

Salt Effects in Isobaric Vapor-Liquid Equilibria of Acetone–Methanol System

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Experimental data are reported on the vapor-liquid equilibria of the acetone–methanol system saturated with the following nonvolatile salts: KSCN, NaSCN, NaI, NaBr, CH₃COOK, and LiCl, at atmospheric pressure. Observed effects include salting-out, crossover between salting-in and salting-out, and azeotrope disappearance. The various patterns of behavior of these systems are analyzed and qualitatively discussed.

This paper reports on the first series of experimental observations obtained in the course of a research program on the investigation of vapor-liquid equilibria at constant pressure in the presence of nonvolatile salt compounds.

A noteworthy research effort has been devoted in recent years to the variations of volatility of systems containing electrolyte solutions. Among the reasons for this interest, it might be pointed out that several systems which entail difficulties in fractionation because of azeotropic effects can profit by the enhancement of relative volatilities caused by salts in an extractive distillation operation.

The IHI Co. has investigated on a pilot scale such systems and reached the conclusion that remarkable advantages can be gained through the use of an agent such as calcium chloride instead of benzene in the extractive distillation of the isopropyl alcohol–water system (7).

A thorough coverage of the literature on this subject has been published by Sergeeva (10) and by Furter and Cook (7). Theoretical endeavors in this field have met with scant success, so far. The variety of molecular interactions in the liquid phase, already hard to cope with in the absence of electrolytes, due to polarity and association effects, are made more complex by the presence of the ionic component.

Semiempirical correlations have been developed, but they cannot avoid using ternary system equilibrium data [solvent(1)–solvent(2)–salt]. Among these, one of the most accurate is the Hala method of correlation (2). Such procedures, validated only for isothermal systems, are inappropriately applied to constant pressure systems as well. In the latter, great uncertainty can be caused by lack of knowledge about the important thermal effects in the mixing of this kind of solution. The extension of the scaled particle theory to estimate the limit coefficient of salt–solvent interaction at vanishingly small salt concentrations is of interest (5, 11, 12). The conclusions of Masterton and Lee (5) have been extended by Wilcox and Schrier (12) to polar systems (water–alcohol); acceptable agreement with experimental observations was reached. A general extension of the theory is hindered by the possibility of specific chemical associations which require a different theoretical treatment in each specific instance.

The great majority of the systems studied are water-containing solutions. The present report concerns a nonaqueous system, namely, that constituted by two commonplace solvents: acetone and methyl alcohol. This binary mixture is of

interest because of its low relative volatility and the presence of a homogeneous azeotrope.

Therefore, eventual effects of salting-out, observed in the majority of the experimental systems, that is, the increase of volatility of the component in which the salt is less soluble—acetone in our case—would be particularly evident.

We investigated saturated liquid solutions at their boiling temperature. These conditions are hardly comparable to the operating behavior of a fractionation column with an excess of undissolved salt. However, this type of measurement can show the maximum effect of relative volatility variation.

The system in question also has the experimental advantage of having a wide spectrum of salt solubilities in pure methanol and acetone, the solubilities in acetone being lower.

Experimental

The experimental assembly was essentially that used by Johnson and Furter (4), that is, an improved version of the classical Othmer recirculation still (8). Burner holes below the still were distributed on a circular section to evenly distribute the heat transfer and improve the mixing action due to boiling.

A magnetic stirrer was used to maintain a sufficient homogeneity of the liquid and to improve salt dissolution. At the same time it decreased irregularities in the boiling behavior such as blanketing, chugging, and sputtering. The sample was constituted by a few drops collected from the condensate chamber. It contained only the solvents, since the salts were nonvolatile. Distillate compositions were determined by means of a refractometer thermostated at 20 °C; bottom compositions were obtained from a material balance based on the quantities and weight concentrations of the starting components. To avoid a variation of the thermal sensor position, with regard to the free liquid surface, only one addition

Table I. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System at 758 ± 1 mm Hg

| <i>T</i> , °C | <i>x</i> ₁ ^a | <i>y</i> ₁ ^a |
|---------------|------------------------------------|------------------------------------|
| 67.7 | 0 | 0 |
| 64.0 | 0.020 | 0.042 |
| 62.8 | 0.062 | 0.132 |
| 61.8 | 0.097 | 0.187 |
| 60.95 | 0.130 | 0.240 |
| 60.35 | 0.165 | 0.285 |
| 58.4 | 0.282 | 0.405 |
| 57.4 | 0.382 | 0.475 |
| 56.85 | 0.445 | 0.532 |
| 56.35 | 0.515 | 0.587 |
| 55.8 | 0.628 | 0.663 |
| 55.65 | 0.720 | 0.730 |
| 55.65 | 0.800 | 0.800 |
| 55.6 | 0.805 | 0.805 |
| 55.95 | 0.910 | 0.900 |
| 56.40 | 0.977 | 0.970 |
| 56.5 | 1 | 1 |

^a Mole fractions.

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was carried out in each experiment before preparing a fresh experimental batch of known amount and composition.

The precise location of the temperature sensor, especially important because of the vertical temperature gradients, was determined by a calibration, using high-purity boiling water at a known pressure. The uncertainty of temperature measurements was thus limited to 0.1 °C, this error being comparable to the intrinsic temperature fluctuation due to atmospheric pressure. The runs were carried out with pressures varying within 3 mm Hg of their mean value. For systems without salt, the liquid-phase composition was analyzed by refractometry as well. Errors on phase compositions, due to hold-up in the condensation chamber and in the condenser and to the few drops withdrawn for sampling, are estimated as being less than 0.001 mol fraction, that is, within experimental uncertainties.

Temperature and composition readings were performed about 20 min after attainment of equilibrium conditions, that is, after reaching a stable temperature and checking on the presence of undissolved solid. Each of the determinations, i.e., temperatures and concentrations, were carried out with several repetitions. The standard deviation was derived and yielded reproducibilities in each case of the order of the cited uncertainties.

Methanol and acetone purity was 99.9 wt %; salts, 99 wt %; and NaSCN and KSCN, respectively, 98.5 and 99.5 wt %. Determination of the solubility of the salts at pure solvent boiling temperatures was performed by sampling about 10 cc of boiling liquid and weighing the sample and the residue after thorough evaporation of the solvent.

Table II. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System Saturated with KSCN at 757 ± 3 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 70.9 | 0 | 0 |
| 70.5 | 0.028 | 0.040 |
| 68.3 | 0.156 | 0.220 |
| 65.75 | 0.315 | 0.413 |
| 65.45 | 0.332 | 0.430 |
| 63.5 | 0.463 | 0.554 |
| 63.1 | 0.492 | 0.595 |
| 61.45 | 0.636 | 0.705 |
| 60.85 | 0.682 | 0.735 |
| 60.2 | 0.756 | 0.798 |
| 59.5 | 0.813 | 0.835 |
| 59 | 0.866 | 0.880 |
| 58 | 1 | 1 |

Table III. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System Saturated with NaSCN at 757 ± 2 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 79.7 | 0 | 0 |
| 77.4 | 0.159 | 0.232 |
| 77.15 | 0.168 | 0.238 |
| 74.5 | 0.332 | 0.475 |
| 74.3 | 0.355 | 0.490 |
| 71.2 | 0.534 | 0.660 |
| 70.5 | 0.577 | 0.700 |
| 67.6 | 0.761 | 0.845 |
| 66.5 | 0.804 | 0.890 |
| 65.5 | 0.906 | 0.958 |
| 62.0 | 1 | 1 |

Table I contains the experimental vapor-liquid equilibrium data for the acetone(1)–methanol(2) mixtures without salt. Tables II–VII show the experimental data with the six salts at saturation. Table VIII shows the salt solubilities in the pure solvents.

Discussion

Figure 1 shows the equilibrium data for the pure acetone–methanol system in $y_1 - x_1$ coordinates together with data from other authors as related by Hala et al. (3). Besides a relative volatility with slightly lower values in the region of inter-

Table IV. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System Saturated with NaI at 757 ± 2 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 80.4 | 0 | 0 |
| 79.95 | 0.029 | 0.053 |
| 77.5 | 0.137 | 0.220 |
| 74.85 | 0.230 | 0.380 |
| 74.25 | 0.224 | 0.398 |
| 70.7 | 0.389 | 0.568 |
| 69.7 | 0.417 | 0.605 |
| 67.15 | 0.531 | 0.725 |
| 66.1 | 0.573 | 0.755 |
| 63.4 | 0.720 | 0.845 |
| 62.3 | 0.783 | 0.885 |
| 59.65 | 0.956 | 0.980 |
| 59.1 | 1 | 1 |

Table V. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System Saturated with NaBr at 759 ± 1 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 67.3 | 0 | 0 |
| 66.2 | 0.030 | 0.076 |
| 62.4 | 0.158 | 0.298 |
| 62.1 | 0.167 | 0.307 |
| 58.95 | 0.330 | 0.470 |
| 58.6 | 0.353 | 0.490 |
| 56.8 | 0.532 | 0.608 |
| 56.5 | 0.575 | 0.634 |
| 55.8 | 0.741 | 0.745 |
| 55.75 | 0.799 | 0.800 |
| 56.0 | 0.922 | 0.915 |
| 56.45 | 1 | 1 |

Table VI. Vapor-Liquid Equilibrium Data of Acetone(1)–Methanol(2) System Saturated with CH_3COOK at 754 ± 1 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 73.7 | 0 | 0 |
| 68.55 | 0.075 | 0.235 |
| 68.1 | 0.086 | 0.245 |
| 64.95 | 0.146 | 0.362 |
| 64.7 | 0.152 | 0.375 |
| 59.5 | 0.321 | 0.536 |
| 59.2 | 0.334 | 0.550 |
| 57.3 | 0.466 | 0.622 |
| 57.0 | 0.496 | 0.640 |
| 56.05 | 0.645 | 0.702 |
| 55.8 | 0.692 | 0.731 |
| 55.6 | 0.780 | 0.775 |
| 55.65 | 0.843 | 0.815 |
| 55.8 | 0.912 | 0.901 |
| 56.25 | 1 | 1 |

Table VII. Vapor-Liquid Equilibrium Data of Acetone(1)-Methanol(2) System Saturated with LiCl at 757 ± 3 mm Hg

| $T, ^\circ\text{C}$ | x_1 | y_1 |
|---------------------|-------|-------|
| 96.4 | 0 | 0 |
| 93.2 | 0.029 | 0.150 |
| 96.8 | 0.071 | 0.330 |
| 84.6 | 0.100 | 0.410 |
| 83.6 | 0.110 | 0.455 |
| 82.8 | 0.117 | 0.481 |
| 74.8 | 0.216 | 0.678 |
| 73.0 | 0.236 | 0.705 |
| 69.2 | 0.284 | 0.755 |
| 68.85 | 0.303 | 0.755 |
| 65.65 | 0.371 | 0.831 |
| 63.7 | 0.413 | 0.860 |
| 60.65 | 0.535 | 0.885 |
| 59.55 | 0.570 | 0.895 |
| 57.7 | 0.732 | 0.925 |
| 57.15 | 0.794 | 0.941 |
| 56.65 | 0.892 | 0.965 |
| 56.55 | 0.914 | 0.975 |
| 56.4 | 1 | 1 |

mediate composition, a general agreement with our data is observed also for the azeotropic composition.

Figures 2-4 show the $y_1 - x_1$ equilibrium curves at atmospheric pressure with sodium and potassium thiocyanate, sodium iodide, sodium bromide, potassium acetate, and lithium chloride dissolved at saturation, obtained by smoothing the experimental results.

The behavior of NaSCN and KSCN is similar due to the close chemical characteristics and the nearly identical difference between their solubilities in pure boiling methanol and acetone.

Besides the azeotrope disappearance, a simultaneous presence of salting-in and salting-out effects can be observed, respectively, at the lower and higher acetone concentrations. This type of behavior was previously observed by several authors, as reported by Meranda and Furter (6), who classified this fact as the first type of anomaly with respect to the common rule of salting-out. It thus appears that the molecular interactions in the liquid phase are strongly composition dependent. In this case, it is possible to presume the existence of a strong association bond between ions and acetone molecules, which at lower acetone concentrations have a greater influence than the common effect of salting-out due to the greater solubility of the salts considered in methanol. The effect of NaI is qualitatively analogous to that of thiocyanates; the larger effect of the increase of the volatility and the shorter range of concentrations in which salting-in can be observed may be attributed to the greater difference between solubilities in pure methanol and acetone.

CH_3COOK and NaBr salts do not appreciably affect the azeotrope concentration; in the case of CH_3COOK , this can be explained because of a compensation of the acetone relative volatility increase, for $x_1 < x_{1 \text{ azeotr.}}$, with the increase of the methanol relative volatility for $x_1 > x_{1 \text{ azeotr.}}$. The variations of volatility in the two ranges depend upon the large difference of solubilities in the solvents. The very high solubility of LiCl at saturation in pure methanol causes an exceptional increase of the relative volatility of acetone.

The solutions containing NaI and LiCl were also experimentally investigated by Proszk and Kollar (9) at a constant salt concentration of 1 mol/l. These authors do not report numerical data, but it is possible to see an acceptable qualitative agreement with our measurements.

Table VIII. Salt Solubility Data (g of Salt/100 g of Solvent) in Pure Boiling Acetone and Methanol at 760 mm Hg

| | Acetone | Methanol |
|--------------------------|---------|----------|
| NaSCN | 26.5 | 63.9 |
| KSCN | 13.7 | 50.1 |
| NaI | 27.9 | 87.8 |
| NaBr | 0.1 | 16.5 |
| CH_3COOK | 0.1 | 99.4 |
| LiCl | 0.7 | 107.9 |

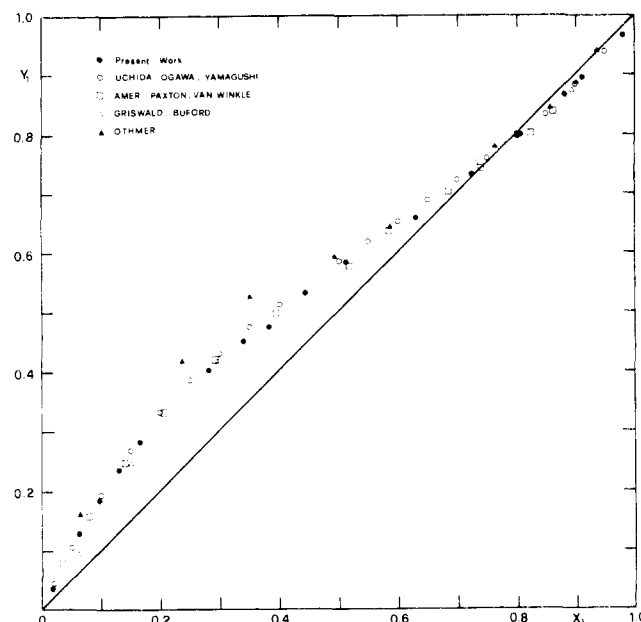


Figure 1. Vapor-liquid equilibrium of acetone(1)-methanol(2) system at 1 atm

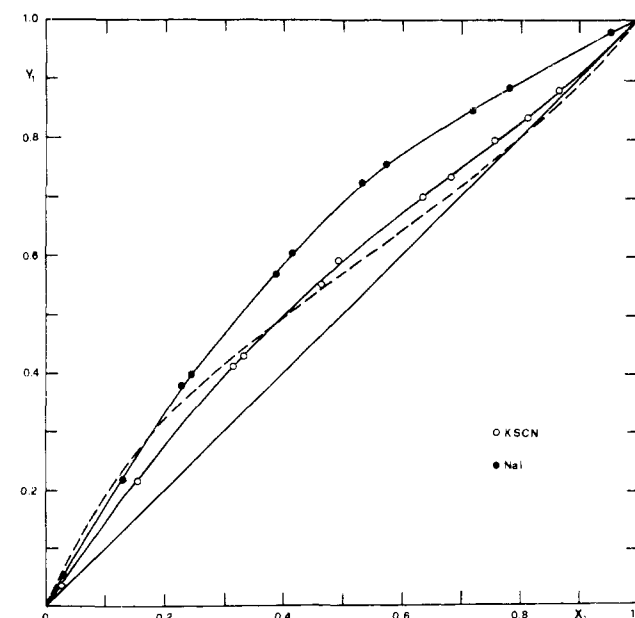


Figure 2. Acetone-methanol system saturated with KSCN and NaI

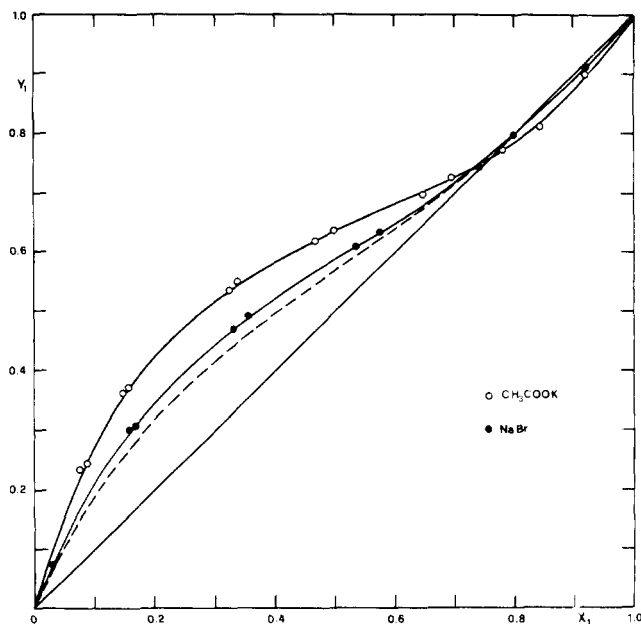


Figure 3. Acetone-methanol system saturated with CH_3COOK and NaBr

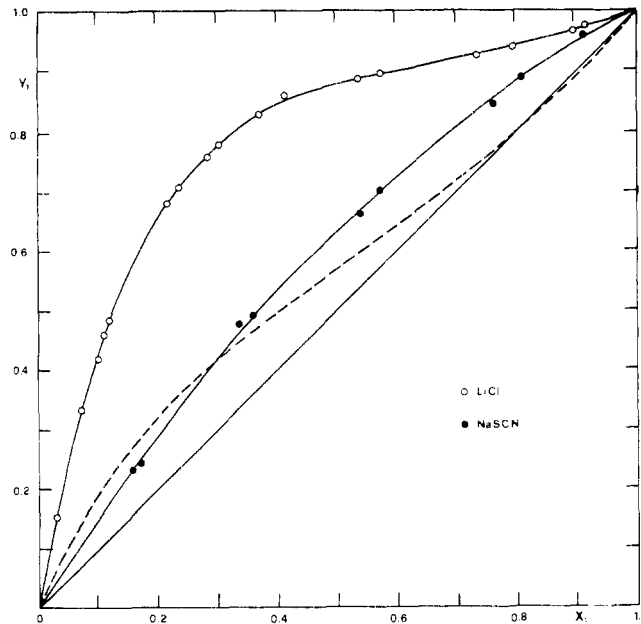


Figure 4. Acetone-methanol system saturated with LiCl and NaSCN

The crossover effect, verified by Prosz and Kollar, appears at saturation only in the case of NaI and does not appear in the case of LiCl which has a very large solubility at saturation in pure methanol.

Besides the practical utility of the reported experimental data, it is to be hoped that the various patterns of behavior of these systems could provide information needed for a breakthrough in understanding the salt solutions.

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Densities of Benzene-*n*-Alkane Mixtures

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Densities of mixtures of benzene with four *n*-alkanes C_6 , C_7 , C_{10} , and C_{16} were determined at 25 and 50 °C using a pycnometric method. The density measurements were used to extend the corresponding states method of Rowlinson and coworkers to systems containing benzene and long-chain hydrocarbons.

Densities of mixtures are required in chemical engineering design calculations. They are also of importance in the theoretical investigation of excess thermodynamic properties of mixtures. Recently, Mollerup and Rowlinson (4) have shown that the corresponding states method of Rowlinson and Watson (6) may be used to predict densities of liquefied natural

gases and of lower molecular weight hydrocarbons. The method is extended here to mixtures containing benzene and the higher molecular weight *n*-alkanes. Experimental data for the mixtures investigated are limited [Nigam et al. (5), Yuan et al. (8)]; therefore, an experimental study was also undertaken.

Experimental Method

Density measurements were made using 1- and 5-ml pycnometers. The side arms were 80 mm long with 0.7-mm diameter bore in both pycnometers. Measurements of volume were made with the pycnometers held in a constant temperature tank in which a NPL calibrated mercury in glass thermometer having 0.1 °C increments was used to measure the bath temperature. The temperature in the bath was kept constant to ± 0.1 °C.