Vapor-Liquid Equilibrium in Alcohol-Water Systems Containing Dissolved Acetate Salts

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Isobaric vapor-liquid equilibrium data at atmospheric pressure are reported for seven systems, each consisting of water, an alcohol (methanol or ethanol), and an anhydrous acetate salt (of sodium, potassium, barium, or calcium) dissolved to saturation in the boiling liquid phase. These systems are intended to complete a matrix about the single system ethanol-water-potassium acetate for which data were reported previously.

Solubility data are reported in terms of saturation salt concentration as a function of alcohol-water proportionality in the liquid. Sodium acetate as well as potassium acetate was found capable of eliminating completely the ethanol-water azeotrope.

Major differences in the effects of these salts as compared to those reported for other salts in the salt-effect literature were observed. Systems were discovered in which the salt appeared to cause both salting out and salting in of the alcohol in differing composition regions of the same system, the predominating effect depending on the relative proportions of alcohol and water. Systems were also discovered in which the salt salted-in the component in which it was less soluble. Both observed effects are in contradiction with previously accepted theories of salt effect in vapor-liquid equilibrium.

In a previous study (*1*), potassium acetate dissolved to saturation was observed to exert a very large effect on the relative volatility of the ethanol-water system. Relative volatility was enhanced as much as fourfold and more at certain ethanol-water ratios. The magnitude of the effect was attributed to a combination of the very high solubility of potassium acetate in the system and the large difference in solubilities of potassium acetate in pure water and pure ethanol. Such a system consists of a two-component vapor phase and a three-component liquid phase, a consequence of the salt being nonvolatile and hence appearing only in the liquid.

Extractive distillation employing a dissolved salt as separating agent is a novel unit-operation of great promise for application in certain specific systems where relatively small concentrations of salt are capable of effecting, through selective association in the liquid phase, large alterations in the vapor-liquid equilibrium relationship. One advantage of using a dissolved salt rather than a liquid is that an overhead product completely free of separating agent is yielded directly from the rectification column, a consequence of the separating agent's residing in its entirety in the liquid phase. Another lies in substantially lower energy requirements for achievement of the separation. A typical application, based on the system of the previous study (*1*), has been described by Cook and Furter (*2*).

Recent interest in extractive distillation by salt effect has led to an expansion of the ethanol-water-potassium acetate system to a matrix of eight systems involving water, two alcohols, and four acetates. Of the seven additional systems, isobaric vapor-liquid equilibrium data have been reported for only one, the ethanol-water-sodium acetate system, by Dobroserdov and Il'yina (*3*) who employed a constant salt concentration of 1 g.mole/liter of solution. At this concentration, the azeotrope was observed to be eliminated completely by sodium acetate, even though this salt was somewhat less effective than potassium acetate in the ethanol-water system.

THEORY

The equation describing salt effect in vapor-liquid equilibrium derived by Johnson and Furter (*4, 5*) predicts the change in equilibrium vapor composition (as a function of salt concentration) occurring when a given salt is dissolved in a given two-component solvent at a fixed composition of the solvent, i.e., at a fixed value of x_2

$$\ln \frac{\alpha_s}{\alpha} = k_3 N_3 \qquad (1)$$

The constancy of the salt effect parameter k_3 is rigorous thermodynamically only for a given system and then only when N_3 is varied with x_2 held constant. The value of k_3

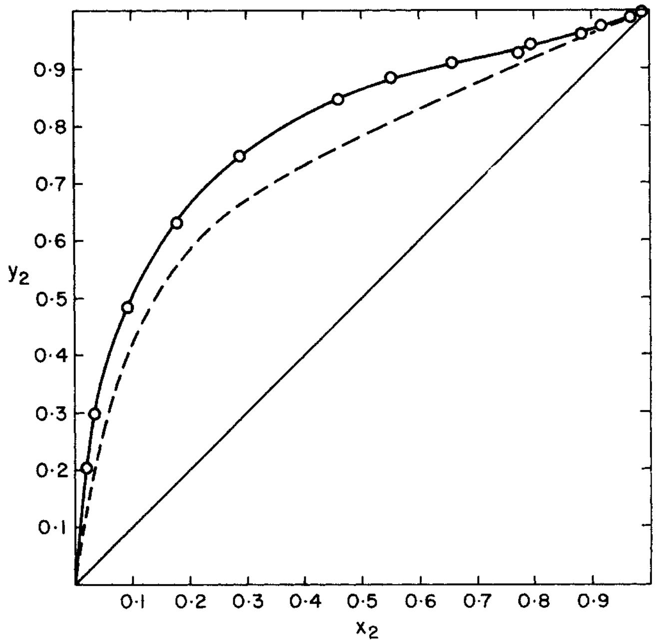

Fig. 1. Data for the system methanol-water saturated with sodium acetate.

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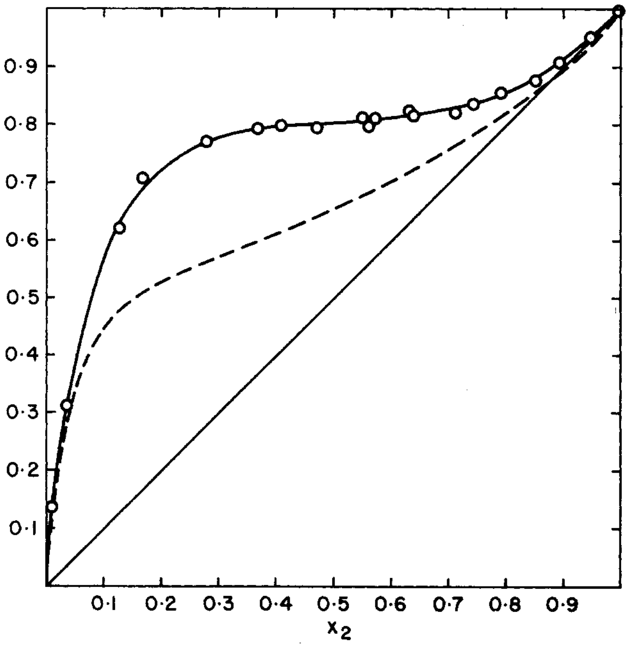

Fig. 2. Data for the system ethanol-water saturated with sodium acetate.

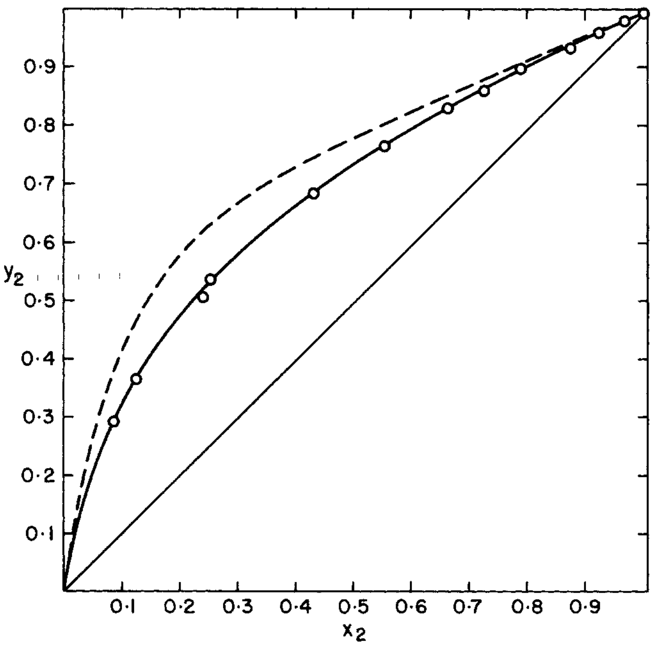

Fig. 3. Data for the system methanol-water saturated with calcium acetate.

would not be expected to remain constant even in a given system as x_2 is varied, because not only degree of salt dissociation but also all interactions between components of the liquid phase, both volatile and nonvolatile, are composition-dependent. These interactions include not only associations of each type of salt particle present (anions, cations, and/or molecules) with the molecules of each volatile component, but also the effect of salt on the water-water, water-alcohol, and alcohol-alcohol interactions of the present systems and all possible interaction combinations as well. All are believed dependent on degree of salt dissociation and, in turn, on the alcohol-water proportionality x_2 in the liquid phase.

Unexpectedly, the value of k_3 was found to remain substantially constant in certain systems as the proportions of the two volatile components of the solvent were varied throughout their entire range. This effect is attributed to an apparent balancing of the interaction mechanisms involved in salt effect as the value of x_2 is altered. Johnson and Furter (Fig. 9 in reference *5*) observed this balancing effect to exist to a remarkable degree in 24 systems, each consisting of an alcohol, water, and a moderately soluble inorganic salt. Yoshida (*6*) made similar observations with various salts in the methanol-water system, but did not observe the apparent balancing to exist to nearly the same extent in the acetic acid-water system. Meranda and Furter's (*1*) observation of a large variation in the value of k_3 with x_2 in the ethanol-water-potassium acetate system led to their extension of the study.

Investigators have agreed generally that magnitude of salt effect in vapor-liquid equilibrium depends on the degree of both solubility of the salt in the liquid phase and selectivity of the salt for selective association. The latter is reflected empirically in the degree of difference between its solubility in each of the two volatile components in their pure states under boiling conditions. It has been conceded generally that the vapor phase will be enriched in that volatile component whose molecules or groupings of molecules are less attracted into associations with the salt, e.g., the volatile component of the solvent pair in which the salt is less soluble.

Literature pertaining to salt effect in vapor-liquid equilibrium and to extractive distillation employing salt-effect was reviewed recently by Furter and Cook (*7*), Furter later reviewing the detailed theory and technical aspects (*8*). Comprehensive data were compiled in a book by Ciparis (*9*).

APPARATUS AND METHOD

The improved Othmer recirculation still (*10*) was modified for salt-effect studies by Johnson and Furter (*4, 11*).

For each experimental run, the equilibrium compositions of all components in each phase were measured and the accuracy checked by mass balance. Experimental and analytical procedures have already been described (*1*), but in this study salt solubility determinations were carried out integrally with the vapor-liquid equilibrium measurements rather than as separate experiments.

Equilibrium liquid phase samples were separated quantitatively into salt and alcohol-water fractions by a total distillation technique of evaporation to dryness. The alcohol-water fraction was collected quantitatively, condensed, weighed, and then analyzed by specific gravity determination for alcohol-water ratio. The salt fraction was determined gravimetrically and dissolved in a known volume of distilled water; results were checked by conductometric titration with hydrochloric acid. In all cases the two methods showed very close agreement. Knowing the weight and composition of the alcohol-water fraction and the weight of the salt fraction, the composition of the liquid phase sample was established. Equilibrium vapor condensate samples were analyzed by specific gravity determination. Weight fraction data thus obtained were then converted to mole fraction.

Anhydrous methanol of 99.8 wt. % purity was from Anachemia Chemicals Limited. Anhydrous ethanol of 99.99 wt. % purity was from Commercial Alcohols Limited. The water was laboratory distilled. The potassium acetate was "Baker Analyzed" crystal reagent grade, the sodium and barium acetates were BDH Analytical Reagent grade, and the calcium acetate was BDH Laboratory Reagent grade. All four salts were anhydrous.

RESULTS

Isobaric vapor-liquid equilibrium data at atmospheric pressure for the seven systems are plotted separately Figures 1 to 7. In all cases the salt was present at saturated (rather than constant) concentration throughout the range of alcohol-water proportionality x_2. The best curves have been drawn through the points, which represent the raw experimental data.

In each figure the dashed line represents the equilibrium curve for the alcohol-water system alone (*4, 5, 11*). Solubility data for these systems (with the exception of methanol-water-calcium acetate[*]) and for the previously studied system (*1*) included for comparison are plotted as smoothed curves in Figure 8, as a function of the relative proportions of alcohol and water in the boiling liquid phase. Boiling temperature-composition data are tabulated (Tables 1-7[†]) for reasons of conciseness. Composition and temperature data are determined at ± 0.005 mole fraction and ± 0.1°C., respectively.

Various unstable boiling phenomena were observed. Bumping and bursting to the point of explosive flash vaporization occurred with some salts and appeared to be unrelated to salt solubility. Such phenomena were observed in the alcohol-rich as well as in the water-rich regions of solution composition.

Problems associated with the extremely high solubility of potassium acetate in water-rich solutions of ethanol-water at the boiling point have previously been reported (*1*). Similar difficulties were encountered with this salt in the methanol-water system. The solubility of potassium acetate in boiling water is approximately mole for mole, resulting in a boiling point rise of about 60°C. The densities of saturated solutions of this salt in boiling, water-rich, aqueous alcohol solutions are such that the slight excess of solid salt particles present to ensure saturation tend to float on top of the boiling mixture rather than to disperse. The high viscosities of such mixtures result in local superheating, uneven boiling, and in poor mixing with the recirculated condensate which may tend to flash-vaporize when contacted with the much higher boiling salt solution. Tendencies toward bumping and flash vaporization are both diminished by reducing the recirculation rate. Too rapid a heating rate can also initiate recirculation holdup due to the large density and viscosity differences between the saltfree condensate and the salt-saturated liquid in the still. Recirculation stoppages can be cleared by gentle heating of the condensate return line. The removing of samples from water-rich, salt-saturated mixtures and their analyses also presented major problems, resulting in some scatter of solubility data in these regions. Such mixtures tend to gel when cooled even slightly below their boiling points. Sodium acetate, substantially less soluble in water than potassium acetate, did not exhibit such troublesome phenomena to nearly the same extent.

DISCUSSION

Although the acetates of both sodium and potassium were successful in breaking the ethanol-water azeotrope to the extent of eliminating it completely, the acetates of neither calcium nor barium exerted appreciable effects on its composition. One reason for this difference undoubtedly lies in the low but still substantial solubilities of the former two salts at the ethanol-rich azeotrope composition as compared with the almost total insolubilities of the latter pair in this composition region.

The boiling temperature vs. liquid composition (x_2) curves for all systems of the present investigation exhibited generally similar characteristics: concave-upward shapes with increasing inflexion in the water-rich region. However, the salt solubility vs. liquid composition curves (Figure 8) did not exhibit nearly the same degree of similarity from system to system; they ranged in shape from slightly convex-upward, to approximately linear, to strongly concave-upward.

Figure 8 shows that the acetates of sodium and potassium are highly soluble in water and of low solubility in both alcohols, whereas the acetates of barium and calcium are only moderately soluble in water and of negligible solubility in both alcohols. It should be pointed out that although salt concentration N_3 appears in Equation (1) as an independent variable, the N_3 values shown in Figure 8 and in Tables 1 to 7 are all those of saturation, that is, the solubility of the salt at that particular temperature and mixed solvent composition x_2. Because all four salts are more soluble in water than in either alcohol, they therefore would be expected to "salt out" the alcohol—to enhance the vapor phase in concentration of alcohol and hence the value of relative volatility (both alcohols being more volatile than water). Such, however, was not found to be entirely the case, for several anomalies, some of them quite remarkable, were observed.

Indeed, both the potassium and sodium acetates did conform to expected behavior in certain respects. Both salts enhanced relative volatility in both of the alcohol-water systems as predicted by salt effect generalizations. Potassium acetate, which is more soluble in both of the alcohol-water systems than is sodium acetate, had the larger effect in both systems. On the other hand, the shapes of the salt solubility vs. liquid composition curves for potassium acetate in the two alcohol-water systems differed widely from each other, while the curves for sodium acetate in the two mixed solvents were quite similar in shape (Figure 8). The degree of difference exhibited by potassium acetate in two such reasonably similar mixed solvents as those of aqueous methanol and aqueous ethanol was unexpected. Another unusual observation was that although sodium acetate was found to be more soluble in boiling methanol than in boiling ethanol as expected, the reverse was found true for potassium acetate.

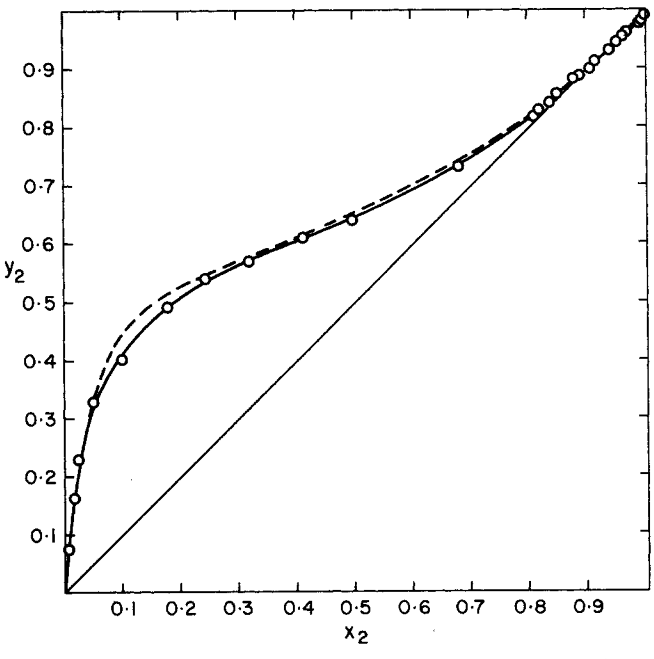

Fig. 4. Data for the system ethanol-water saturated with calcium acetate.

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[*] In the case of the methanol-water-calcium acetate system, salt concentration data were not measured because solutions containing small excesses of solid salt to ensure saturation would not settle when boiling was discontinued prior to sampling.

[†] Tabular material has been deposited as document No. 01249 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

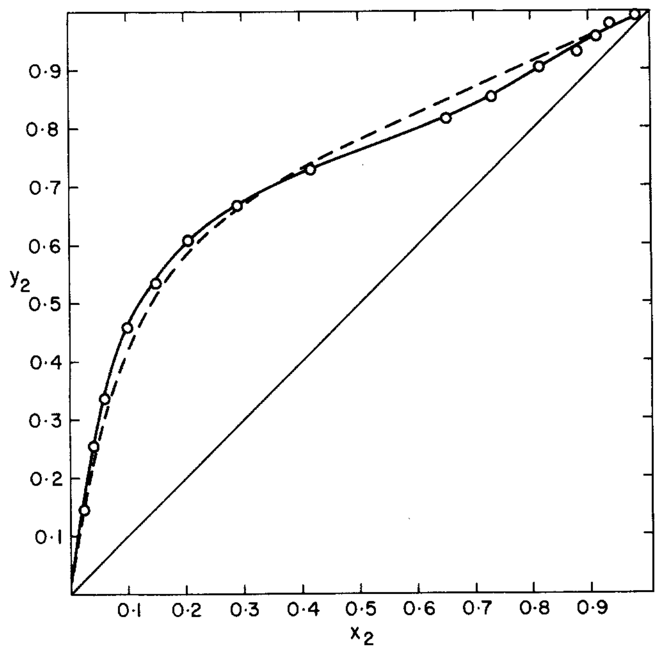

Fig. 5. Data for the system methanol-water saturated with barium acetate.

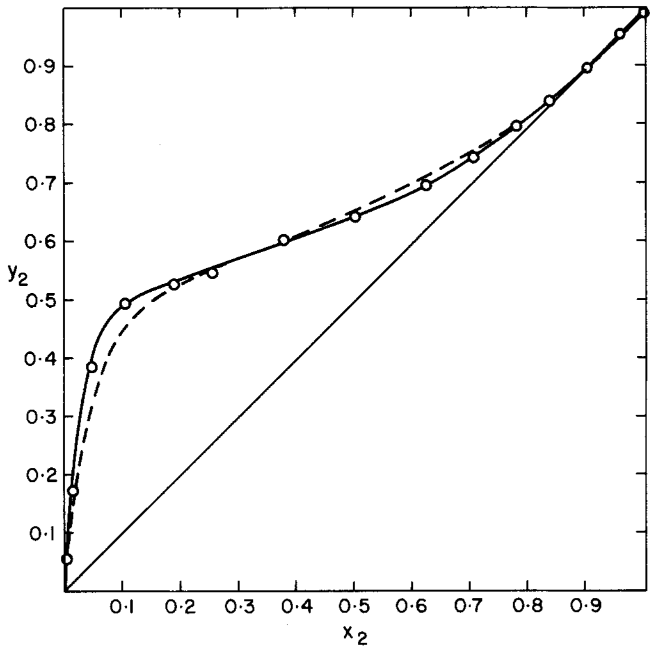

Fig. 6. Data for the system ethanol-water saturated with barium acetate.

In summary, it can be said that, compared with sodium acetate, potassium acetate is more soluble in both water and ethanol, and causes a greater increase in relative volatility throughout the ethanol-water system. Sodium acetate, however, was found to be considerably more soluble than potassium acetate in boiling aqueous methanol solutions, despite the opposite being true in pure water. The effects of the two salts in the methanol-water system are therefore less easy to compare.

Another interesting anomaly is observed in the behavior of barium acetate in both alcohol-water systems. Although of low solubility in water and extremely low solubility in both alcohols, barium acetate is clearly still more soluble in water than in either alcohol. Nevertheless, the data indicate that in both alcohol-water systems, barium acetate appears to cause salting out of the alcohol (enhancement of relative volatility) in the water-rich region of liquid composition, but salting in of the alcohol (decrease in the value of relative volatility) in the alcohol-rich region of the same system. The effects, although not large, are visible in Figures 5 and 6. In these systems it can be speculated that at least two major interaction mechanisms involving the salt occur in the structure complex of the liquid phase; each is composition-dependent, each has an effect quite different from that of the other and each dominates the overall salt effect in a different region of the range of mixed solvent composition x_2. Prausnitz and Targovnik (*12*) observed a similar crossover between salting out and salting in to exist in the water-pyridine system with sodium iodide and also with sodium sulfate. Each salt salted out pyridine at high pyridine concentrations but salted it in slightly at low pyridine concentrations.

A more remarkable phenomenon was observed to occur in both alcohol-water systems containing calcium acetate. Data of the present investigation show that anhydrous calcium acetate is more soluble in water than in ethanol. Although salt solubility data as a function of liquid composition were not measured for the system methanol-water-calcium acetate, Seidell (*13*) lists the solubility of hydrated calcium acetate in boiling water as 29.7 g./100 g. water, and in boiling methanol as 1.0 g./100 g. methanol.

Instead of enriching the vapor phase in alcohol, and thus enhancing the value of relative volatility as might be expected, calcium acetate is observed to salt in the alcohol and hence decrease the value of relative volatility. This holds true for both of the alcohol-water systems over their entire ranges of mixed-solvent composition x_2 in the liquid phase. Here a salt more soluble in the less volatile component is seen to decrease relative volatility over the entire range of x_2 in both systems. The effect is clearly visible in the methanol-water-calcium acetate system, as seen in Figure 3, and to a lesser extent in the ethanol-water-calcium acetate system, as seen in Figure 4. In the past, salting in in aqueous alcohol systems over their entire composition ranges had been observed only when the salt is more soluble in the alcohol than in water, as in the case of mercuric chloride with the ethanol-water system.

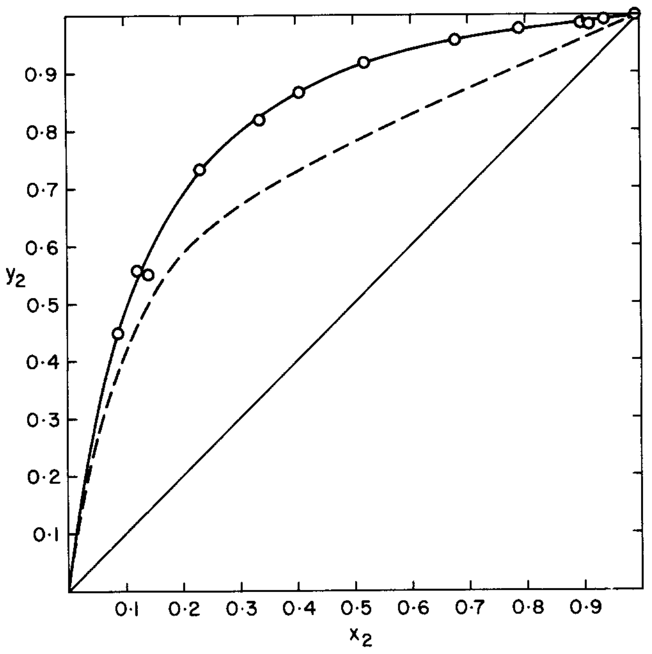

Fig. 7. Data for the system methanol-water saturated with potassium acetate.

The anomalous behavior of these acetate salts on vapor-liquid equilibrium in the two alcohol-water systems is further illustrated in Figure 9 (constructed from the smoothed vapor-liquid equilibrium curves of Figures 1 to 7) showing the salt-effect parameter k_3 as a function of mixed solvent composition x_2. Error analysis has been employed to determine the point at which each curve should be discontinued; indeterminate data result from an excessively low concentration of any one component of the liquid phase e.g., water, alcohol, or salt). In their respective solubilities as a function of x_2 in the two alcohol-water systems (Figure 8), the relative similarity for sodium acetate and the large disparity for potassium acetate are also evident in the behavior of their salt-effect parameters (Figure 9). The k_3 values of sodium acetate in both systems remain relatively uniform with x_2, exhibiting to a reasonable extent the apparent balancing effects reported in the 24 systems investigated by Johnson and Furter. However, the k_3 value of potassium acetate, as reported previously, undergoes a major variation with x_2 in the ethanol-water system and an extremely large variation in the methanol-water system.

Also in Figure 9 can be seen the transitions from salting out to salting in by barium acetate and the anomalous salting in caused by calcium acetate, as reflected in negative values for the salt-effect parameter.

It is evident that acetate salts in boiling alcohol-water mixtures produce effects different from those reported previously in the literature of salt effect in vapor-liquid equilibrium and most of which has involved inorganic salts.

α_s/α = "improvement factor" for extractive distillation,

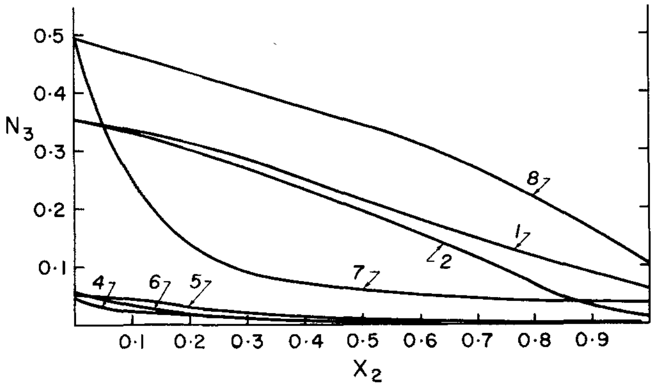

Fig. 8. Salt Solubilities in boiling alcohol-water mixtures, showing curves refering to systems as follows: (1) methanol-water-sodium acetate, (2) ethanol-water-sodium acetate, (4) ethanol-water-calcium acetate, (5) methanol-water-barium acetate, (6) ethanol-water-barium acetate, (7) methanol-water potassium acetate, and (8) ethanol-water-potassium acetate (reference 1).

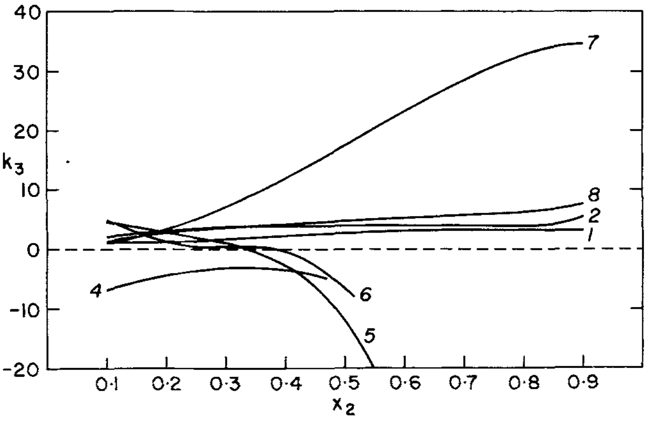

Fig. 9. Variation of salt effect parameter k_3 with liquid phase composition (on saltfree basis) x_2 (curves numbered as in Fig. 8).

ACKNOWLEDGMENTS

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NOTATION

k_3 = salt effect parameter, as defined by Equation (1)

N_3 = mole fraction salt in alcohol-water-salt liquid phase:

$$\frac{\text{moles salt}}{\text{moles water + moles alcohol + moles salt}}$$

T = temperature, °C.

x_2 = mole fraction alcohol in alcohol-water-salt liquid phase, calculated on a salt-free basis:

$$\frac{\text{moles alcohol}}{\text{moles water + moles alcohol}}$$

y_2 = mole fraction alcohol in alcohol-water vapor phase:

$$\frac{\text{moles alcohol}}{\text{moles water + moles alcohol}}$$

α_s = relative volatility of alcohol/water in alcohol-water-salt system, calculated on a saltfree basis

α = relative volatility of alcohol-water system without salt

NOTE: Relative volatilities, both in the presence and absence of salt, are calculated from the expression:

$y_2(1 - x_2)/(1 - y_2)x_2$

$\frac{\alpha_s}{\alpha}$ = "improvement factor" for extractive distillation, both values of relative volatility being calculated at the same value of x_2

Subscripts

1 = water
2 = alcohol
3 = salt

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