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Vapor–Liquid Equilibrium Data for the Systems Acetone–Methanol and Methanol–Benzene in the Presence of Dissolved Salts

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The vapor–liquid equilibrium data at 760 mmHg pressure have been determined experimentally for the two binary systems, viz., acetone–methanol saturated with cadmium acetate and methanol–benzene saturated with magnesium acetate. The data obtained by using a Smith and Bonner type of equilibrium still were found to be thermodynamically consistent.

The advantages of using a salt as a separating agent in extractive distillation have been discussed by a few investigators (*2–5*). It has also been shown that a few systems, both aqueous and nonaqueous, exhibit departure from the general theory of salt effect in vapor–liquid equilibrium (*3*, *12–15*), vis., the presence of a dissolved salt would result in an increase in concentration in the equilibrium vapor of the component in which the salt was less soluble, due to the lowering of the vapor pressure of the other component in which it is more soluble. This work presents the isobaric vapor–liquid equilibrium data for two nonaqueous binary systems: (i) acetone–methanol saturated with cadmium acetate and (ii) methanol–benzene saturated with magnesium acetate. Both the salts were found to be soluble in methanol and only very sparingly soluble in the other components. The nonaqueous systems have been chosen in this work for the reason that these have not been studied for the effect of salt to the extent the aqueous systems have been investigated (*6*, *7*).

Experimental Section

The vapor–liquid equilibrium data were determined in a Smith and Bonner type of still with an arrangement for magnetic stirring the description of which is given elsewhere (*16–18*). The experimental technique and procedure were the same as outlined in earlier papers of one of the authors (*14*, *15*) excepting for the modification in the liquid composition estimation method. In this investigation, the liquid-phase composition was determined at the end of the run by evaporating to dryness the liquid mixture and then analyzing the condensate for composition by the density measurement at 30 ± 0.05 °C. The equilibrium data were determined at atmospheric pressure which remained constant in the range 760 ± 3 mmHg. To ensure saturation of the boiling liquid mixture with salt, the latter was added slightly in excess before starting every run.

Table I. Physical Properties of Solvents

	lit. (*19*, *20*)			obsd		
solvent	bp, °C	sp gr at 30 °C	RI[a] at 30 °C	bp, °C	sp gr at 30 °C	RI[a] at 30 °C
acetone	56.1	0.7790	1.3536	56.2	0.7780	1.3539
methanol	64.5	0.7825	1.3262	64.6	0.7821	1.3260
benzene	80.1	0.8684	1.4952	80.1	0.8681	1.4875

[a] RI = refractive index.

The components purified by fractional distillation were used in the work. The physical properties of these components measured at 30 °C are shown compared with the corresponding literature values (*19*, *20*) in Table I. These chemicals were supplied by B.D.H. (Ltd.), Bombay, and Sarabhai Merck Ltd., Bombay. The salts used in this work were of AnalaR/laboratory grade and supplied by Sarabhai Merck Chemicals and B.D.H. (Ltd.), Bombay. The performance of the equilibrium still for the determination of data in the presence of dissolved salts was earlier assessed by studying the system cyclohexane–carbon tetrachloride–ammonium sulfate. The data thus obtained compared well with the reported data (*15*) for this system.

Presentation and Discussion of the Results

The experimental data in the presence of salts are shown in Tables II and III and plotted as x-y and t-x-y diagrams with the compositions expressed on a salt-free basis in Figures 1–4. The reported y-x data for the two systems without salt (*8*) are also shown in respective figures. Besides these, the figures

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Table II. Vapor-Liquid Equilibrium Activity Coefficient Data (Experimental and Calculated) for the System Acetone (1)-Methanol (2) Saturated with Cadmium Acetate

exptl					calcd				
x_1	y_1	t, °C	γ_1	γ_2	γ_1	γ_2	t, °C	y_1	y_2
0	0	70.6							
0.110	0.255	63.9	1.901	1.0828	2.123	1.019	64.3	0.2884	0.7126
0.325	0.492	60.5	1.382	1.1170	1.414	1.136	60.0	0.4934	0.5076
0.455	0.571	59.1	1.208	1.2360	1.225	1.245	58.8	0.5748	0.4277
0.510	0.612	58.3	1.179	1.2883	1.1706	1.298	58.4	0.6074	0.3947
0.571	0.655	58.2	1.137	1.3040	1.123	1.363	58.0	0.6432	0.3574
0.871	0.871	58.8	0.995	1.6380	1.009	1.781	57.4	0.8643	0.1367
1.000	1.000	57.9							

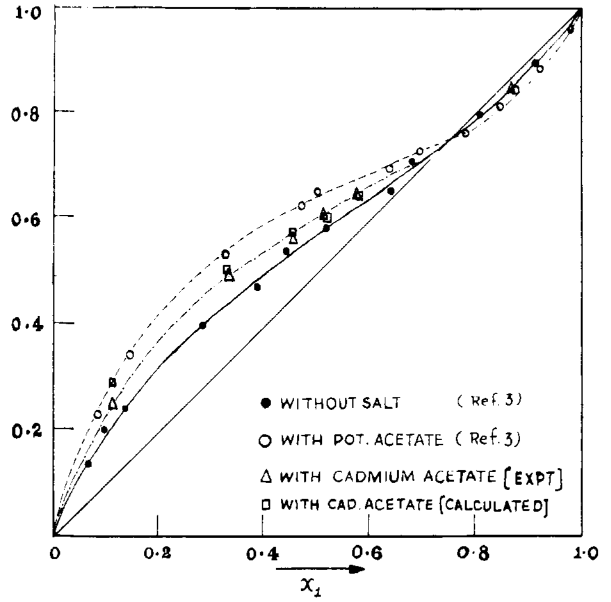

Figure 1. y-x data for acetone (1)-methanol (2)-cadmium acetate (experimental and calculated): ●, without salt (3); ○, with potassium acetate (3); △, with cadmium acetate (experimental); □, with cadmium acetate (calculated).

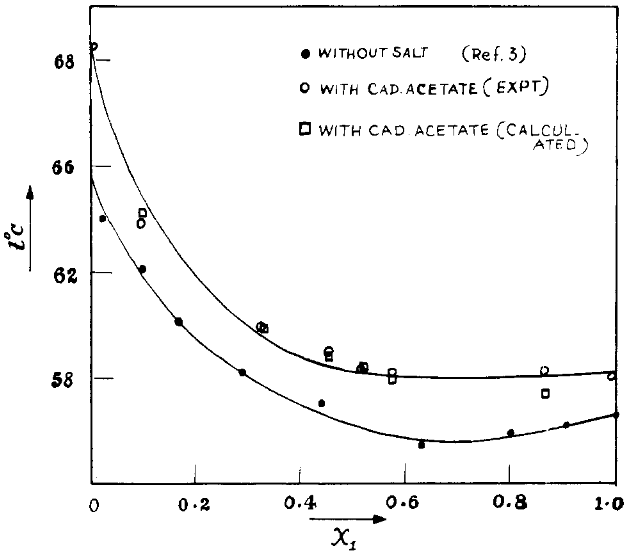

Figure 2. t-x diagram for acetone (1)-methanol (2)-cadmium acetate (experimental and calculated): ●, without salt (3); △, with cadmium acetate (experimental); □, with cadmium acetate (calculated).

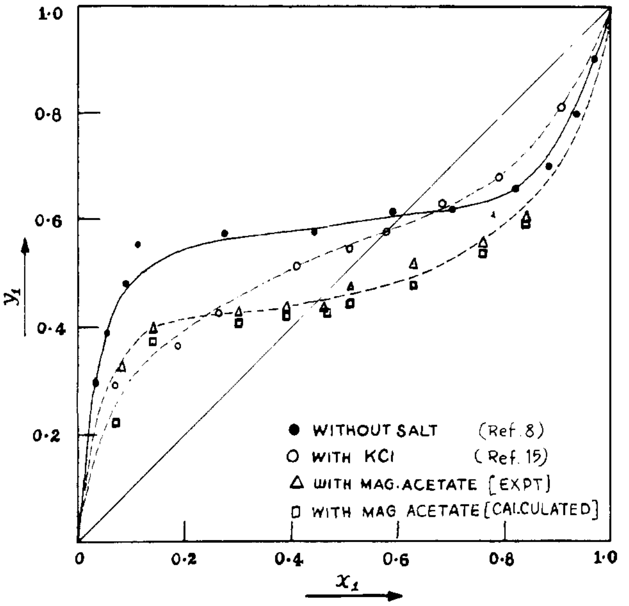

Figure 3. y-x data for methanol (1)-benzene (2)-magnesium acetate: ●, without salt (8); ○, with KCl (15); △, with magnesium acetate (experimental); □, with magnesium acetate (calculated).

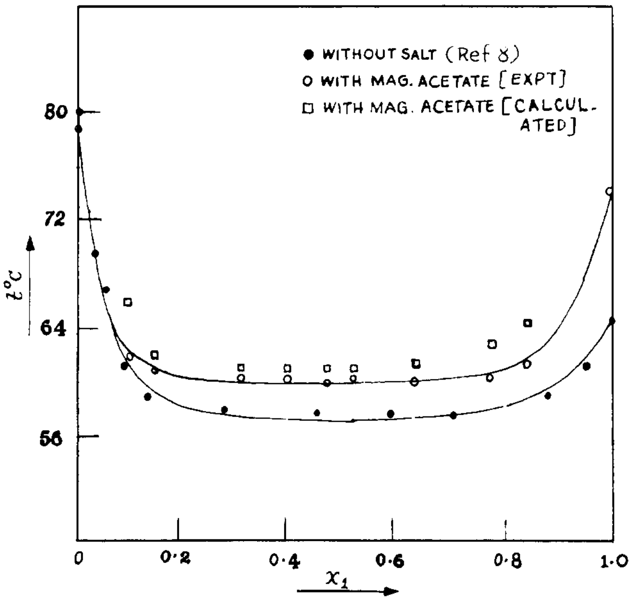

Figure 4. t-x diagram for methanol (1)-benzene (2)-magnesium acetate: ●, without salt (8); △, with magnesium acetate (experimental); □, with magnesium acetate (calculated).

show the reported data for the respective systems in the presence of other salts. In the case of acetone-methanol-cadmium acetate there is practically no change in the azeotropic composition and there is only an increase in the relative volatility of acetone with respect to methanol, while for methanol-benzene the azeotropic composition gets shifted from 0.605 without salt to 0.440 mole fraction of methanol on adding the magnesium acetate salt to saturation level. In addition there is a significant decrease in the relative volatility of methanol.

The liquid-phase activity coefficient was computed by applying the correction for saturation vapor pressure of components in

Table III. Vapor-Liquid Equilibrium and Activity Coefficient Data (Experimental and Calculated) for the System Methanol (1)-Benzene (2) Saturated with Magnesium Acetate

exptl					calcd				
x_1	y_1	t, °C	γ_1	γ_2	γ_1	γ_2	t, °C	y_1	y_2
0.075	0.315	62.1	6.659	1.275	4.0206	1.246	66.3	0.2248	0.7742
0.141	0.395	60.9	4.462	1.360	4.2240	1.252	62.0	0.3750	0.6230
0.305	0.430	60.2	2.330	1.512	2.2020	1.500	61.3	0.4114	0.5895
0.385	0.440	60.0	1.470	1.688	1.7992	1.668	61.2	0.4226	0.5780
0.465	0.455	59.8	1.697	1.901	1.5372	1.874	61.2	0.4361	0.5698
0.511	0.431	60.0	1.450	1.978	1.4260	2.013	61.2	0.4445	0.5546
0.625	0.515	59.6	1.440	2.432	1.2290	2.447	61.6	0.4760	0.5240
0.761	0.552	60.2	1.235	3.451	1.0890	3.213	62.9	0.5406	0.4600
0.840	0.590	61.6	1.132	4.489	1.0395	3.868	64.5	0.6070	0.3900

the presence of dissolved salts suggested by Furter et al. (*10*). The relationship used was

$$\gamma_i = y_i P / x_i P_i'$$

where x and y are on a salt-free basis and p_i' is the corrected vapor pressure given by $p_i' = p_i^0 \epsilon_i$ in which p_i^0 is the saturation vapor pressure in the absence of salts at system temperature and ϵ_i the correction factor. The correction factors for the components as determined by the method followed by Furter (*10*) are as follows: for acetone (1)-methanol (2)-cadmium acetate $\epsilon_1 = 0.9441$, $\epsilon_2 = 0.7993$; for methanol (1)-benzene (2)-magnesium acetate $\epsilon_1 = 0.7020$, $\epsilon_2 = 1.048$. The vapor pressure values at the desired temperatures were computed by the Antoine equation with the constants taken from literature (*11*). The activity coefficients thus determined (assuming the vapor phase to be ideal) are presented in Tables II and III.

The thermodynamic consistency of the experimental equilibrium data was assessed by the Black test (*1*), that is, by plotting $(\log \gamma_1)^{0.5}$ against $(\log \gamma_2)^{0.5}$. The above plot resulted in straight lines for both the systems showing consistency of the data with van Laar equations. Herington's criteria (*9*) were also applied to both binary systems to check the thermodynamic consistency. The values of the D and J terms for the two systems are as follows: acetone (1)-methanol (2)-cadmium acetate $D = 10.15$, $J = 2.716$; methanol (1)-benzene (2)-magnesium acetate $D = 10.30$, $J = 1.12$. It can be seen from the above that the relation $J + 10 > D$ is satisified for both systems.

In the present investigation the experimental y-x data were correlated with the two-constant Wilson equations (*21*) with the constants in these equations obtained by a least-squares fit of the experimental activity coefficient using a nonlinear multiple regression technique on an IBM 1130 computer.

The constants Λ_{12} and Λ_{21} of the correlating equation used in this investigation are as follows: acetone (1)-methanol (2)-cadmium acetate $\Lambda_{12} = 0.3499$, $\Lambda_{21} = 0.9498$; methanol (1)-benzene (2)-magnesium acetate $\Lambda_{12} = -0.0517$, $\Lambda_{21} = 0.4703$.

On the basis of the values of calculated activity coefficients, the calculated values of vapor compositions and the corresponding equilibrium temperatures were obtained, the calculated values of equilibrium temperatures being established by adjusting them such that the constraint $y_1 + y_2 = 1.0$ is met for all the selected liquid compositions. The calculated vapor compositions and equilibrium boiling temperatures are shown in Tables II and III for the two systems studied. The average deviation was calculated as

$$\text{average deviation} = (\Sigma\sigma^2/n)^{1/2}$$

where $= \gamma_{i(\text{exptl})} - y_{i(\text{calcd})}$ and n = number of experimental points. The average deviations are given in Table IV.

Table IV. Average Deviation

system	vapor mole fraction y_i	equilibrium temp, °C
acetone (1)-methanol (2)-cadmium acetate	0.01489	0.647
methanol (1)-benzene (2)-magnesium acetate	0.0360	2.226

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Glossary

D	percentage deviation $(10^2 I/\Sigma)$
I	difference between the area above and below the abscissa of the plot $\log \gamma_1/\gamma_2$ vs. x_1 or $I = \int_0^1 \log \gamma_1/\gamma_2 \, dx_1$
J	$150\theta/T_{\min}$
P	system pressure, mmHg
P_i^0	saturation vapor pressure of component i in the absence of salts
P_i'	corrected vapor pressure of component i
$T_{\max}$	highest boiling temperature in the system, K
$T_{\min}$	lowest boiling point in the system, K
x_i	mole fraction of component i in the liquid phase on a salt-free basis
y_i	mole fraction of component i in the vapor phase on a salt-free basis

Greek Letters

γ_i	activity coefficient of component i
θ	difference between the maximum and minimum boiling points
ϵ_i	correction factor for the computation of the activity coefficient given by P/p_i^0 where p_i^0 is the vapor pressure of the pure component i at the temperature at which component i boils in the presence of salt under a saturated condition.
Σ	area above the 0 axis of $\log \gamma_1/\gamma_2$ plus the area below it without regard to sign

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Effect of Sodium Nitrate on the Vapor–Liquid Equilibria of the Methanol–Water System

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The effect of sodium nitrate on the vapor–liquid equilibria of the methanol–water system has been investigated under the atmospheric conditions of 760 ± 3 mmHg pressure by using a Smith and Bonner type of equilibrium still. Experiments were carried out at various concentrations of salt. The addition of increased amounts of salt enhanced the relative volatility of methanol and seemed to decrease the activity coefficients of the components of the system. The results obtained are indicative of the possible hydration and hydrotropism of ions for the methanol–water system. The improvement factor (i.e., the ratio of relative volatilities with and without salt present) could be correlated semiempirically as a function of salt concentration in the manner suggested by Johnson and Furter, showing a linear dependence of the salt effect on the salt concentration of the liquid.

An important technique in extractive distillation is the use of inorganic salt as extractive agent to modify the relative volatility of the binary mixture. As the addition of salt to a binary solution has a notable effect on the vapor–liquid equilibrium of the system, it has been the normal tendency for investigators to conduct these studies under saturated conditions of the salt though the addition of relatively small amounts of salts may serve the purpose in either shifting appreciably or breaking the azeotrope in the case of binary azeotropic systems or in enhancing the relative volatility of the desired component in the case of nonazeotropic systems comprising components exhibiting almost the same volatilities. It would also be desirable to ascertain in such studies how the improvement factor varies with varying concentrations of the salt in question. A few investigations reported (*1*, *5*, *9*, *11*, *13*, *17*) about the effect of the addition of salts of varying concentrations have also included correlation of salt effect with the salt concentration of the liquid. Both methods of correlation, the "improvement factor" method and the "special binary" method have been dealt with in detail by Furter (*2*, *3*). The results from a similar study of the effect of sodium nitrate on the vapor–liquid equilibrium relationships of methanol–water systems are described in this presentation.

Experimental Section

The vapor–liquid equilibrium data were determined by using a Smith and Bonner type of still with an arrangement for magnetic stirring. The description and working of the still have been detailed elsewhere (*15*, *16*). The experimental technique and procedure were the same as described in earlier papers (*12*, *13*) except for the modification in the liquid composition estimation method. The liquid sample at the end of each run was analyzed for its methanol content on a salt-free basis by first separating it quantitatively into salt and methanol–water fractions by a total distillation technique of evaporation to dryness and then analyzing for the alcohol–water ratio. The vapor samples were analyzed directly by the specific gravity–composition method with the specific gravities determined at 30 ± 0.05 °C. The vapor–liquid equilibrium data for the methanol–water system were obtained at three concentrations of sodium nitrate salt, the concentrations being 0.05, 0.07, and 0.08 mole fraction of salt in the ternary mixture. The salt concentrations in the liquid were established by adding known weights of dried salt to known quantities and compositions of alcohol–water mixtures previously prepared. The equilibrium data were determined at atmospheric pressure which remained constant in the range 760 ± 3 mmHg. The methanol and sodium nitrate used were BDH AnalaR reagent grade and the water was laboratory distilled.

The performance of the equilibrium still for the determination of data in the presence of dissolved salts was earlier assessed by measuring data for the system cyclohexane–carbon tetrachloride–ammonium sulfate, the salt being present under saturated condition. The vapor–liquid equilibrium data obtained compared well with the reported data (*13*) for this system.

Results

The experimental results on the vapor–liquid equilibrium of methanol–water at three concentrations of sodium nitrate, viz., 0.05, 0.07, and 0.08 mole fraction, are presented on a salt-free basis in Table I and plotted as an x–y diagram in Figure 1. The binary data (i.e., without sodium nitrate present) reported in ref 4 and those of Johnson and Furter (*8*) under saturated sodium nitrate have also been included in the figure for comparison purpose. To study the effect of salt, we computed the improvement factor which is the ratio of relative volatilities with and without salt present for varying concentrations of the salt at various fixed values of x_1, the methanol mole fraction employing the data in the presence of salt obtained in this investigation and the reported binary data (*4*) in the absence of salt. The values of $\ln (\alpha_S/\alpha)$ thus calculated and presented in Table II are also plotted against salt concentrations for the various

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