Vapor-Liquid Equilibrium in Alcohol-Water Systems Containing Dissolved Halide Salts and Salt Mixtures

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Isobaric vapor-liquid equilibrium data at atmospheric pressure are reported for 17 systems, each consisting of water, an alcohol (methanol or ethanol), and either a salt or a mixed pair of salts having a common anion, dissolved to saturation in the boiling liquid phase. The matrix of four salts employed consisted of the sodium and potassium bromides and iodides. Solubility data are reported in terms of saturation salt concentration as a function of alcohol-water proportionality in the liquid.

Some of these salts and salt mixtures were found capable of eliminating the ethanol-water azeotrope completely. Relative volatility was observed to be enhanced by as much as threefold in certain cases. Orders of effectiveness of both the cations and anions were in agreement with those observed by previous investigators of the effects of electrolytes in mixed solvents. The value of the salt effect parameter was observed to undergo major variation as a function of alcohol-water mixed solvent proportionality in the methanol-water-salt systems, but to be remarkably constant throughout the ethanol-water-salt systems. Synergistic effects of mixed salts on vapor-liquid equilibrium were observed in certain systems despite their apparent lack in the corresponding salt solubility relationships. In systems where synergistic effects did exist they were found to be dependent strongly on liquid composition, largely lacking in water-rich regions, and evident only in midrange and alcohol-rich regions of binary solvent composition. In some of these systems 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 present. This latter effect is in general contradiction with the accepted theories of salt effect in vapor-liquid equilibrium.

The unit operation of extractive distillation employing dissolved salts, rather than liquid solvents, as separating agents for effecting separations in systems exhibiting either azeotropes or low relative volatility in composition regions critical to the separation is an unusual operation which has been a subject of continuing interest in the literature.

Recent industrial interest in achieving extractive distillation by salt effect has led to the present investigation into the efficacies of mixed salts, as compared with single salts, to serve as separating agents for such an operation. For this study, a matrix of systems was chosen, each consisting of water, an alcohol (methanol or ethanol), and either a single salt or a mixture of two salts having a common anion, dissolved to saturation in the boiling liquid phase. The individual salts employed were sodium bromide, potassium bromide, sodium iodide, and potassium iodide. The mixed salt pairs used were the two bromides and the two iodides. All salts were anhydrous. In all, the matrix consisted of 17 separate systems, eight with single salts and nine with mixed salt pairs. Each system was studied with the salt concentration maintained at saturation throughout the entire x_2 composition range of alcohol-water proportionality in the boiling liquid phase, under conditions of atmospheric pressure. Such systems, while containing either three or four chemical components in the liquid phase, possess a vapor phase consisting only of alcohol and water.

The purpose of using saturated salt concentrations throughout the entire liquid-phase composition range of the binary solvent is to measure the largest salt effect possible at each value of liquid composition. It is to be noted, however, that this condition is not representative of salt concentration in an extractive distillation column using dissolved salt as the separating agent. Rather, molal salt concentration in the liquid phase would remain essentially constant from tray to tray within each of the rectifying and stripping sections; just as constant, in fact, as the assumption of constant molal overflow is valid. From a knowledge of salt effect at saturation, however, its effect at a constant concentration below saturation can be calculated using the salt effect equation, which is referred to later in the paper.

Rius Miro and associates (*1*) reported isobaric vapor-liquid equilibrium data at 700 mm. for the system ethanol-water-potassium iodide, and for the alcohol-rich region only of the system ethanol-water-sodium iodide. Mischenko (*2*) made isothermal vapor-liquid equilibrium measurements on the system methanol-water-sodium bromide at 25° and 40°C., employing various salt concentrations. Unfortunately, because of either the conditions or salt concentrations employed in previous investigations, no direct comparison with the data of the present investigation is possible.

Literature pertaining to salt effect in vapor-liquid equilibrium and to extractive distillation employing salt effect was reviewed recently by Furter and Cook (*3*), and the theory and technical aspects by Furter (*4*). A comprehen-

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sive compilation of equilibrium data has been published in book form by Ciparis (*5*). A recent book on the subject of extractive distillation by salt effect has been published by Ciparis, Dobroserdov, and Kogan (*6*).

Most previous studies have involved investigation of the effects of individual salts on the vapor-liquid equilibrium relationship of a mixed solvent, the latter consisting usually of a binary system comprising two volatile liquid components. However there have been investigations in which mixtures of two or more salts, rather than single salts, were employed. Baranov and associates studied the nitric acid-water system in the presence of mixtures of magnesium and zinc nitrates (*7*), and mixtures of calcium and zinc nitrates (*8*). They compared the effectiveness of these salt mixtures with that of sulfuric acid, the conventional separating agent for the concentration of aqueous nitric acid. Proinova and Toncheva (*9*), studying techniques for ethanol recovery in the process for preparing double superphosphate from apatite and nitric acid, made vapor-liquid equilibrium measurements in the ethanol-water system containing calcium and ammonium nitrates dissolved together in the liquid phase at relatively low concentrations.

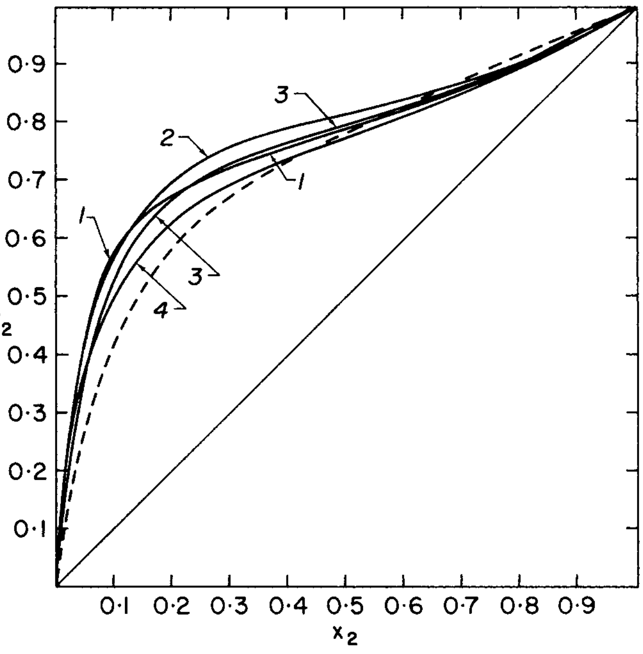

Fig. 1. Vapor-liquid equilibrium data for the methanol-water system saturated with bromides of sodium and potassium and their mixtures. Curve 1 is for NaBr alone, curve 2 for a 2:1 mole mixture of NaBr:KBr, curve 3 for a 1:1 ratio, and curve 4 for KBr alone.

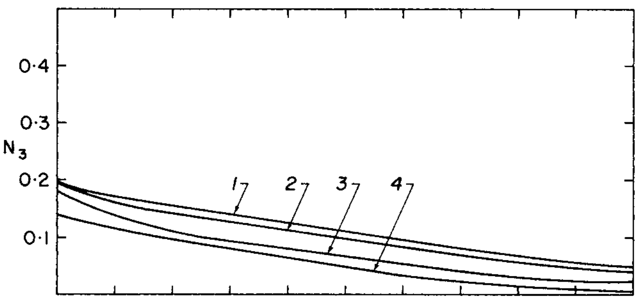

Fig. 2. Salt solubility data for boiling methanol-water mixtures saturated with the bromides of sodium and potassium and their mixtures. The numbering scheme for the curves is the same as in Figure 1.

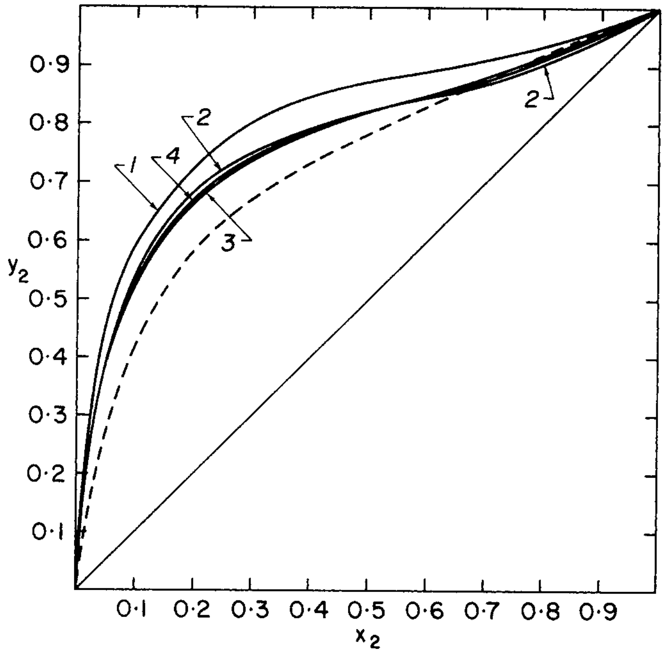

Fig. 3. Vapor-liquid equilibrium data for the methanol-water system saturated with the iodides of sodium and potassium and their mixtures. Curve 1 is for NaI alone, curve 2 for a 2:1 mole mixture of NaI:KI, curve 3 for a 1:1 ratio, and curve 4 for KI alone.

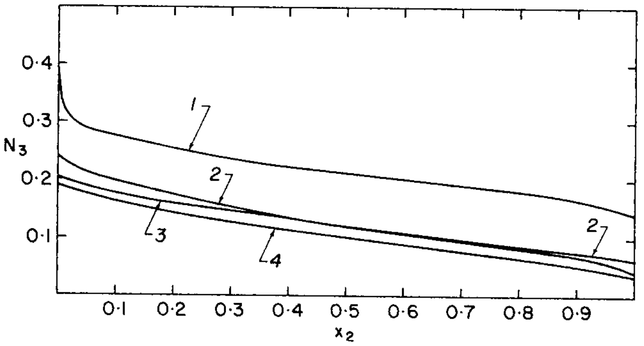

Fig. 4. Salt solubility data for boiling methanol-water mixtures saturated with the iodides of sodium and potassium and their mixtures. The numbering scheme for the curves is the same as in Figure 3.

Gorhan registered several patents (*10* to *16*) describing an extractive distillation process and apparatus for the production of absolute ethanol using salts such as nitrates, chlorides, formates, acetates, and propionates, either singly, in pairs, or in threes as the separating agent. The basis of Gorhan's process was to melt the salt in order to expel all moisture of hydration, and to dissolve the fused salt into the reflux stream at the top of a spray rectification column. Aqueous ethanol vapor was stripped of water as it passed up the column by countercurrent contact with the spray of reflux. Gorhan did not publish either process or equilibrium data to support his patent claims.

The Hiag process (*17, 18*) of Degussa, based on Gorhan's proposals, went into wide-scale use during the 1930's, with individual units producing up to 13,200 gal./day of absolute alcohol, for use as a motor fuel admixture in countries where petroleum was costly. The process involved the addition of a molten mixture of acetate salts to the reflux of an extractive distillation column. Both lower capital costs and lower energy requirements were claimed in comparison with conventional processes which use benzene or ethylene glycol as the separating agent, and the 99.8% ethanol so produced required no further purification or solvent knockback to rid it of traces of separating agent. Over 100 such plants were built by Degussa.

EXPERIMENTAL

The apparatus employed was the improved Othmer recirculation still (*19*), as modified for salt effect studies by Johnson and Furter (*20*, *21*). In the experiments where salt pairs were used, the salts were premixed by mechanical agitation in the desired mole ratio prior to charging. As with single salts, small amounts were added progressively until an exceedingly small excess of solid salt persisted in the still. The experimental procedure was the same as described previously (*22*), with the exception that the salt fractions separated quantitatively by total distillation from equilibrium liquid-phase samples were determined gravimetrically, and then were dissolved in distilled water and the iodide and bromide ions determined by titration with silver nitrate solution using eosin as indicator (*23*) to check the results.

RESULTS

Isobaric vapor-liquid equilibrium data at atmospheric pressure for the 17 systems of the present investigation are plotted in family groupings in Figures 1, 3, 5, and 7. In all cases the salt or salt mixture was present at saturated (rather than constant) concentration in the boiling liquid phase throughout the x_2 range of alcohol-water proportionality. 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 or solubility of the mixed salt pair as a function of alcohol-water proportionality x_2 in the boiling liquid phase, are plotted in the same family groupings in Figures 2, 4, 6, and 8.

Because of the large quantity of data presented in each of Figures 1 to 8, the individual data points have been omitted for reasons of clarity. The raw experimental data, consisting of vapor-liquid equilibrium compositions, equilibrium boiling temperatures, and salt solubilities for the 17 systems, are contained in Tables 1 to 17.[*]

DISCUSSION

The boiling temperature versus liquid composition (x_2) curves for all systems exhibited generally similar characteristics: concave-upward shapes with increasing inflection in the water-rich region. The salt solubility versus liquid composition curves also exhibited reasonable similarity from system to system, ranging in shape for the most part from slightly concave upward to approximately linear.

In respect to the two cations, sodium and potassium, tested in the salt matrix, the two sodium salts were observed to exert larger effects on equilibrium vapor composition than the two potassium salts, in both alcohol-water systems. This observation is consistent with the electrostatic theory and with the general order of cation effectiveness observed by previous investigators (*21*, *24*). Glasstone (*25*) lists the crystallographic ionic radii of sodium and potassium as 0.95 and 1.33 Å., respectively. The smaller ion, by allowing a closer approach to its charge center, would exert a stronger attractive force for molecular association in solution.

However, in respect to the two anions tested, bromide and iodide, the two iodide salts each exhibited considerably larger effects on vapor-liquid equilibrium in both alcohol-water systems than did the two bromides. The general order of anion effectiveness observed by previous investigators places the bromide ion ahead of the iodide ion in terms of effectiveness. However the greater effects of the iodides over the bromides in the present systems undoubtedly are related strongly to their considerably greater solubilities. It is necessary to differentiate between the meanings of the terms effect and effectiveness, the former being the product of the amount of salt present, that is, in this case its solubility, and the effectiveness of its ions in complexing selectively with molecules of one or the other component of the binary solvent or otherwise altering liquid phase structure. Orders of ion effectiveness are meaningful only if ion concentration is not a parameter. Indeed, in both alcohol-water systems the values of the salt effect parameter k_3, the meaning and significance of which are referenced below, were slightly higher for the bromide salts than for the respective iodides, thus being in agreement

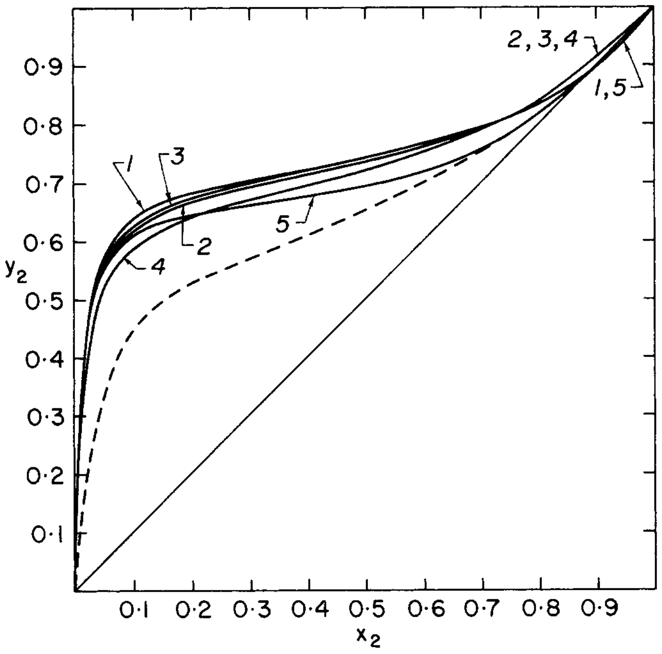

Fig. 5. Vapor-liquid equilibrium data for the ethanol-water system saturated with the bromides of sodium and potassium and their mixtures. Curve 1 is for NaBr alone, curve 2 for a 3:1 mole mixture of NaBr:KBr, curve 3 for a 2:1 ratio, curve 4 for a 1:1 ratio, and curve 5 for KBr alone.

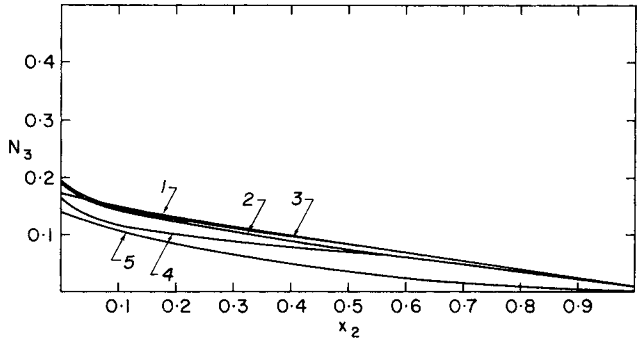

Fig. 6. Salt solubility data for boiling ethanol-water mixtures saturated with the bromides of sodium and potassium and their mixtures. The numbering scheme for the curves is the same as in Figure 5.

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[*] Tabular material has been deposited as Document No. 01615 with the ASIS National Auxiliary Publications Service, c/o CCM Information Services Inc., 909 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.40 for photocopies.

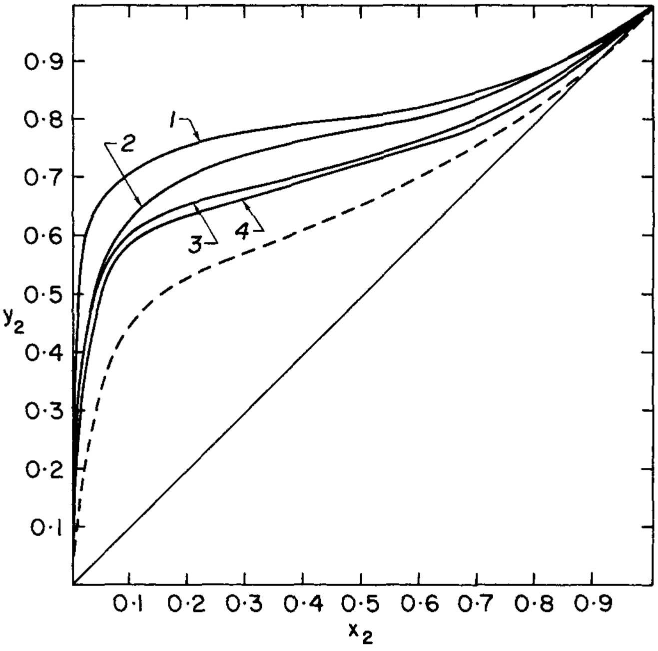

Fig. 7. Vapor-liquid equilibrium data for the ethanol-water system saturated with the iodides of sodium and potassium and their mixtures. Curve 1 is for NaI alone, curve 2 for a 2:1 mole mixture of NaI:KI, curve 3 for a 1:1 ratio, and curve 4 for KI alone.

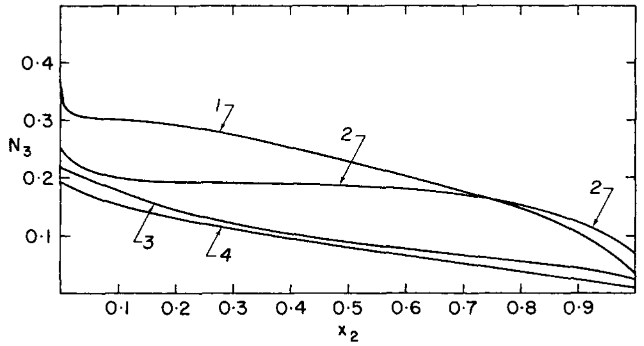

Fig. 8. Salt solubility data for boiling ethanol-water mixtures saturated with the iodides of sodium and potassium and their mixtures. The numbering scheme for the curves is the same as in Figure 7.

with the generally observed anion order of effectiveness.

It also must be emphasized that the orders of ion effectiveness reported in the literature are only approximate, with frequent exceptions existing in specific cases. More important, the observed orders of salt effectiveness in the present investigation are in accord with the order of solubility of the four salts involved, an agreement expected for reasons which will be discussed in a later paragraph. All four salts were more soluble in water than in either alcohol. In both alcohol-water systems, the two sodium salts were more soluble at all alcohol-water proportionalities, that is, at all values of x_2, than were the respective potassium salts, and the two iodides were more soluble at all values of x_2 than were the respective bromides.

The equation describing salt effect in vapor-liquid equilibrium (*21, 24*), has been described and discussed recently by the authors in this *Journal* (*22*). In the present investigation, the salt effect parameter k_3 was observed to vary widely with x_2 in the methanol-water-salt systems, ranging in value from about $+4$ to -10 with both bromide salts, and from about $+3$ to -3 with both iodide salts. On the other hand, in the ethanol-water-salt systems, k_3 was found to be remarkably invariant with x_2, having an essentially constant value of about $+5$ for both bromides and about $+4$ for both iodides. In the ethanol-water-salt systems of the present investigation, the value of k_3 is sufficiently constant that the salt effect equation using a single value of k_3 per system is capable of representing the data to within $\pm 1\%$.

The well-known common ion effect predicts the amount by which the solubility of a salt in a given solvent will be altered by the addition of a second salt having one ion (usually the anion) in common with the first salt. Glasstone (*26*) indicates that in certain systems in which the two salts possess a common ion, a maximum may be exhibited as a result of complex ion formation. By a maximum is meant that at a certain ratio the mixture of the two salts would be more soluble in a given solvent than either salt alone. The increase of solubility is believed due to the removal of the simple ions by the formation of complex ions. There appears to be essentially no occurrence of such a synergistic effect in mixed-salt solubility in the systems of the present investigation, although a 2:1 ratio of NaI:KI does appear to be more soluble than sodium iodide alone in alcohol-rich regions of the ethanol-water system (Figure 8). The relatively unconventional shapes of the solubility curves of the iodides and their mixtures in the ethanol-water system are also visible in this figure, as is the sharp upturn of the solubility curve for pure sodium iodide in the strongly water-rich region. The solubility of sodium iodide exhibits a similar upturn in the methanol-water system, as seen in curve 1 of Figure 4.

The term salt effect as used in the present context refers to the effects of the salt on the volatile components of the binary solvent. The particular salt effect under study is the effect of salt dissolved in the liquid phase on the composition of the equilibrium vapor. The salt also affects the mutual solubility of the solvent components in each other, in effect salting in or salting out one volatile component in respect to the other. The effect on the mutual solubility of binary solvent components in the systems of the present investigation is insufficient to cause partial miscibility to occur in any of them, and has not been studied. However, creation of partial miscibility even in such highly soluble systems as boiling mixtures of ethanol and water by certain dissolved salts has been observed (*21, 24*). The term salt effect can also be used to describe the effect of the presence of one salt on the solubility of the other salt when a pair of salts are dissolved in a solvent. In such a case a positive effect would be called salting in of one salt by the other, and a negative effect would be referred to as salting out. The differences in usage above require clarification, since both solvent pairs and salt pairs are employed in the present investigation.

Another matter of semantics requiring clarification is the perhaps improper use of the terms saturation and solubility as they apply to mixed salt pairs, by the authors in the present investigation. As used here they apply to the appearance of the first sign of solid salt persisting in the liquid as the solid salt mixture is progressively added, providing a concept of saturation that may be used to compare the effects of the mixture with those of the two salts individually. The concepts of saturation and solubility cannot be employed in their full thermodynamic sense to the mixture of salts of two different solubilities as a whole, since the mixture is not a single component of the solution. The precipitate which first appears as the salt mixture is progressively dissolved is almost certainly not of the same composition as that of the mixture. It may not even consist wholly of the less soluble component of the mixture, as a result of the salt effect of one salt on the other. At this point, more of the more soluble member of the salt pair could probably still be added to the solution without more precipitate forming, and hence the solution cannot be thought of as saturated individually in both salts. The salt pair, after all, is only a mechanical mixture of solids. However if more of the more soluble salt were added after the first traces of solid salt persisted, by dissolving it would alter the ratio of the two salts in solution from that of the salt mixture being charged. (A similar result would be obtained if additional salt mixture were added to the solution after the first traces of solid appeared.) Therefore the point of persistent appearance of the first traces of solid in fact represents the maximum amount of a given salt mixture that can be dissolved in a given solvent without causing alteration in the salt pair composition in solution, and it is in this context that the terms saturation and solubility have been used in reference to mixed salt pairs.

A synergistic effect of mixed salts on vapor-liquid equilibrium does appear to exist in certain systems of the present investigation, notwithstanding the lack of its evidence in the solubility curves. The effect is most clearly evident in both alcohol-water systems containing the bromide salts and their mixtures, and is exhibited mainly in the midrange and alcohol-rich regions of alcohol-water proportionality. For instance, in the ethanol-water system saturated with sodium and potassium bromides and their mixtures, although no significant synergistic effect on vapor-liquid equilibrium appears to exist in water-rich regions, the effect is sufficiently pronounced in ethanol-rich regions that all three mixtures of the two salts exerted effects sufficient to completely eliminate the azeotrope although neither salt alone was capable of so doing. In the ethanol-rich region, the solubilities of the three salt mixtures are seen in Figure 6 to be almost identical with that of the more soluble salt of the pair, a phenomenon almost certainly related to their effects on the composition of the equilibrium vapor.

Investigators have agreed generally that magnitude of salt effect in vapor-liquid equilibrium depends both on the degree of solubility of the salt in the liquid phase and the degree of difference between its solubility in each of the two volatile components in their pure states under boiling conditions. The vapor phase will be enriched in the component of the binary solvent whose molecules or groupings of molecules are less attracted into associations with the salt. Solution theory predicts that this will be the component in which the salt is less soluble. Previous experimental findings have tended to support the theory in this regard.

In the systems comprising the matrix of the present investigation, all four salts are more soluble in water than in either alcohol under boiling conditions. All, therefore, would be expected to salt out the alcohol, that is, to enhance the vapor phase in concentration of alcohol and hence to enhance the value of relative volatility (both alcohols being more volatile than water). Such, however, was found not to be the case for some of the systems of the present investigation in certain regions of alcohol-water proportionality. An interesting anomaly is observed in the behavior of the systems containing methanol. Although all four of the salts investigated are clearly more soluble in water than in methanol, and although all of their solubilities decrease as alcohol-water proportionality x_2 is increased, certain salts and their mixtures were observed to cause salting-out of methanol (enhancement of relative volatility) in water-rich regions, while salting in the methanol (decreasing the value of relative volatility) in methanol-rich regions. A similar crossover effect has been observed by Prausnitz and Targovnik (*27*) in the pyridine-water system with sodium iodide, in the isopropanol-water system with sodium chloride, and in the dioxane-water system with each of sodium chloride and sodium acetate. In all systems except the first, the crossover appeared related to the salt causing formation of two liquid phases. Crossover effects have also been observed in the methanol-water system with lithium chloride, lithium iodide, and sodium iodide by Proszt and Kollar (*28*), and in the methanol-water and ethanol-water systems with barium acetate by the authors (*22*, *29*). In these systems it can be speculated that at least two distinct and major it can be speculated 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 mixed solvent composition x_2. The crossover effect is most noticeable in the present investigation in the methanol-water system with sodium and potassium bromides and their mixtures. In the alcohol-rich region, as seen in Figure 1, both salts and all of their mixtures salted in the methanol, reducing rather than increasing the value of relative volatility. A lesser crossover effect is caused in methanol-water by the iodide pair, as seen in Figure 3. Sodium iodide appears to cause salting out of methanol throughout the entire range of x_2 values, whereas potassium iodide and its mixtures with sodium iodide exhibited mild salting in of methanol in alcohol-rich regions. There was no sign of a crossover effect existing in any of the present systems containing ethanol.

Some of the salt effects observed in the present investigation were quite substantial. The largest were observed in the ethanol-water system saturated with the iodides, where sodium iodide, potassium iodide, and all of their mixtures tested eliminated the azeotrope completely. The effect of sodium iodide in this system was sufficiently large that relative volatility, the parameter indicating by its magnitude the relative ease of separation of a system by distillation, was increased by as much as two- and even threefold over most of the x_2 range.

ACKNOWLEDGMENT

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NOTATION

k_3 = salt effect parameter, as defined elsewhere (*22*, *24*)
N_3 = mole fraction salt in alcohol-water-salt liquid phase = moles salt/(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 = moles alcohol/(moles water + moles alcohol)
y_2 = mole fraction alcohol in alcohol-water vapor phase = moles alcohol/(moles water + moles alcohol)

Subscripts

1 = water
2 = alcohol

3 = salt

Note: the term salt as used above also refers to the mixed salt pair collectively in those systems containing mixed salts

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On Intrinsic Errors in Pressure-Hole Measurements in Flow of Polymer Melts

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In order to investigate the possibilities of pressure-hole errors in the measurement of wall normal stresses in the flow of polymer melts, a 2.280-in. long slit die has been designed, having a slot with a rectangular cross section, 0.050 in. by 1.000 in. Three transducers were mounted on each of the two long sides of the rectangular slot along the longitudinal center line of the die and located so that each transducer was directly opposite another in the opposite side. The three transducers on one side were flush mounted. Those on the other side were mounted through pressure-holes with different diameters (0.017, 0.034, and 0.050 in.). Measurements of wall normal stresses were made with high density polyethylene and polypropylene melts at 200°C., following the experimental procedure described in the author's earlier papers. The present study indicates that pressure measurements made through pressure-holes are essentially the same as those made flush-mounted instruments, and that there are *no* pressure hole errors in the measurements of wall normal stresses, insofar as polymer melts are concerned.

In recent years several authors (*1* to *5*) studying the rheological properties of viscoelastic fluids have questioned the validity of normal stress measurement obtained by pressure transducers mounted on duct walls through pressure-holes. In most cases, such pressure measuring devices are connected to small pressure-holes. These holes are drilled through the wall normal to the surface mainly because the sensing device is much larger than the capillary diameter (or the gap between two plates).

Kaye et al. (*2*) reported that they found a systematic error in their pressure measurements using a cone-and-plate rheometer, and they attributed the error to the existence of small pressure-holes. They then presented an empirical correlation between the pressure-hole error and the shear stress by

$$p_H = -3.0\,|\tau_w| + 414 \qquad (1)$$