$$\overline{YAC} = \frac{Y}{N_{D1}\left[\left\{\phi - \phi^2\left(1 - \frac{1}{N_{Sh1}}\right) + \frac{1}{N_{D1}}\right\} + N_{D22}\overline{SRC}\left\{\omega + \omega^2\left(\frac{1}{N_{Sh1}} - 1\right)\right\} \cdot \left\{\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right\}\right]}$$

$$Y \cdot \frac{\left[\phi - \phi^2\left(1 - \frac{1}{N_{Sh1}}\right) + \frac{1}{N_{D1}}\right] + N_{D22}\overline{SRC}\left[\omega + \omega^2\left(\frac{1}{N_{Sh1}} - 1\right)\right]\left[\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right] - \left[\left(\phi - \phi^2 + \frac{1}{N_{D1}}\right) + N_{D22}\overline{SRC}\left\{\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right\}(\omega - \omega^2)\right]\frac{\Theta}{\Psi}}{\left[\phi - \phi^2\left(1 - \frac{1}{N_{Sh1}}\right) + \frac{1}{N_{D1}}\right] + N_{D22}\overline{SRC}\left[\omega + \omega^2\left(\frac{1}{N_{Sh1}} - 1\right)\right]\left[\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right]} = \overline{\Delta Y}$$

$$+ \left[\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right]$$

$$\left[\frac{N_{D22}}{N_{D21}}\left\{\omega - \omega^2\left(\frac{1}{N_{Sh1}} - 1\right)\right\} - Y\left(\omega + \omega^2\left\{\frac{1}{N_{Sh2}} - 1\right\}\right)\right]$$

$$C = \frac{-Y}{N_{D21}}\left[\phi\left(1 - \frac{\phi}{\omega}\right) + \frac{1}{N_{D1}}\right]$$

In defining these quantities, a new variable $\overline{SRC}$ appears which is the normalized pellet SO_2 concentration at the sulfation interface within the pellet. It is defined as

$$\overline{SRC} = \frac{S}{1 + N_{D21}\,(\overline{YRC})\,[\omega + \omega^2\,(1/N_{Sh2} - 1)]}$$

The expressions for the preceding variables are derived by solving the Laplace equations which result from the pseudo steady state pellet gas phase material balances and their boundary conditions (Bourgeois, 1972).

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Salt Effects on Vapor-Liquid Equilibrium: Some Anomalies

Experimental data are presented for five systems, each consisting of water, an alcohol (methanol or ethanol), and an inorganic salt dissolved to saturation in the boiling liquid phase. The data confirm and extend knowledge of recently discovered anomalies to the general theory of salt effect in vapor-liquid equilibrium. A partial accounting for the observed anomalies is attempted based on recent advances in the understanding of the structural nature of alcohol-water mixtures.

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SCOPE

Extractive distillation employing a dissolved salt in place of the conventional liquid solvent as the separating agent is capable of yielding higher separation efficiency, and with lower energy requirements, than conventional extractive distillation processing. A recent review of the theoretical and technical aspects of extractive distillation by salt effect has been published (Furter, 1972). Before large-scale commercialization is feasible, however, the theory of salt effect on vapor-liquid equilibrium must be better understood than at present.

When a salt is dissolved in a boiling solution of two liquid components, there are several salt effects that may occur. These include alterations in the boiling point, in the mutual solubilities of the two liquid components in each other, and in the composition of the equilibrium vapor phase. It is with the latter effect that this paper is concerned. Studies of salt effect in vapor-liquid equilibrium involve, in the simplest case, a two-component vapor phase in equilibrium with a three-component liquid phase, one of the components of the latter being the dissolved salt. The salt does not appear in the vapor.

At least until recently, it has been generally held that the presence of a salt in the liquid would result in an increase in concentration, in the equilibrium vapor, of the component in which the salt was less soluble, with

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a corresponding decrease occurring in the vapor concentration of the component in which the salt was more soluble. Such a prediction is the result of combining the probability that salt ions will tend to cluster preferentially with molecules of the more polar component and hence reduce its volatility in relation to that of the other, with the probability that the salt will be more soluble in the former component which it tends to resemble chemically more than the latter. It has also been held, in general, that the selectivity and hence magnitude of salt effect on vapor composition depends among other things more or less directly on the degree of difference between the solubilities of the salt in the two volatile components separately. Both of these predictions of salt behavior are now challenged by the discovery of systems where they seem to apply either only partially or not at all.

CONCLUSIONS AND SIGNIFICANCE

Three types of anomalous behavior to the predictions described above have been identified.

Type 1 is a crossover in salt effect between salting in and salting out, as liquid composition is varied, even though the salt is clearly more soluble in one component than in the other.

Type 2 is the enrichment of vapor composition throughout, in the component in which the salt is more, rather than less, soluble.

Type 3 is a relatively large effect on vapor composition caused by a salt having little difference in solubility between the two components.

The effects of salts on vapor-liquid equilibrium in systems as polar as methanol-water or ethanol-water no doubt are related to the previously existing liquid association structures which they alter or destroy when they are added, as well as to the clustering they create by their presence. Hence it seems probable that at least the Type 1 crossover anomalies are related to maxima or minima occurring in other physical properties of alcohol-water solutions as functions of liquid composition, such as volume change on mixing, heat of mixing, and sound absorption, and hence related to structural changes occurring in the liquid phase with composition. The complex mechanisms which make up salt effect in vapor-liquid equilibrium must be better understood before a sound approach can be made to the design of extractive distillation processes using this effect.

SALTING IN AND SALTING OUT

The vapor-liquid equilibrium relationships in a system of two volatile components are complicated greatly by the addition of a dissolved salt since the liquid phase then becomes a concentrated solution of an electrolyte whose degree of dissociation in turn is a function of the relative proportions of the other two components. The salt may affect the activities of the two volatile components either through the formation of association complexes or by otherwise altering the structure of the binary solvent mixture. Generally, the particles (molecules or ions or both) of dissolved salt tend to attract the molecules of one component of the binary more strongly than those of the other, tending to form association complexes preferentially, but not necessarily solely, with the former. Normally, the added component will tend to associate preferentially with that member of the binary system with which it is more similar chemically (like associates with like), thus affecting the volatilities of the two original components by differing amounts. Preferential attraction by the electrostatic fields of salt ions would normally be for the more polar component of the binary solvent. Since the added agent is likely to complex to some extent with both liquid components, the volatilities of both will most likely tend to be lowered, but by differing amounts depending on how selective the agent is. If the association preference of the salt is for the less volatile of the two liquid components, then its volatility will be reduced by an amount proportionally greater than that of the more volatile component, resulting in an increase in the value of relative volatility and enrichment of the equilibrium vapor in the more volatile component. Likewise, if the association preference of the salt is for the more volatile component, the value of relative volatility will be decreased and the vapor composition will be enriched in the less volatile component.

A common rule of physical chemistry states that like dissolves like, meaning that things tend to be most soluble in those solvents with which they are most similar chemically, that is, most similar in terms of molecular nature and structure. When like dissolves like is combined with like associates with like, the empirical rule of salt effect theory results which predicts that the vapor phase will be enriched in that component of the binary solvent in which the salt is less soluble. In other words, if the salt is more soluble in the less volatile component, the value of relative volatility will be increased by the salt. Conversely, if the salt is more soluble in the more volatile component, relative volatility will be decreased. In the former case the more volatile component is said to be salted-out by the salt, and in the latter, to be salted-in. Previous experimental findings have tended to support the above theory of salt effect as general. Experimental observation that salts enriched the vapor in the component in which they were less soluble was first made by Kablukov (1891, 1903, 1904) in Russia, and by Miller (1897) in Canada. Both studied the ethanol-water system with various salts added. Gross and Halpern (1934a, 1934b) in Vienna and Butler (1930, 1933) in England refined the liquid phase model relating salt effect on vapor composition to association-complexing in the liquid phase. Empirically it has been concluded that the magnitude of salt effect on the activity coefficients of the volatile components, for a given salt in a given system, will depend on the concentration of salt present in solution, and on a salt effect parameter (Furter, 1958; Johnson and Furter, 1960) which is a function of such factors as degree of difference of solubility of the salt in the two pure components, degree of dissociation of the salt in solution, ion charge, ion radius, and others.

ANOMALIES TO THE GENERAL RULE

More recently, anomalies have been observed which challenge the validity of the general prediction that a salt will enrich the vapor in that component of the binary in which it is less soluble. Systems have been observed in which certain salts have increased relative volatility in one part of the composition range of the system and decreased it in another composition region of the same system, while at the same time being clearly more soluble in one pure component than in the other. This type of anomaly hereafter will be referred to as Type 1. Prausnitz and Targovnik (1958) observed this crossover in salt effect to exist in the isopropanol-water system with sodium chloride, in pyridine-water with sodium iodide, in dioxane-water with sodium chloride and potassium benzoate, and in dioxane-water with sodium acetate. They suggested that the crossover effect was related to the observed formation of two liquid phases and its result on the shape of the equilibrium curve.

In recent investigations we have observed the Type 1, or crossover, effect to exist in the methanol-water system with the sodium and potassium bromides and iodides and certain of their mixtures (Meranda and Furter, 1972). We have also observed crossovers with the salt barium acetate (Meranda and Furter, 1971) in methanol-water and in ethanol-water. In none of our systems exhibiting crossovers was formation of two liquid phases observed. We have speculated (Meranda and Furter, 1971, 1972) that at least two distinct and major interaction mechanisms involving the effect of the salt on the structure complex of the liquid phase exist, each composition-dependent, each having an effect quite different from that of the other, and each dominating the overall salt effect in a different region of the range of binary liquid composition.

Proszt and Kollar (1958) in Hungary observed the existence of crossover effects in the acetone-methanol system with each of lithium chloride, lithium iodide, and sodium iodide.

An even more curious anomaly, referred to hereafter as Type 2, has been observed recently by us (Meranda and Furter, 1971; Newstead and Furter, 1971). In the methanol-water system, the salt calcium acetate, while clearly more soluble in water than in methanol, was observed to enrich the equilibrium vapor in water rather than in methanol throughout the entire range of binary liquid composition, thus reducing rather than enhancing the value of relative volatility throughout the entire composition range of the system. The solubility curve for calcium acetate in boiling methanol-water solutions (Newstead and Furter, 1971) confirms that this salt is substantially more soluble in water than in methanol under the conditions employed. This effect, which we have also observed to exist in the system ethanol-water-calcium acetate but to a lesser extent (Meranda and Furter, 1971), is in total contradiction with the prediction that a salt will enrich the vapor in the component in which it is less, rather than more, soluble.

EXPERIMENT

The apparatus employed was the improved Othmer recirculation still (Othmer, 1948), as modified for salt effect studies by Johnson and Furter (1957, 1960). For each experimental run, the equilibrium compositions of all components in each phase were measured, and the results checked by mass balance. Experimental and analytical procedures were as described in detail previously (Meranda and Furter, 1966), with the exception that in the present study salt solubility determinations were carried out integrally with the vapor-liquid equilibrium measurements rather than as separate experiments.

Briefly, the analytical techniques were as follows. The equilibrium liquid phase samples were separated into salt and alcohol-water fractions by quantitative total distillation, and the salt fractions determined gravimetrically. The alcohol-water fraction of each liquid sample was weighed and then analyzed by specific gravity determination. 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.

All salts employed in the study were anhydrous.

RESULTS

Isobaric vapor-liquid equilibrium data at atmospheric pressure for the five systems of the present investigation are plotted in Figures 1 to 5. In all cases the salt was

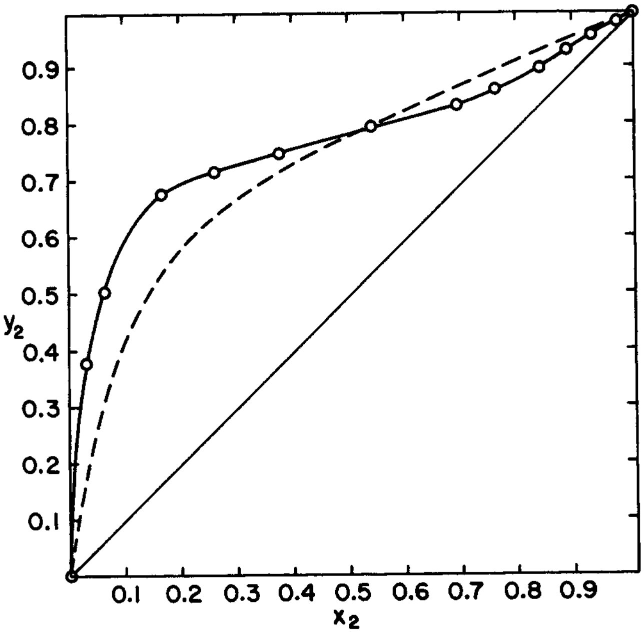

Fig. 1. Methanol-water saturated with potassium nitrate.

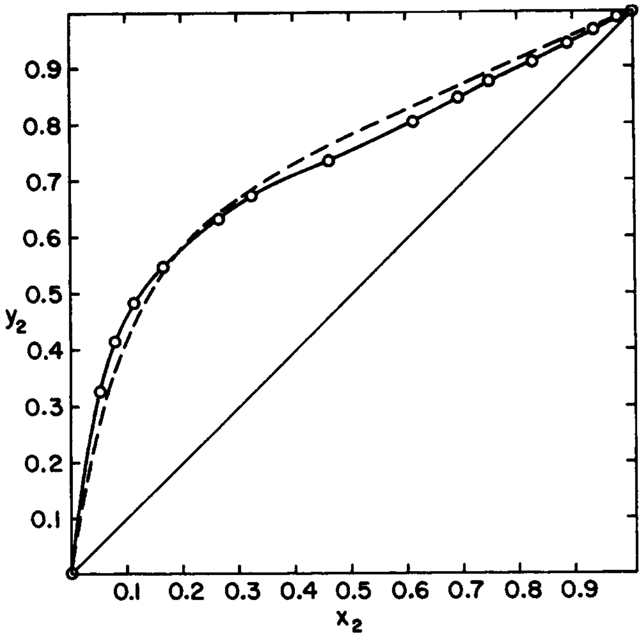

Fig. 2. Methanol-water saturated with potassium sulfate.

present at saturated (rather than constant) concentration in the boiling liquid phase throughout the x_2 range of alcohol-water proportionality. The best curves have been drawn through the points, which represent the raw experimental data. For the system ethanol-water-cupric chloride, the only one of the five which had been studied previously, data reported by Costa and Moragues (1952) in Madrid are also plotted. Costa and Moragues did not, however, measure salt concentration data for their system. The dashed line in each figure represents the vapor-liquid equilibrium curve for the alcohol-water system alone. Solubility data for these systems, reported in terms of the solubility of the salt as a function of alcohol-water proportionality x_2 in the boiling liquid phase, are plotted as smoothed curves in Figure 6. Boiling temperature-composition data have not been plotted for reasons of conciseness but are tabulated. Tables 1 to 5* contain the experimental vapor-liquid equilibrium data, boiling point temperature data, and salt solubility data for the five systems investigated.

DISCUSSION

The boiling temperature versus liquid composition (x_2) curves for all five systems exhibited generally similar characteristics: concave-upward shapes with increasing inflexion in the water-rich region.

The salt solubility versus liquid composition curves for the methanol-water system with three of the salts, potassium nitrate, potassium sulfate, and sodium sulfate, exhibited the concave-upward shape with increasing inflexion in the water-rich region expected of salts soluble in water but essentially insoluble in methanol, as can be seen in Figure 6. Cupric chloride, on the other hand, which appears to be slightly more soluble both in methanol and ethanol than in water although possessing sub-

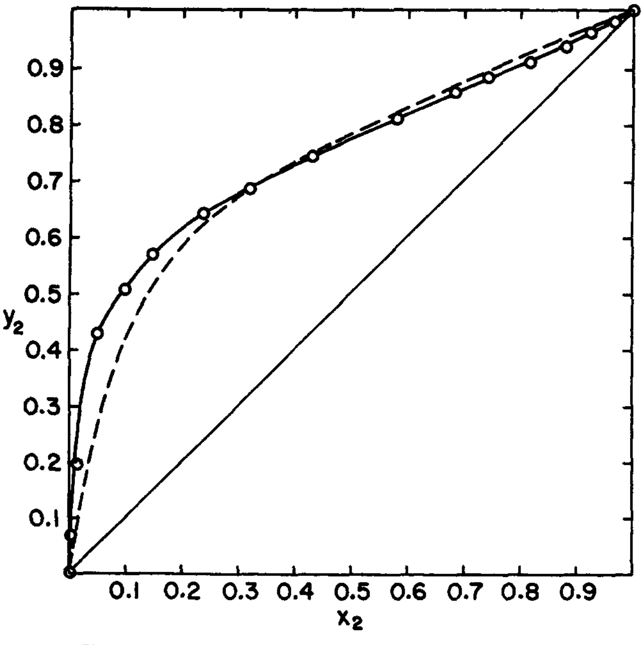

Fig. 3. Methanol-water saturated with sodium sulfate.

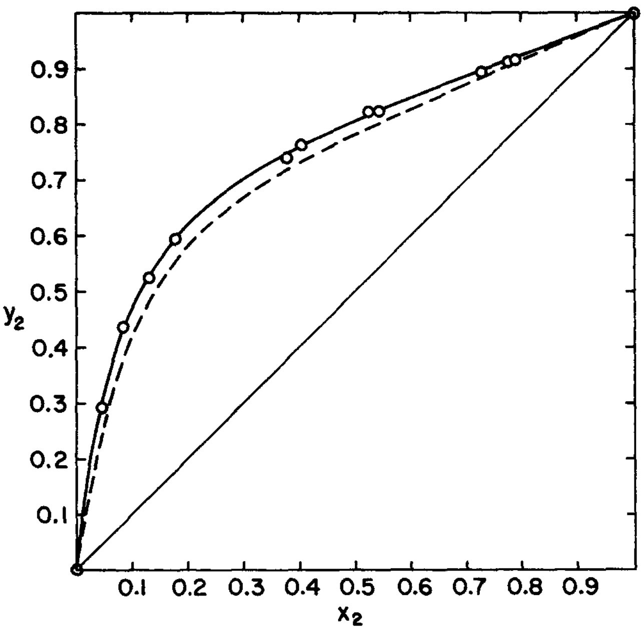

Fig. 4. Methanol-water saturated with cupric chloride.

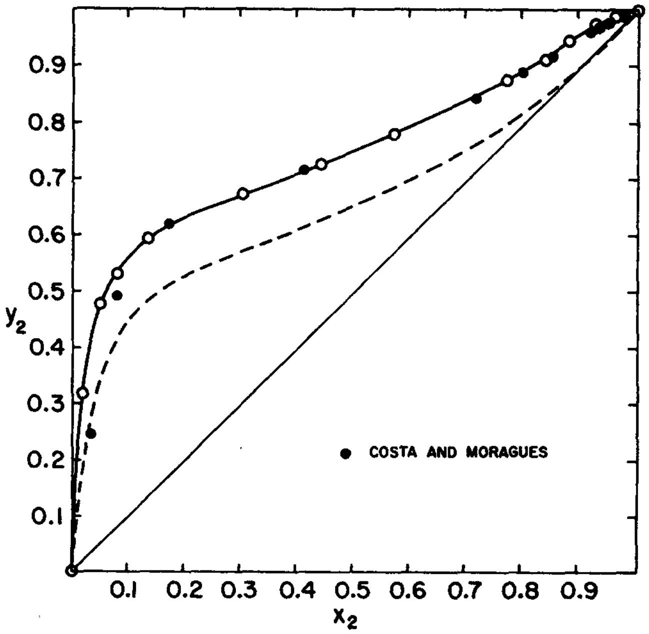

Fig. 5. Ethanol-water saturated with cupric chloride.

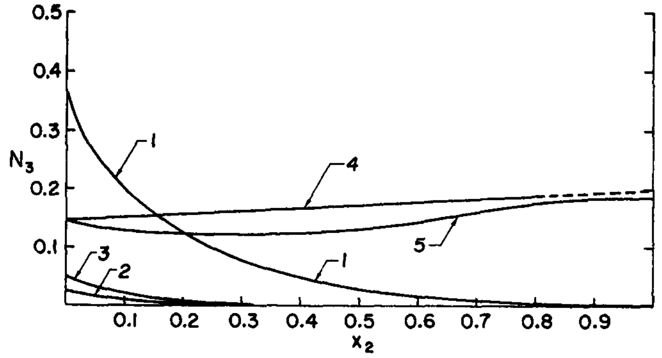

Fig. 6. Salt solubilities as functions of binary composition, for systems numbered as follows: (1) methanol-water-potassium nitrate, (2) methanol-water-potassium sulfate, (3) methanol-water-sodium sulfate, (4) methanol-water-cupric chloride, and (5) ethanol-water-cupric chloride.

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[*] Tables 1 to 5 have been deposited as Document No. 02293 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., New York, N. Y. 10017 and may be obtained for $1.50 for microfiche or $2.00 for photocopies.

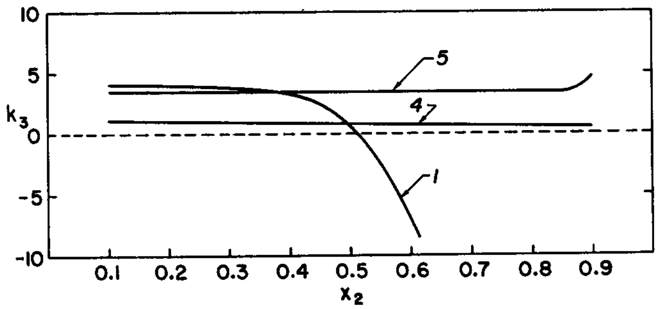

Fig. 7. Variation of salt effect parameter with binary composition. (Curves numbered as in Figure 6).

stantial degrees of solubility in all three, exhibited an almost linear solubility relationship in both alcohol-water systems.

In none of the five systems was formation of two liquid phases observed to occur in any portion of the liquid composition range. With the possible exception of potassium nitrate in methanol-water, none of the salts were of a solubility level sufficiently high in their respective systems that reduction to partial miscibility would be deemed likely to occur. In fact, formation of two liquid phases in the boiling methanol-water system caused by any salt is extremely improbable due to the high degree of chemical similarity and hence mutual solubility between these two chemicals.

The salt effect parameter k_3, which has been derived and discussed elsewhere (Furter, 1958; Johnson and Furter, 1960; Meranda and Furter, 1971), is plotted for the three systems of the present investigation which possess salt solubilities sufficiently high for the salt parameter data to be determinate in Figure 7. Statistical 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 component of the liquid phase; alcohol, water, or salt. For cupric chloride with both methanol-water and ethanol-water, the salt effect parameter remained relatively uniform in value with alcohol-water proportionality x_2, exhibiting the apparent balancing effects observed in many similar systems by Johnson and Furter (1960). On the other hand, a wide variation is observed for methanol-water-potassium nitrate, as with some other systems studied recently by the authors (Meranda and Furter, 1971).

In each of three of the systems investigated, namely methanol-water with each of potassium nitrate, potassium sulfate, and sodium sulfate, a Type 1 anomaly, or crossover in salt effect, was observed to occur despite all three salts being clearly more soluble in water than in methanol. These three add to the list of systems observed previously that partially contradict the prediction that a salt will enrich the vapor, in all composition regions of a given system, in that component of the binary in which it is less soluble. All three salts are observed to salt-out methanol (that is, increase relative volatility) in water-rich composition regions and to salt it in (that is, decrease relative volatility) in methanol-rich regions. The magnitude of the salt effect on the vapor-liquid equilibrium relationship of methanol-water is quite considerable with potassium nitrate, a salt of substantial solubility in the system, and considerably less with the much less soluble salts potassium sulfate and sodium sulfate, as expected. The respective effects can be seen in Figures 1 to 3, and also for methanol-water-potassium nitrate in the salt effect parameter plot of Figure 7.

In the other two systems studied in the present investigation, namely cupric chloride with each of methanol-water and ethanol-water, the Type 2, or total contradiction anomaly was observed to exist. As seen in Figures 4 and 5 and in the salt solubility curves of Figure 6, cupric chloride is more soluble in both alcohols than in water. Yet in both cases the vapor has been enriched throughout in the alcohol rather than in water, in other words, in the component in which it is more, rather than less, soluble.

In the latter two systems, still another type of anomalous behavior appears to exist. This will be referred to as Type 3. Cupric chloride is substantially soluble in water as well as in the two alcohols and is only slightly more soluble in them than in water. Yet it causes a fairly substantial effect on vapor composition, particularly in ethanol-water where it has eliminated the azeotrope. The data of Costa and Moragues (1952) are seen in Figure 5 to confirm the magnitude of the effect in the latter system, although they did not report salt solubility data. Thus the behavior of these two systems is in apparent contradiction to that portion of the theory which relates the degree of selectivity of the salt for preferential association, and hence the magnitude of its effect on vapor composition, to the degree of difference in solubility of the salt in the two liquid components.

RELATION TO CLUSTERING THEORY

As mentioned earlier, a common rule of physical chemistry is that *Similia Similibus Solvunar* (like dissolves like) and also most probably that like associates with like. In the case of salts more soluble in water than in alcohol it has been postulated that the salt ions form more stable cluster complexes with water than with the alcohol, thus expelling alcohol molecules from ionic regions of the liquid phase into higher activity in the remainder of the liquid phase, and thus salting-out the alcohol and raising the relative volatility of the alcohol-water solvent pair.

Clustering in water, alcohol, and water-alcohol mixtures occurs without the necessity of adding salt. In the water-rich region, clustering of the more-polar water molecules has a predominant effect, accounting for the high volatility of ethanol relative to water in this region. In effect, the ethanol molecules, dispersed at low concentration among water molecules tending more strongly to cluster with themselves than with the ethanol molecules, are prevented from clustering with other ethanol molecules because of their degree of dilution and hence separation from each other. However, in the alcohol-rich region, the opposite effect occurs (albeit with lesser strength due to the lower polarity of ethanol), and the concentrated ethanol molecules cluster either among themselves or with water, liberating unclustered water molecules which are more volatile than the ethanol clusters or ethanol-water clusters. At the crossover point between the two competing effects, the ethanol-water azeotrope occurs. The situation in the methanol-water system is postulated to be quite different because of the much greater degree of molecular similarity (and hence in polarity) existing between water and methanol than between water and ethanol. Hence it can be postulated that methanol and water molecules are more interchangeable in the clusters and that the degree of preferential competition in forming clusters is much less than in the ethanol-water system. This postulate is supported by the lack of an azeotrope existing in the methanol-water system.

The clustering model becomes much more complex when salt is added to the liquid phase because of the short-range electrostatic fields of the salt ions and their interactions with each other and with polar molecules. It is believed that salt ions tend to promote the clustering of the more polar component about them. However, the effect is also a function of the relative proportions of the two volatile components present and may possibly reverse when one or the other of the volatile components is dilute in concentration. Hence the relative interchangeability of methanol with water molecules in salt-associated clusters may explain the Type 1 anomaly, or reversal from salting-out to salting-in, observed with certain salts as the methanol concentration is increased. Also, the lesser degree of interchangeability of ethanol with water molecules in such clusters, due to the greater chemical dissimilarity of water with ethanol than with methanol, may explain why crossovers in salt effect have been observed very seldomly in the latter system.

In recent studies of the structural properties of alcohol-water mixtures, Franks and Ives (1966) have postulated that some quite strong, but as yet unidentified water-water interaction other than hydrogen bonding may exist, becoming predominant at elevated temperatures. In alcohol-rich regions their evidence indicates that water has been depolymerized or become unclustered considerably, while strong and well-organized alcohol-water associations have formed, the latter however being thermally vulnerable and decreasing with increasing temperature. Pure water can be considered as existing in a quasi-equilibrium between structured and unstructured regions. Addition of alcohol to water, according to Franks and Ives, initially shifts the equilibrium further toward structured, actually increasing the structured state of water at first, and then decreasing it later, with depolymerization of water setting in progressively as more and more alcohol is added. The more foreign or different the alcohol molecule is to water, that is, the higher its molecular weight, the earlier the maximum occurs. This structure mechanism is evident in the occurrence of maxima or minima in the relationships of various properties of alcohol-water solutions with liquid composition, such as volume change on mixing, heat of mixing, sound absorption, and others, and occurs at an alcohol concentration of about 0.3 mole fraction for methanol-water and 0.15 to 0.2 for ethanol-water. Although Franks and Ives do not discuss the effects of addition of electrolytes to alcohol-water systems, a relation can be speculated to exist between the crossovers in effect on vapor composition caused by certain salts in such systems and the maximums exhibited in degree of association even without salt present. Further study of the effects of salts on liquid phase structure is necessary before a more general theory encompassing the anomalies recently and currently observed can be derived.

ACKNOWLEDGMENT

The continuing research programs on extractive distillation by salt effect and on salt effect in vapor-liquid equilibrium at the Royal Military College of Canada are supported by the Defence Research Board of Canada.

NOTATION

k_3 = salt effect parameter (Furter, 1958; Johnson and Furter, 1960)

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

$$= \frac{\text{moles salt}}{(\text{moles water} + \text{moles alcohol} + \text{moles salt})}$$

T = temperature, °C

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

$$= \frac{\text{moles alcohol}}{(\text{moles water} + \text{moles alcohol})}$$

y_2 = mole fraction alcohol in alcohol-water vapor phase

$$= \frac{\text{moles alcohol}}{(\text{moles water} + \text{moles alcohol})}$$

Subscripts

1 = water
2 = alcohol
3 = salt

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