.069
0.308	0.967	14.09	1.544	0.943
0.400	0.974	16.32	1.386	0.991
0.497	0.977	18.63	1.275	1.191
0.595	0.984	21.25	1.223	1.172
0.693	0.988	23.90	1.184	1.302
0.794	0.992	26.00	1.129	1.407
0.895	0.994	27.26	1.051	2.167

Table 6. Fitted Parameters (A_{12}, A_{21}) and Average Absolute Deviations in the Vapor-Phase Mole Fraction (Δy_1) for the Binary Systems at 298.15 K

model	A_{12}	A_{21}	Δy_1
Methyl Acetate (1) + 2-Methoxyethanol (2)			
Wilson	180.98	123.74	0.0014
NRTL	99.598	187.81	0.0014
NRTL-m	110.39	182.60	0.0014
van Laar	0.9283	0.8507	0.0014
Methyl Acetate (1) + 2-Ethoxyethanol (2)			
Wilson	-51.784	551.50	0.0030
NRTL	577.62	-180.91	0.0032
NRTL-m	509.62	-121.71	0.0031
van Laar	0.4901	1.4076	0.0032

Inasmuch as the method does not provide the total vapor pressures, the values of P, as well as those of the activity coefficients, were derived from the x–y–T data and from the vapor pressures of the pure components, by means of an iterative procedure which requires an algebraic expression for dimensionless excess Gibbs energy. For this purpose the four-parameter Margules equation (*5*) was used. The flow chart of the computation program was shown in a previous paper (*2*). The following values for the vapor pressures (kPa) of the pure components at 298.15 K were taken from the literature: 28.82 for methyl acetate (*6*), 16.93 for methanol (*7*), 1.29 for 2-methoxyethanol (*8*), and 0.71 for 2-ethoxyethanol (*8*).

The thermodynamic consistency of the results was satisfactorily checked using the method proposed by Gess et al. (*9*); the average difference in vapor-phase composition between experimental and reduced data was in all four binary systems less than 0.01 mole fraction. In addition, no systematic deviations were observed when these deviations were plotted against the liquid mole fraction.

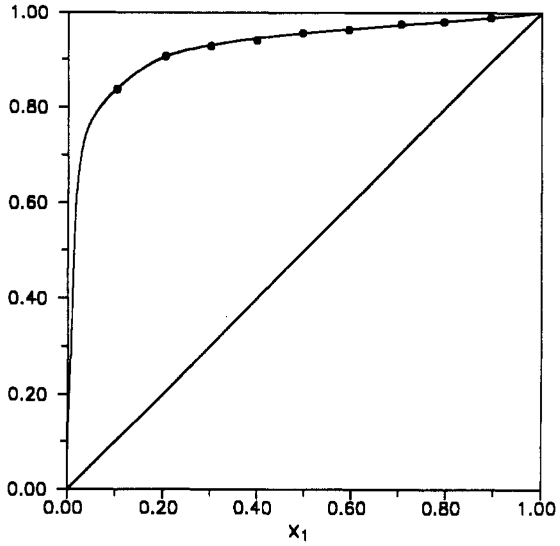

Figure 1. Equilibrium diagram for the methyl acetate (1) + 2-methoxyethanol (2) system. The continuous line corresponds to the correlation with the Wilson equation.

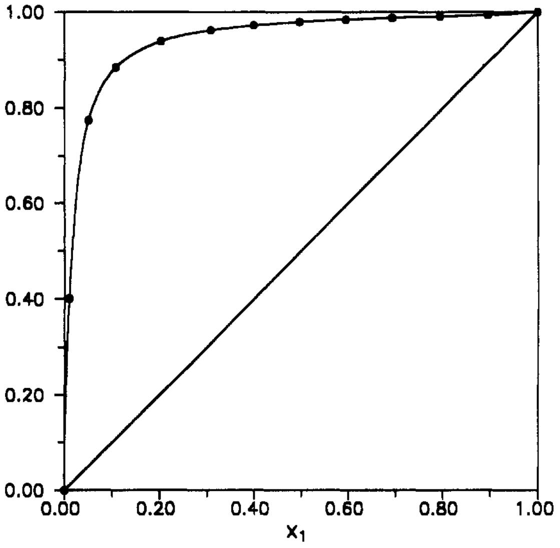

Figure 2. Equilibrium diagram for the methyl acetate (1) + 2-ethoxyethanol (2) system. The continuous line corresponds to the correlation with the Wilson equation.

The experimental activity coefficients of the binary systems containing methyl acetate were used to fit the adjustable parameters in the van Laar (*10*), Wilson (*11*), NRTL (*12*), and NRTL-m (a modified NRTL equation) (*13*) equations by a nonlinear regression method. For this purpose the following objective function, OF, was minimized:

$$\mathrm{OF} = \sum_{i=1}^{N}\left[\left(\frac{\gamma_{1,\mathrm{e}} - \gamma_{1,\mathrm{c}}}{\gamma_{1,\mathrm{e}}}\right)^2 + \left(\frac{\gamma_{2,\mathrm{e}} - \gamma_{2,\mathrm{c}}}{\gamma_{2,\mathrm{e}}}\right)^2\right]$$

where N is the number of experimental data points and the subscript e and c mean experimental and calculated values, respectively. The other two binary systems containing methanol were not correlated because of their ideal behavior.

The NRTL-m equation is a modification of the original NRTL, proposed by Mato et al. (*13*), where the nonrandomness parameter α_{ij} is expressed as a function of the other two binary interaction parameters G_{ij} and G_{ji}:

$$\alpha_{ij} = \frac{1}{2 + G_{ij}G_{ji}}$$

Table 6 summarizes the results of the correlation for the two binary systems containing methyl acetate, where A_{ij} is the fitted parameter of the corresponding model and Δy_1 is the average absolute deviation in the vapor-phase mole fraction of the ester. The unit of the parameters A_{ij} in Table 6 is kelvin for the Wilson, NRTL, and NRTL-m models; they are dimensionless for the van Laar model. The results obtained with all the models are in good agreement with the experimental values. Experimental data and their correlation with the Wilson equation are plotted for these systems in Figures 1 and 2.

Registry Numbers Supplied by Author. Methyl acetate, 79-20-9; methanol, 67-56-1; 2-methoxyethanol, 109-86-4; 2-ethoxyethanol, 110-80-5.

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