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Vapor–Liquid Equilibrium Measurements at 101.32 kPa for Binary Mixtures of Methyl Acetate + Ethanol or 1-Propanol

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Isobaric vapor–liquid equilibrium data at 101.32 ± 0.02 kPa are reported for methyl acetate (1) + ethanol (2) or + 1-propanol (2). The results are compared with those predicted by the UNIFAC and ASOG methods. The methyl acetate (1) + ethanol (2) system forms an azeotrope at 329.8 K and a molar concentration of x_1 = 0.958. Both methods predict the vapor-phase compositions equally well, with overall mean errors of less than 5%.

Introduction

In continuation of our studies (*1*, *2*) on isobaric vapor–liquid equilibrium (VLE) data for binary mixtures of esters with 1-alkanols, we have determined VLE for methyl acetate + ethanol or + 1-propanol.

Nagata et al. (*3*) have reported isothermal VLE data for methyl acetate + 1-propanol. Isothermal or isobaric experimental data exist for methyl acetate + ethanol (see refs 4 and 5). However, the literature data are not sufficient to define the exact behavior of these systems.

In our previous studies (*1*, *2*), the UNIFAC and ASOG methods were found to adequately fit isobaric equilibrium data, with average absolute percent errors in vapor mole fraction, $\bar{e}(y_1)$, of less than 5%. In consequence, these models were also used in the present work.

Experimental Section

Commercially available methyl acetate, ethanol, and 1-propanol of the highest quality were used. The source and physical properties of the alkanols have been described previously (*2*). Methyl acetate, Fluka AG HPLC grade material, was degassed with ultrasound and dried over molecular sieves. The density ρ and refractive index n_D of the purified product, ρ(298.15 K)/(kg m^{-3}) = 926.99 and n_D(298.15 K) = 1.3593, differ slightly from literature values: 927.9 and 1.3589 (*6*).

The equilibrium data were obtained in a modified version of the small-capacity equilibrium described earlier (*1*). The equilibrium compositions of the liquid phase, x and the vapor phase, y, were determined (*1*) from (x, ρ) curves, obtained previously. The mole fractions are accurate to ±0.001 for the liquid phase and ±0.002 for the vapor phase. The accuracy of the variations in pressure was better than ±0.02 kPa. The temperatures were read with an accuracy of ±0.01 K (*1*).

Results and Discussion

The isobaric VLE data are given in Table I. Both systems show positive deviations of Raoult's law. Methyl acetate (1) + ethanol (2) forms an azeotrope at an acetate concentration x_1 = 0.958 and at a temperature of 329.8 K. These values agree almost exactly with those proposed by Horsley (*7*), x_1 = 0.953 and T = 330.05 K.

The concentration data obtained experimentally were fit to the equation applied in earlier works (*1*, *2*):

$$y_1 - x_1 = x_1 x_2 \sum A_i [x_1/(x_1 + kx_2)]^i \qquad i = 0\text{-}3 \quad (1)$$

Table I. Experimental Vapor–Liquid Equilibrium T–x–y Data and Activity Coefficients γ_i at 101.32 ± 0.02 kPa

T/K	x_1	y_1	γ_1	γ_2
Methyl Acetate (1) + Ethanol (2)				
351.46	0.0000	0.0000		1.000
345.75	0.0688	0.2483	2.204	1.007
341.75	0.1543	0.4032	1.800	1.033
340.75	0.1776	0.4382	1.752	1.042
340.15	0.1906	0.4560	1.731	1.050
339.55	0.2090	0.4798	1.692	1.053
336.75	0.3055	0.5770	1.520	1.096
335.85	0.3432	0.6043	1.458	1.126
335.15	0.3721	0.6243	1.421	1.152
334.45	0.4090	0.6463	1.369	1.187
334.15	0.4339	0.6586	1.328	1.212
333.55	0.4733	0.6792	1.280	1.256
333.05	0.5229	0.7002	1.214	1.324
332.55	0.5669	0.7223	1.174	1.380
332.05	0.6292	0.7430	1.106	1.525
331.15	0.7248	0.7915	1.054	1.733
330.85	0.7674	0.8123	1.032	1.870
330.55	0.8069	0.8388	1.023	1.960
330.15	0.8456	0.8727	1.029	1.970
329.98	0.8859	0.8997	1.019	2.116
329.85	0.9237	0.9288	1.013	2.259
329.82	0.9432	0.9450	1.010	2.348
329.80	0.9541	0.9544	1.010	2.411
329.79	0.9624	0.9621	1.009	2.447
329.81	0.9700	0.9692	1.008	2.490
329.82	0.9796	0.9784	1.007	2.567
329.85	0.9880	0.9867	1.006	2.683
329.82	1.0000	1.0000	1.000	
Methyl Acetate (1) + 1-Propanol (2)				
370.35	0.0000	0.0000		1.000
361.85	0.0705	0.3112	1.723	1.019
360.15	0.0870	0.3654	1.715	1.021
358.65	0.1026	0.4109	1.702	1.024
357.45	0.1191	0.4472	1.648	1.027
356.65	0.1292	0.4706	1.634	1.027
355.25	0.1462	0.5049	1.609	1.037
354.15	0.1618	0.5354	1.590	1.037
353.35	0.1755	0.5537	1.550	1.047
351.35	0.1946	0.5899	1.549	1.044
350.95	0.2123	0.6114	1.514	1.054
349.95	0.2288	0.6343	1.499	1.057
347.85	0.2699	0.6839	1.456	1.056
346.85	0.2934	0.7048	1.421	1.064
342.35	0.4022	0.7822	1.316	1.131
340.25	0.4685	0.8142	1.254	1.194
339.35	0.5035	0.8300	1.223	1.218
338.60	0.5367	0.8418	1.191	1.258
338.05	0.5623	0.8496	1.167	1.298
337.25	0.5956	0.8619	1.147	1.339
336.65	0.6231	0.8712	1.129	1.378
336.10	0.6528	0.8800	1.108	1.430
335.55	0.6827	0.8905	1.091	1.465
334.95	0.7111	0.8991	1.078	1.526
334.45	0.7373	0.9061	1.065	1.599
333.95	0.7694	0.9167	1.049	1.655
333.25	0.8086	0.9289	1.035	1.760
332.65	0.8390	0.9394	1.028	1.836
332.15	0.8693	0.9498	1.020	1.919
331.55	0.9061	0.9624	1.011	2.060
330.85	0.9412	0.9756	1.010	2.209
330.65	0.9573	0.9820	1.006	2.267
330.40	0.9711	0.9874	1.006	2.373
329.82	1.0000	1.0000	1.000	

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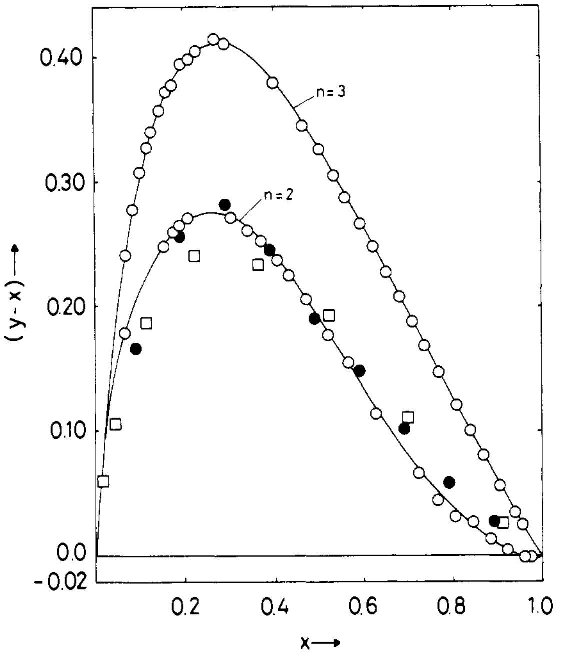

Figure 1. Experimental vapor-liquid equilibrium ($y_1 - x_1$) data at 101.32 kPa for binary systems, $H_3CCOOCH_3$ (1) + $C_nH_{2n+1}OH$ (2): ○, this work (n = 2,3); ●, Nishi (*8*) (n = 2); □, Perelygin and Volkov (*9*) (n = 3).

The coefficients A_i in eq 1 were determined by a least-squares method for a value of k optimized to yield the smallest standard deviation $s(y_1 - x_1)$. The values obtained are as follows: for methyl acetate (1) + ethanol (2), $A_0 = 5.954$, $A_1 = -14.355$, $A_2 = 18.273$, $A_3 = -9.893$, $k = 0.144$, and $s(y_1 - x_1) = 0.002$; for methyl acetate (1) + 1-propanol (2), $A_0 = 5.179$, $A_1 = -5.810$, $A_2 = 2.601$, $A_3 = -1.400$, $k = 0.193$, and $s(y_1 - x_1) = 0.001$. Figure 1 shows that for the methyl acetate + ethanol system our results are in good agreement with those of Nishi (*8*) at low, but not at high, ester concentration, the latter affecting the coordinates of the azeotrope defined for this mixture. Likewise, our experimental results show large differences from those presented by Perelygin and Volkov (*9*, cf. ref 4) (see Figure 1).

The activity coefficients γ_i were calculated (*1*) by taking into account the nonideality of the vapor phase (Table I). The vapor pressures of the pure component were calculated by means of the Antoine equation, using the constants extracted from ref 6. The virial coefficients were determined by the method of Tsonopoulos (*10*).

The area consistency tests of Herington (*11*) and Fredenslund et al. (*12*) are satisfied by our data. The mean absolute deviation between measured and estimated vapor concentration, $(\sum |y_{1,\mathrm{exptl}} - y_{1,\mathrm{calcd}}|)/N$, was smaller than 0.01 mole fraction.

Finally, following the good results obtained with ASOG and UNIFAC in our previous paper (*2*), we applied again these models to the systems studied, using the ester/alkanol interaction parameters set forth in the literature.

Using the ASOG method, with the OH/COO parameters as given by Kojima and Tochigi (*13*), we obtained the following results in the prediction of the vapor-phase composition: (a) for methyl acetate (1) + ethanol (2) system, the mean error was 2.6% (the azeotrope was at $x_1 = y_1 = 0.886$, somewhat different from the experimental value), and (b) for methyl acetate (1) + 1-propanol (2), the mean error was 3.1%.

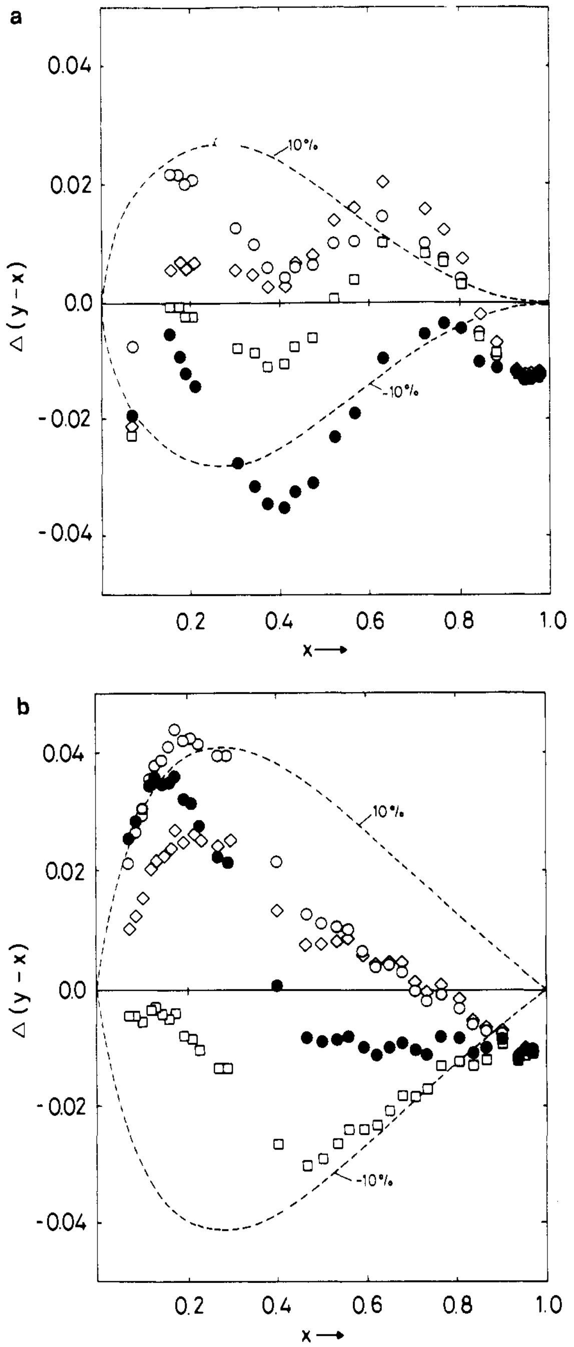

Figure 2. Representation of the differences indicated by eq 3, using the ASOG and UNIFAC models for (a) methyl acetate (1) + ethanol (2) and (b) methyl acetate (1) + 1-propanol (2). The curves fitted to experimental points are situated on the x-axis: ●, ASOG; □, UNIFAC with the pair CCOH/COOC; ◇, UNIFAC with the pair COH/COO; ○, UNIFAC with the pair OH/COOC.

Various types of ester/alkanol interaction parameters were taken into account when applying the UNIFAC method: COH/COO (Fredenslund et al. (*14*)), OH/COOC (Skjold-Jorgensen et al. (*15*)), and CCOH/COOC (Fredenslund et al. (*16*)). The UNIFAC predictions present a mean estimation error for the vapor-phase composition of 2–4% with the azeotrope at $x_1 = y_1 = 0.897–0.905$.

Parts a and b of Figure 2 show the deviations between the estimated data and the smoothed experimental data, eq 3. The deviations were expressed, respectively, by

$$\Delta(y_1 - x_1) = (y_1 - x_1)_{\mathrm{estd}} - (y_1 - x_1)_{\mathrm{exptl}} \quad (2)$$

$$\Delta y_1 = y_{1,\mathrm{estd}} - y_{1,\mathrm{exptl}} \quad (3)$$

Summing up, the present analysis does not provide a sufficient basis for deciding which of the two predictive models is better, since they are formally equivalent and therefore yield similar results. In any case, both methods produce overall errors of less than 5% in the vapor-phase composition, which is considered quite acceptable for this type of estimation.

Glossary

A_i	coefficients of eq 1
$\bar{e}(y_1)$	mean error in y_1, $(\sum\|y_{1,\text{exptl}} - y_{1,\text{calcd}}\|/y_{1,\text{exptl}})100/N$
k	parameter in eq 1
N	number of experimental points
s	standard deviation, $\|\sum(\text{exptl} - \text{calcd})^2/N\|^{1/2}$
T	temperature, K
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

γ_i	activity coefficient of component i
ρ	liquid density, kg m^{-3}

Registry No. $H_3CCOOCH_3$, 79-20-9; ethanol, 64-17-5; 1-propanol, 71-23-8.

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Equilibrium Diagrams at 25 °C of Water–Oxalic Acid–2-Methyl-1-propanol, Water–Oxalic Acid–1-Pentanol, and Water–Oxalic Acid–3-Methyl-1-butanol Ternary Systems

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The purpose of this work is to study the oxalic acid recovery possibilities from wastewater of the ozonization process of wood sawdust through a liquid-liquid extracting process. 2-Methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol may be suitable as extracting solvents. Water–oxalic acid–alcohol ternary system solubility diagrams and tie lines were established at the temperature of 25 °C. Partition coefficients are comprised between 0.28 and 0.81. 1-Pentanol is the most selective solvent with regard to oxalic acid.

Introduction

Oxalic acid is principally manufactured from propylene. It is an organic acid used in the metal treatment, coating process, and anodizing industries (*1*). In order to recover oxalic acid from ozonization wastewater of poplar sawdust, which is present at a concentration rate of about 7 g/100 g of wood sawdust dried (*2*), we considered the possibility of using the liquid–liquid extracting process. The solvation character of oxygen atoms tied to the carbon chain lends especially to alcohols extracting properties with regard to acids. Thus we have selected 2-methyl-1-propanol, 1-pentanol, and 3-methyl-1-butanol for use in this work.

Experimental Section

Chemicals. Solvents, with a minimum purity of 98%, have been obtained from Prolabo. Oxalic acid (Prolabo) had a purity of 99%.

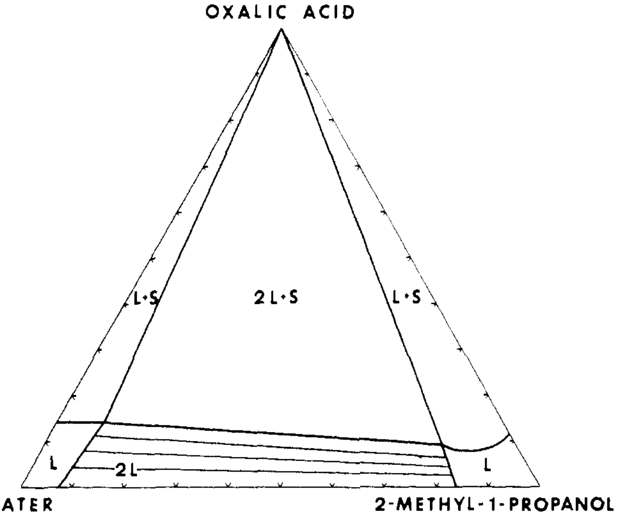

Figure 1. Water–oxalic acid–2-methyl-1-propanol phase diagram with tie lines at 25 °C: S = solid; L = liquid.

Experimental Procedures. Solubility isotherms and tie-line data were determined with an experimental device maintained at the constant temperature of 25 ± 0.1 °C in a thermostated vessel. Several oxalic acid solutions at different concentrations were prepared to determine the tie lines.

The solutions were mixed in glass-stoppered separatory funnels and then added to the solvent and shaken for 4 h.

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