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Salt Effects in Vapor–Liquid Equilibria. Effects of Dissolved Salts on the Vapor–Liquid Equilibrium Relationships of Three Miscible Nonaqueous Binary Systems and One Partially Miscible Binary System

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The vapor–liquid equilibrium (VLE) data determined experimentally at 760 torr for three nonaqueous and completely miscible binary systems, viz., (I) carbon tetrachloride–2-propanol saturated with calcium chloride, (II) acetone–carbon tetrachloride saturated with potassium iodide, and (III) acetone–chloroform saturated with potassium iodide, and for the partially miscible binary system methyl ethyl ketone–water saturated with sodium chloride are reported. The second and third miscible systems exhibit anomalous behavior (viz., crossover effect) from the general theory of salt effects in vapor–liquid equilibria. The data for the three miscible systems have been checked for their thermodynamic consistency and also correlated satisfactorily by choosing the Wilson model for the activity coefficient–composition relationship.

Introduction

A salt dissolved in a mixed solvent is capable, through preferential association or other structure-related effects in the liquid phase, of altering the composition of the equilibrium vapor phase. Hence, salt effects on vapor–liquid equilibrium relationships provide a potential technique of extractive distillation for difficult separations. A good amount of work has been reported in the literature concerning salt effects on the vapor–liquid equilibria for many binary systems with a variety of salts (*1–3*). However, much of the reported work covers mainly aqueous miscible systems, and data on nonaqueous and partially miscible systems are rather fragmentary.

In a continuing study (*4–9*) of salt effects on the VLE of nonaqueous binary systems and salt-mixture effects on aqueous ones, the following systems have been studied in the present investigation: (i) carbon tetrachloride–2-propanol* in the presence of calcium chloride, (ii) acetone*–carbon tetrachloride in the presence of potassium iodide, and (iii) acetone*–chloroform in the presence of potassium iodide again, the salts being present under saturated conditions. To find out the effect of dissolved salt on the VLE of a partially miscible system, we have also studied the system methyl ethyl ketone–water*–sodium chloride. The asterisks shown above denote the components in which the salt in question is more soluble.

Table I. Physical Properties of Solvents

solvent	lit. (*10, 11*) bp, K	lit. sp gr at 303.2 K	lit. n^a at 303.2 K	obsd bp, K	obsd sp gr at 303.2 K	obsd n^a at 303.2 K
acetone	329.2	0.7790	1.3536	329.3	0.7780	1.3539
carbon tetrachloride	349.9	1.5748	1.4519	350.1	1.5625	1.452
chloroform	334.3	1.4706	1.3886	334.3	1.4685	1.360
methyl ethyl ketone	352.8	0.7946	1.3760	352.8	0.7905	1.373
2-propanol	355.7	0.7770	1.3732	355.7	0.7724	1.3715

[a] Refractive index.

Experimental Section

Chemicals. The components (both the liquid and the solid) used in the present investigation were of the AnalaR/LR quality. The solvents were further purified by fractional distillation. The physical properties of these solvents measured at 30 °C are compared with the corresponding literature values (*10*, *11*) in Table I.

Equilibrium Still and Analytical Technique. The vapor–liquid equilibrium data were determined in a Smith and Bonner type (*12*) of still with an arrangement for magnetic stirring the description of which is given elsewhere (*13*, *14*). This type of still was chosen so as to enable the study of the partially miscible system also. The experimental procedure and the analytical technique for the liquid- and vapor-phase samples were the same as outlined by one of us in earlier papers (*6–8*).

The equilibrium data were obtained at atmospheric pressure, viz., 760 ± 3 torr. The saturated condition of the salt in the liquid mixture was ensured by adding the salt slightly in excess before starting every run. As for the partially miscible system methyl ethyl ketone–water (in the presence of dissolved sodium chloride), cloudy or two-phase samples were analyzed by the density–composition method, after the addition of measured quantities of distilled water to bring them within the homogeneous region. The boiling temperature and concentration measurements for all of the systems studied were generally accurate to ±0.1 K and ±0.005 mole fraction, respectively.

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Table II. Vapor-Liquid Equilibrium and Activity Coefficients (Experimental and Calculated) for the System Carbon Tetrachloride (1)-2-Propanol (2) Saturated with Calcium Chloride

	exptl				calcd			
x_1	y_1	t, K	γ_1	γ_2	γ_1	γ_2	t, K	y_1
0	0	357.2						
0.0325	0.1300	352.8	3.7550	1.075	3.3846	1.0010	354.7	0.1239
0.1260	0.3600	347.8	3.1417	1.0825	2.9224	1.0137	349.5	0.3550
0.1900	0.4400	345.0	2.7606	1.1562	2.6545	1.0321	347.1	0.4517
0.3900	0.6180	342.3	2.0580	1.1835	2.0059	1.1592	342.9	0.6149
0.5270	0.6780	341.7	1.6970	1.3350	1.6823	1.3471	341.8	0.6712
0.6500	0.7110	341.5	1.4553	1.6250	1.4506	1.6680	341.3	0.7043
0.7775	0.7450	341.8	1.2644	2.2163	1.2551	2.4122	341.3	0.7287
0.8100	0.7500	341.95	1.2160	2.5270	1.2112	2.7668	341.4	0.7335
0.8750	0.7775	343.4	1.1124	3.1920	1.1299	4.0371	341.6	0.7428
0.9280	0.8200	345.0	1.0534	4.1810	1.0693	6.7740	341.8	0.7494
1.0000	1.0000	350.7						

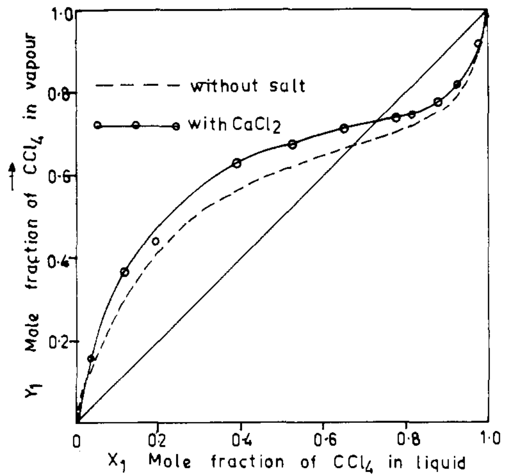

Figure 1. Plot of y_1 vs. x_1 for carbon tetrachloride (1)-2-propanol (2)-calcium chloride.

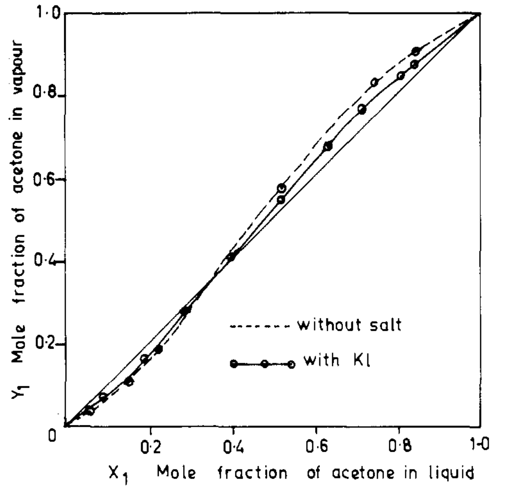

Figure 3. Plot of y_1 vs. x_1 for acetone (1)-chloroform (2)-potassium iodide.

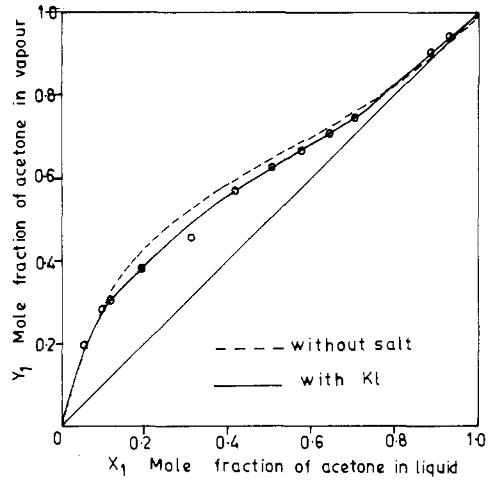

Figure 2. Plot of y_1 vs. x_1 for acetone (1)-carbon tetrachloride (2)-potassium iodide.

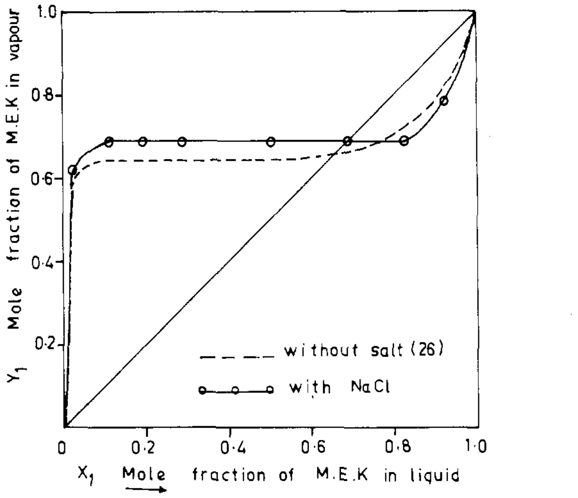

Figure 4. Plot of y_1 vs. x_1 for methyl ethyl ketone (1)-water (2)-sodium chloride.

Presentation and Discussion of the Results

The experimental VLE data in the presence of dissolved salts for the four systems studied in the present work are shown in Tables II-V and plotted as x-y diagrams in Figures 1-4, the compositions being expressed on a salt-free basis. These figures also contain the reported data for the corresponding four systems without salt (*15*).

The system carbon tetrachloride-2-propanol in the presence of saturated calcium chloride exhibits behavior which is in conformity with salt-effect generalizations on vapor-liquid equilibria in that the calcium chloride "salts in" the component (in this case 2-propanol) in which it is more soluble. There is also significant change in the azeotropic composition, from 0.667 mole fraction of carbon tetrachloride in the absence of salt to 0.725 in the presence of calcium chloride.

In the case of the acetone-carbon tetrachloride system, the salt potassium iodide "salts in" acetone, in which it is more soluble, in the carbon tetrachloride rich region and "salts out" acetone (enhancement of relative volatility) in the acetone-rich region. In other words, it exhibits the anomaly of a "crossover effect" as the liquid composition is varied. Furter and Meranda (*16*) categorize this as type 1 anomalous behavior. Hence, in this system it can be safely conjectured that at least two major interaction mechanisms involving the salt occur in the structure

Table III. Vapor-Liquid Equilibrium and Activity Coefficients (Experimental and Calculated) for the System Acetone (1)-Carbon Tetrachloride (2) Saturated with Potassium Iodide

	exptl				calcd			
x_1	y_1	t, K	γ_1	γ_2	γ_1	γ_2	t, K	y_1
0	0	349.4						
0.0980	0.2800	342.3	1.9225	0.9917	2.3495	1.0252	339.87	0.3154
0.1150	0.3030	341.1	1.8948	1.0217	2.2021	1.0331	339.13	0.3388
0.1900	0.3800	338.6	1.5205	1.0770	1.7543	1.0757	336.9	0.4150
0.3030	0.4550	335.7	1.2542	1.2111	1.4036	1.1557	334.8	0.4950
0.4125	0.5750	333.7	1.2436	1.1986	1.226	1.2452	333.5	0.5623
0.5050	0.6200	332.5	1.1400	1.3250	1.1361	1.3276	332.6	0.6190
0.5730	0.6670	331.7	1.1100	1.3834	1.0912	1.3914	332.0	0.6620
0.6400	0.7040	331.3	1.0635	1.4788	1.0391	1.4569	331.5	0.7063
0.7000	0.7500	330.9	1.0499	1.5196	1.038	1.5174	331.2	0.7480
0.7920	0.8170	330.3	1.0316	1.6380	1.0164	1.6134	330.7	0.8170
0.8150	0.8400	330.2	1.0342	1.6158	1.0127	1.638	330.7	0.8351
0.8925	0.9100	330.0	1.0300	1.575	1.0039	1.7225	330.4	0.9002
0.9370	0.9450	329.9	1.0224	1.6482	1.0013	1.772	330.4	0.9400
1.0000	1.0000	330.3						

Table IV. Vapor-Liquid Equilibrium and Activity Coefficients (Experimental and Calculated) for the System Acetone (1)-Chloroform (2) Saturated with Potassium Iodide

	exptl				calcd			
x	y	t, K	γ_1	γ_2	γ_1	γ_2	t, K	y_1
0	0	334.2						
0.0870	0.0670	335.7	0.6432	0.9740	0.5969	0.9952	335.23	0.0612
0.1900	0.1625	336.5	0.6970	0.9622	0.6671	0.9776	336.25	0.1545
0.2880	0.2775	337.4	0.7615	0.9164	0.7318	0.9496	336.9	0.2626
0.2925	0.2730	337.3	0.7400	0.9310	0.7346	0.9480	337.0	0.2680
0.3930	0.4000	337.3	0.8070	0.8955	0.7969	0.9087	337.2	0.3936
0.5200	0.5510	337.0	0.8483	0.8555	0.8673	0.8463	336.8	0.5593
0.629	0.6850	335.8	0.9067	0.8067	0.9181	0.7837	335.8	0.6939
0.715	0.7625	334.7	0.9205	0.8200	0.9506	0.7298	334.8	0.7887
0.803	0.8580	333.3	0.9660	0.7420	0.9759	0.6118	333.8	0.8810
0.836	0.8900	333.0	0.9425	0.6984	0.9832	0.6496	332.9	0.8980
0.922	0.9480	331.3	0.9962	0.7143	0.9959	0.5921	330.7	0.9896
1.000	1.0000	330.3						

Table V. Vapor-Liquid Equilibrium Data for the System Methyl Ethyl Ketone (1)-Water (2) Saturated with Sodium Chloride

x_1	y_1	t, K	x_1	y_1	t, K
0	0	379.0	0.6900	0.6900	346.6
0.0387	0.6230	349.7	0.7460	0.6900	346.1
0.1100	0.6900	347.4	0.8334	0.6900	347.9
0.1900	0.6890	347.2	0.9128	0.7850	348.7
0.3804	0.6900	347.1	1.0000	1.0000	350.9
0.5050	0.6910	347.3			

complex. Each mechanism should be composition dependent (as evidenced by the behavior of the system), and each should have an effect quite different from that of the other. The individual mechanisms appear to dominate the overall salt effect in a different region of the range of mixed solvent composition. It has also been observed that the addition of potassium iodide under saturated conditions helps in breaking the azeotrope which otherwise is encountered in this system at a mole fraction of 0.952 of acetone.

A similar crossover effect has been noticed in the case of the acetone-chloroform system (a maximum-boiling azeotropic one) when potassium iodide is added under saturated conditions. But the sequence of occurence of salting in and salting out is reversed. Firstly, the acetone component is salted out and then the salting in follows in the acetone-rich region. A slight shift in the azeotropic composition has also been effected.

In the partially miscible system methyl ethyl ketone-water, a shift in the heterogeneous azeotropic composition from 0.665 to 0.690 mole fraction of methyl ethyl ketone is observed in the presence of dissolved sodium chloride. The salt being highly soluble in water enhanced the mole fraction of methyl ethyl ketone in the vapor phase. The temperature and the vapor composition remain constant at 74 °C and 0.690 mole fraction, respectively, throughout the miscibility gap from 0.110 to 0.833 mole fraction of methyl ethyl ketone in the liquid phase.

The liquid-phase activity coefficient (γ) was computed for the three miscible systems by applying the correction for saturation vapor pressure of the components in the presence of dissolved salts by the method suggested by Furter and Jaques (*17*) as detailed in earlier papers by one of us (*4-8*). The correction factors (ϵ's) for the components obtained from the tabulated boiling-point data for each system (Tables II-IV) when x_1 is 0 and 1, using the method of Furter and Jaques (*17*), are as follows: for carbon tetrachloride (1)-2-propanol (2)-calcium chloride, $\epsilon_1 = 0.9712$ and $\epsilon_2 = 0.9298$; for acetone (1)-carbon tetrachloride (2)-potassium iodide, $\epsilon_1 = 0.9673$ and $\epsilon_2 = 1.010$; and for acetone (1)-chloroform (2)-potassium iodide, $\epsilon_1 = 0.9673$ and $\epsilon_2 = 1.0238$. The vapor-pressure values at the desired temperatures were calculated by the Antoine equation with the constants taken from the literature (*18*). The activity coefficients thus determined (assuming the vapor phase to be ideal) are recorded in Tables II-IV for the three miscible systems.

The thermodynamic consistency of the experimental data was assessed by employing both Black's test (*19*) and Herington's criteria (*20*) on the Redlich-Kister area test (*21*), and the data were found to be consistent.

The experimental VLE data for the three miscible systems were correlated by the Wilson equation (*22*) with the constants in the equation obtained by a least-squares fit of the experimental activity coefficients using a nonlinear multiple regression technique on an IBM 1130 computer. The constants Λ_{12} and Λ_{21} of the correlating Wilson equation used in this investigation are as follows: for carbon tetrachloride (1)-2-propanol (2)-calcium chloride, $\Lambda_{12} = 0.01705$ and $\Lambda_{21} = 0.7563$; for ace-

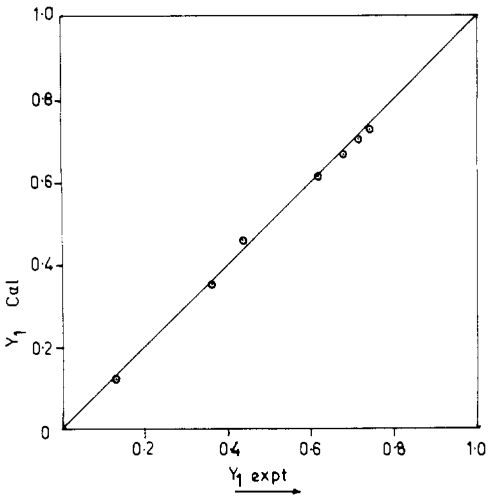

Figure 5. Plot of y_1(exptl) vs. y_1(calcd) for carbon tetrachloride (1)–2-propanol (2)–calcium chloride.

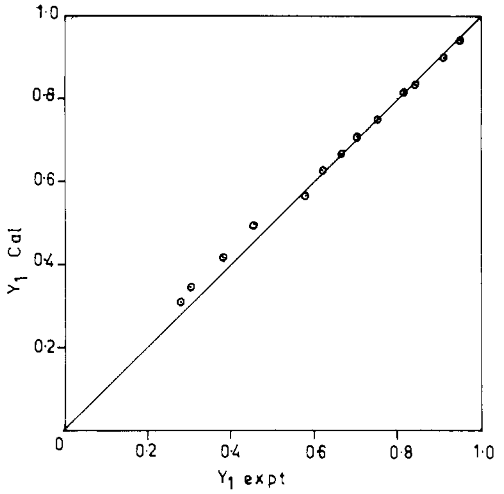

Figure 6. Plot of y_1(exptl) vs. y_1(calcd) for acetone (1)–carbon tetrachloride (2)–potassium iodide.

tone (1)–carbon tetrachloride (2)–potassium iodide, Λ_{12} = 0.2046 and Λ_{21} = 1.201; for acetone (1)–chloroform (2)–potassium iodide, Λ_{12} = 1.3338 and Λ_{21} = 1.3336. On the basis of the values of calculated activity coefficients, the calculated values of vapor compositions y_1 and y_2 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 of the selected liquid compositions. The calculated vapor compositions and the equilibrium boiling temperatures are also shown in Tables II–IV for the systems processed. It can be seen that there is fair agreement between the experimental and calculated values of vapor compositions and equilibrium temperatures. Figures 5–7 show the plot of experimental vs. calculated vapor compositions for the systems studied.

Glossary

t	temperature, 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

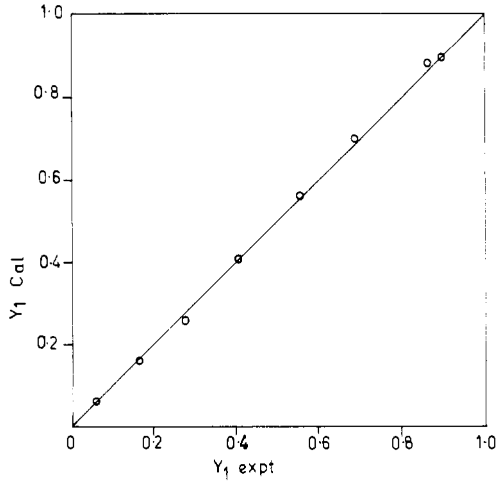

Figure 7. Plot of y_1(exptl) vs. y_1(calcd) for acetone (1)–chloroform (2)–potassium iodide.

Greek Letters

γ_i	activity coefficient of component i in the liquid phase
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 saturated conditions and P, the system pressure, torr
Λ_{ij}	constants in the Wilson equation for any components i and j, dimensionless

Subscripts

1	low-boiling component
2	high-boiling component

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