

Salt Effect on the Vapor-Liquid Equilibrium of Methyl Acetate + Methanol at 298.15 K

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Isothermal vapor-liquid equilibrium was measured at 298.15 K for the systems methyl acetate + methanol and methyl acetate + methanol + CH₃COOK, + LiCl, + CaCl₂, and + Ca(NO₃)₂, by a saturation method. The results have been fitted by using the van Laar, Wilson, NRTL, and NRTL-m (a modified NRTL equation) activity coefficient models.

Introduction

The azeotropic mixture methyl acetate + methanol is involved in the industrial manufacturing process of poly(vinyl alcohol), which is made from poly(vinyl acetate) by alcoholysis with methanol. The resulting methyl acetate is hydrolyzed to obtain methanol, which is recycled to the alcoholysis stage, and acetic acid, which is returned to the vinyl acetate plant.

In previous papers we have reported the results of studies carried out for selection of a third component to enable the separation of the mixture methyl acetate + methanol by azeotropic (1) or extractive distillation (2, 3).

In this paper we present the vapor-liquid equilibrium (VLE) data, at 298.15 K, for the binary mixture methyl acetate + methanol and the ternary mixtures methyl acetate + methanol + CH₃COOK, + LiCl, + CaCl₂, or + Ca(NO₃)₂.

Experimental Section

Materials. The salts CH₃COOK (Panreac), LiCl (Carlo Erba), CaCl₂·2H₂O (Merck), and Ca(NO₃)₂·4H₂O (Panreac) were analytical reagent grade. Anhydrous salts were desiccated in an oven at 393 K until constant mass was obtained. Anhydrous calcium chloride and calcium nitrate were obtained by desiccating the hydrated compounds in a microwave oven. Methyl acetate and methanol were Carlo Erba products, and were purified by rectification at 1 atm of pressure in a packed column. The intermediate fraction distilling at constant temperature was collected. Gas chromatographic analysis failed to show any significant impurities for both compounds.

Apparatus and Procedure. Vapor-liquid equilibrium measurements were made by a saturation method. This method is based on the isothermal saturation of a flow of dry nitrogen passing through the liquid phase embedded in a packed column. The vapor phase is condensed in a liquid air trap, and the condensate is dissolved in an adequate solvent (diethyl ether in this work) for gas chromatography analysis. A more detailed description of the experimental technique and operation procedure can be found in a previous paper (4).

The equilibrium temperature, *T*, was measured accurately to ±0.05 K with a PROTON mercury thermometer previously calibrated with a Hewlett-Packard Model 2804A certified quartz thermometer.

The liquid mixtures were prepared from known masses of methyl acetate and methanol, and the salt was added in excess. The vaporized fraction of the liquid phase being very small (<0.5%), it was not necessary to make corrections for the liquid composition calculated directly from the masses charged to the column. The mole fraction of the liquid phase, *x*, is accurate to within ±0.0002. The composition of the vapor phase was determined by use of a gas chromatograph (Hewlett-Packard Model 5980) equipped with a flame ionization detector and previously calibrated with synthetic mixtures. The column, 30 m long and 0.53 mm in diameter, with Carbowax 20M as the stationary phase, was operated isothermally at 333 K. The chromatographic measurements present good reproducibility, and the mole fraction of the vapor phase, *y*, accurate to within ±0.001, was calculated from the peak area ratio of the samples. The validity of the method has been tested on several other salt systems (5, 6).

Results and Discussion

The experimental data have been interpreted considering the solution of salt in the mixtures of the two volatile components as a pseudobinary system, with each one of the volatile components being salt-saturated. Using this approach, Sada (7) found that the integrated form of the Gibbs-Duhem equation is applicable to salt solutions, whenever the composition of the liquid phase without salt and the vapor pressures of the salt-saturated volatile compounds are used. With this purpose the following values for the vapor pressures (kPa) of methanol solutions saturated with salt at 298.15 K were measured: 13.91 with CH₃COOK, 3.27 with LiCl, 13.33 with CaCl₂, and 5.33 with Ca(NO₃)₂. The salts CH₃COOK, LiCl, and CaCl₂ are very insoluble in methyl acetate, and therefore, the presence of salt does not modify the vapor pressure of pure components. On the contrary, the Ca(NO₃)₂ is also soluble in methyl acetate, 27.5 kPa being the measured value for the vapor pressure of the solution saturated with this salt at 298.15 K.

The thermodynamic consistency of the experimental data was analyzed by using the Redlich-Kister area test (8). The systems methyl acetate + methanol without salt, methyl acetate + methanol + CH₃COOK and methyl acetate + methanol + LiCl were found to be thermodynamically consistent.

The system methyl acetate + methanol + CaCl₂ was found to be slightly nonconsistent. This was attributed to the excess of added salt to attain a completely saturated solution. Further analysis showed that the excess solid salt retained methanol, and therefore, the concentration of this component

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Table 1. Experimental x - y Data and Calculated Values of the Total Pressure (P) and the Activity Coefficients (γ_1 , γ_2) at 298.15 K

x_1	y_1	P/kPa	γ_1	γ_2
Methyl Acetate (1) + Methanol (2)				
0.103	0.337	23.20	2.642	1.011
0.190	0.454	26.43	2.194	1.050
0.309	0.547	28.94	1.778	1.117
0.404	0.592	30.15	1.533	1.215
0.511	0.634	31.10	1.338	1.370
0.600	0.678	31.66	1.240	1.499
0.705	0.721	32.00	1.135	1.781
0.800	0.780	31.98	1.081	2.069
0.878	0.826	31.55	1.029	2.648
Methyl Acetate (1) + Methanol (2) + CH ₃ COOK (3)				
0.104	0.416	21.23	2.957	0.994
0.196	0.544	25.46	2.455	1.036
0.303	0.616	28.38	2.003	1.121
0.394	0.664	29.83	1.744	1.186
0.493	0.699	30.80	1.515	1.311
0.590	0.718	31.43	1.326	1.549
0.691	0.740	31.82	1.181	1.918
0.785	0.778	31.94	1.097	2.362
0.885	0.840	31.51	1.037	3.141
Methyl Acetate (1) + Methanol (2) + LiCl (3)				
0.100	0.765	12.17	3.251	0.974
0.194	0.851	18.87	2.883	1.067
0.305	0.897	22.81	2.333	1.033
0.390	0.898	24.27	1.943	1.240
0.491	0.915	25.60	1.658	1.306
0.593	0.917	26.92	1.446	1.677
0.680	0.931	27.50	1.327	1.839
0.783	0.938	27.92	1.191	2.500
0.878	0.943	28.94	1.078	4.127

decreases in the liquid phase. For this reason, the experiments were made using a very slight CaCl₂ excess. However, the thermodynamic consistency was poor.

On the other hand, when the consistency test is applied to the system methyl acetate + methanol + Ca(NO₃)₂ using the pseudobinary model of Sada (7), the line $\ln(\gamma_1/\gamma_2)$ vs x_1 does not cross the abscissa axis and the ordinate value is always positive. The same behavior has been observed in our previous studies with the systems ethyl acetate + ethanol + ZnCl₂ and 1-propyl acetate + 1-propanol + ZnCl₂. The results appear to indicate that the systems containing bivalent cations do not obey the thermodynamic consistency test. Consequently, the experimental data of the systems methyl acetate + methanol + CaCl₂, + Ca(NO₃)₂ were not correlated with thermodynamic models for the excess Gibbs energy.

Table 1 presents the experimental x - y - T VLE data for the systems methyl acetate + methanol, methyl acetate + methanol + CH₃COOK, and methyl acetate + methanol + LiCl at 298.15 K. Also, Table 1 shows the calculated values of the total vapor pressure, P , and liquid-phase activity coefficients, γ_i . All the vapor-phase fugacity coefficients, estimated from the Peng-Robinson (9) equation of state for this study, were close to 1 and can be ignored. Therefore, data reduction was performed neglecting vapor-phase corrections. The experimental x - y data for the systems methyl acetate + CaCl₂, + Ca(NO₃)₂ are shown in Table 2, and the experimental and calculated x - y data are plotted in Figure 1 for all systems.

Inasmuch as the experimental method does not provide measured total vapor pressures, the values of P , as well as those of the liquid-phase 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 the dimensionless excess Gibbs energy. For this purpose the four-parameter Margules equation (10) has been used. The flow chart of the computation program was shown in a previous paper (2). The following

Table 2. Experimental Equilibrium Vapor (y) and Liquid (x) Mole Fractions for the Systems Methyl Acetate + Methanol + CaCl₂ and + Ca(NO₃)₂ at 298.15 K

x_1	y_1	x_1	y_1	x_1	y_1
Methyl Acetate (1) + Methanol (2) + CaCl ₂ (3)					
0.098	0.574	0.392	0.729	0.691	0.779
0.194	0.665	0.495	0.747	0.786	0.805
0.298	0.707	0.598	0.763	0.882	0.853
Methyl Acetate (1) + Methanol (2) + Ca(NO ₃) ₂ (3)					
0.101	0.428	0.390	0.819	0.691	0.925
0.193	0.617	0.490	0.867	0.785	0.951
0.299	0.750	0.597	0.899	0.879	0.964

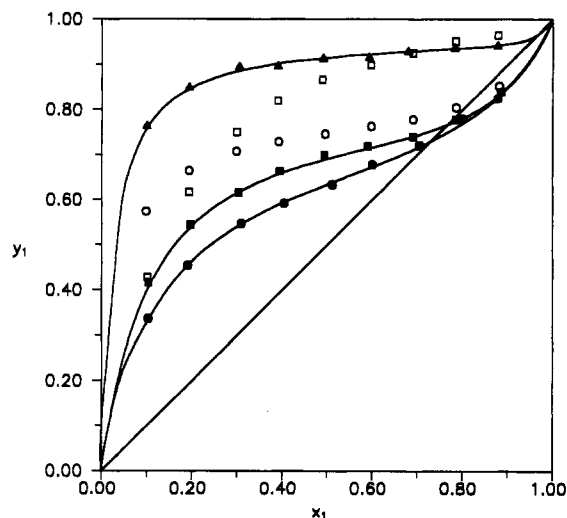


Figure 1. Equilibrium diagrams for methyl acetate (1) + methanol (2) and methyl acetate (1) + methanol (2) + salt (3) systems. Symbols represent experimental values: ●, without salt; ■, + CH₃COOK; ▲, + LiCl; ○, + CaCl₂; □, + Ca(NO₃)₂. The lines correspond to the correlation with the Wilson equation.

values for the vapor pressures (kPa) of the pure components at 298.15 K were taken from the literature: 28.82 for methyl acetate (11) and 16.93 for methanol (12).

The methyl acetate + methanol, methyl acetate + methanol + CH₃COOK, and methyl acetate + methanol + LiCl data were used to obtain the adjustable parameters in the van Laar (13), Wilson (14), NRTL (15), and NRTL-m (a modified NRTL equation) (16) equations by using a nonlinear regression method. For this purpose the following objective function, OF, was minimized:

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

where N is the number of experimental data points and the subscripts e and c mean experimental and calculated values, respectively.

The NRTL-m equation, proposed by Mato et al. (16), is a modification of the original NRTL model of Renon and Prausnitz (15). In the NRTL-m equation the nonrandomness parameter α_{ij} is expressed as a function of the two other parameters:

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

Table 3 summarizes the results of correlation for the systems methyl acetate + methanol (salt-free), + CH₃COOK, and + LiCl, 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. These were the systems previously determined as thermodynamically consistent. The

Table 3. Fitted Parameters (A_{12} , A_{21}) and Average Absolute Deviations in Vapor-Phase Mole Fractions (Δy_1) for Systems at 298.15 K

model	A_{12}	A_{21}	Δy_1
Methyl Acetate (1) + Methanol (2)			
Wilson	-10.371	449.07	0.0038
NRTL	236.06	163.53	0.0046
NRTL-m	236.96	178.01	0.0042
van Laar	1.1621	1.2435	0.0050
Methyl Acetate (1) + Methanol (2) + CH ₃ COOK (3)			
Wilson	-16.943	570.73	0.0055
NRTL	363.15	128.60	0.0052
NRTL-m	350.39	166.78	0.0052
van Laar	1.2619	1.5762	0.0054
Methyl Acetate (1) + Methanol (2) + LiCl (3)			
Wilson	-57.746	921.70	0.0044
NRTL	586.33	65.951	0.0060
NRTL-m	564.01	149.24	0.0056
van Laar	1.2940	2.1467	0.0062

unit of parameters A_{12} and A_{21} is kelvin for the Wilson, NRTL, and NRTL-m models; they are dimensionless for the van Laar model.

The most favorable effect for the separation of the azeotropic mixture methyl acetate + methanol is obtained with calcium nitrate and lithium chloride, since the azeotrope disappears when both salts are added. Calcium nitrate is the most effective salt in the methyl acetate rich concentration range.

Registry Numbers Supplied by Author. Methyl acetate, 79-20-9; methanol, 67-56-1; potassium acetate, 127-08-2; lithium

chloride, 7447-41-8; calcium chloride dihydrate, 10035-04-8; calcium nitrate tetrahydrate, 13477-34-4.

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