Solubility of Calcium Acetate in Boiling Methanol-Water Solutions

W. T. NEWSTEAD and W. F. FURTER
Department of Chemical Engineering
The Royal Military College of Canada, Kingston, Ontario, Canada

The existing theory of salt effect in vapor-liquid equilibrium predicts that when a salt is dissolved in a mixed solvent consisting of two liquid components, the salt, by exhibiting selective association in the liquid phase, will alter the composition of the equilibrium vapor, enriching it in concentration of one component of the mixed solvent and diminishing it in concentration of the other. The molecules of the component in which the vapor is enriched are less attracted into complexes in the liquid phase by the salt than are those of the other solvent. The effect on vapor composition caused by salt addition to the liquid phase results because the volatility of the less attracted component is reduced by an amount less than that by which the volatility of the more attracted component is reduced. When this theory is combined with the liquid solution theory prediction that the salt will associate preferentially with the molecules of that component of the mixed solvent in which it is more soluble, the resulting prediction is that a given salt will enrich the vapor in that component of the binary solvent in which it is less soluble. These theories are reviewed in greater detail elsewhere (*1, 2*).

The data for systems reported in the literature on salt effect in vapor-liquid equilibrium have indeed supported the reasoning that the equilibrium vapor will be enriched in the component in which the salt is less soluble. A recent compilation of data for a total of 188 such systems has been published in book form by Ciparis (*3*). Shemilt, Davies, and Gordon (*4*) presented mathematical validity for this prediction in systems possessing a festoonlike (that is, convex-downward) curve of salt solubility as a function of mixed-solvent composition. The method of application of their development to salt effect in vapor-liquid equilibrium has been presented and discussed previously (*5*).

Two publications (*6, 7*) have reported the effects of acetate salts dissolved to saturation in the liquid phase on isobaric vapor-liquid equilibrium in the systems methanol-water and ethanol-water under boiling conditions at atmospheric pressure. Although some of these systems exhibited salt effects on their vapor-liquid equilibrium relationships of a nature in accordance with the predictions of the theory, one system, that of calcium acetate-water-methanol, acted in a manner believed to be contrary to the predictions (*7*). Anhydrous calcium acetate enriched the equilibrium vapor in water rather than in methanol throughout the entire range of methanol-water proportionality in the liquid phase, thus reducing rather than enhancing the value of relative volatility throughout the entire composition range of the system. The phrase "believed to be contrary" was used in the previous sentence because it was not possible to measure the concentration of calcium acetate in the liquid phase by the method used in the investigation. The only solubility data available in the literature were for *hydrated* calcium acetate as listed by Seidell (*8*), who reported the solubility of $Ca(CH_3COO)_2 \cdot H_2O$ in pure water as 29.7 g./100 g. water, and in pure methanol as 1.0 g./100 g. methanol, at their respective boiling points. If anhydrous calcium acetate were indeed more soluble in water than in methanol, its effect on the vapor-liquid equilibrium relationship of this system would be in clear contradiction with that predicted by the salt effect theory.

Because of the potential importance of this finding on the validity of the existing theory, we decided to measure the solubility of anhydrous calcium acetate in boiling methanol-water solutions. Unlike the solubilities of the other acetate salts, its values had not been determined in the previous investigation because of the discovery that methanol-water-calcium acetate solutions containing very small excesses of solid salt to ensure that saturation had been attained would not settle when boiling was discontinued prior to sampling the liquid phase, forming a gel-like suspension instead.

Current interest in salt effect in vapor-liquid equilibrium has been stimulated by certain highly successful applications in extractive distillation, in which a dissolved salt rather than a liquid additive has been employed as the separating agent. Major advantages in product purity and in reduced requirements both for separating agent and energy have been demonstrated (*9* to *11*).

METHOD AND RESULTS

Anhydrous methanol of 99.8 wt. % purity was from Anachemia Chemicals Ltd. The water was laboratory distilled. The anhydrous calcium acetate was British Drug Houses Laboratory Reagent grade.

For each run, a boiling flask equipped with a total reflux condenser was charged with a methanol-water mixture of known composition, and dry calcium acetate was added until saturation was attained with a very small excess of solid salt persisting in the boiling system. In order to observe the exact point of saturation at which the finely dispersed salt particles

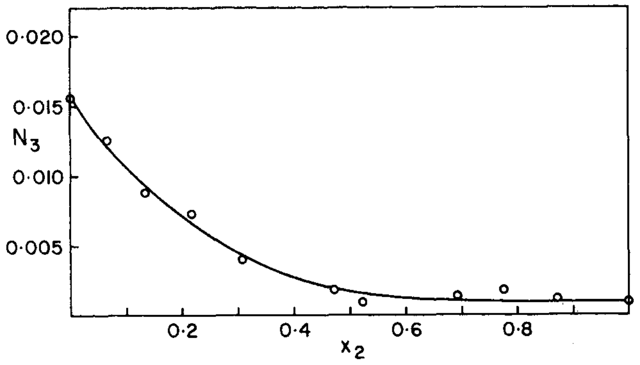

Fig. 1. Solubility of calcium acetate in boiling methanol-water solutions.

TABLE 1. SOLUBILITY OF CALCIUM ACETATE IN BOILING AQUEOUS METHANOL SOLUTIONS UNDER ISOBARIC CONDITIONS AT ATMOSPHERIC PRESSURE

x_2	N_3
0.000	0.0153
0.065	0.0126
0.130	0.0087
0.224	0.0074
0.306	0.0040
0.470	0.0018
0.520	0.0007
0.693	0.0014
0.775	0.0020
0.871	0.0012
1.000	0.0008

began to form, a high intensity lamp was employed. Boiling was then discontinued, and a liquid sample withdrawn immediately in a special pipette of large bore, described previously (*6*) but this time equipped with a filtration device affixed to the ¼ in. O.D. entry tube of the pipette. The filter, designed to block passage of the gel suspension without causing precipitation of dissolved salt, consisted of a 1-in. length of ¼-in. I.D. Tygon tubing, containing a core of packed glass wool bounded on each end by a layer of dense filter paper. To withdraw a saturated liquid sample, the filter-tipped pipette, which had been preheated to the approximate boiling temperature of the solution, was lowered into the solution with only the tip of the filter immersed. The pipette was filled with a suction bulb, removed, the filter detached, and the entire contents transferred immediately to a preweighed sampling bottle. The sample was weighed, dried to constant weight, and weighed again. Knowing the weight of the sample of solution, the weight of the salt contained in it, and the mass composition of the methanol-water solvent, the composition of the sample was established. The data were then converted to mole fraction.

The results of the solubility determinations are given in Table 1 and Figure 1. The data for boiling point temperature as a function of methanol-water proportionality for aqueous methanol solutions saturated with calcium acetate have been reported previously (*7*).

DISCUSSION

Of the solubilities of anhydrous calcium acetate in the two components of the mixed solvent in their pure states measured, that in boiling methanol was approximately equal to the value listed by Seidell for the hydrated salt, but that in boiling water was only half Seidell's listed value for the hydrate. Aside from the obvious chemical difference between the anhydrous and hydrated forms of the salt, it should also be noted that Seidell's value for solubility in boiling water was extracted from a combination of data measured in 1887 and in 1902. Small quantities of potassium or sodium acetates, both of which are much more soluble in water, if present as impurities would greatly affect the measured solubility.

The data of the present investigation show that anhydrous calcium acetate is considerably more soluble in water than in methanol under boiling conditions, thus confirming that in this system the effect of the salt has been to enrich the equilibrium vapor in the component of the binary solvent in which it is more, rather than less, soluble, and contradicting the empirical predictions of the salt effect theory.

Furthermore, the solubility curve as a function of mixed solvent composition has a conventional convex-downward aspect, which contradicts the more rigorous mathematical argument of Gordon.

Therefore, in view of this contradiction, it is now necessary to reexamine the existing theories of salt effect in vapor-liquid equilibrium.

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NOTATION

N_3 = mole fraction calcium acetate in methanol-water-calcium acetate liquid phase, moles calcium acetate/(moles water + moles methanol + moles calcium acetate)

x_2 = mole fraction methanol in methanol-water-calcium acetate liquid phase, calculated on a salt-free basis, moles methanol/(moles water + moles methanol)

Subscripts

1 = water
2 = methanol
3 = calcium acetate

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