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SALT EFFECT IN DISTILLATION: A LITERATURE REVIEW*

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Abstract—A salt dissolved in a mixed solvent is capable, through preferential association in the liquid phase, of altering the composition of the equilibrium vapour phase. Hence salt effect on vapour–liquid equilibrium relationships provides a potential technique of extractive distillation for systems difficult or impossible to separate by normal rectification.

The literature pertaining to salt effect in vapour–liquid equilibrium and in extractive distillation is reviewed.

1. INTRODUCTION

When a salt is dissolved in a mixed solvent consisting of two volatile, miscible liquid components, the salt may affect the activities of the two volatile components through the formation of liquid-phase associations or complexes. If the dissolved salt associates preferentially with the molecules of one component of the solvent compared with those of the other, the solubility relationship between the two volatile components is altered such that one component is "salted out" in respect to the other. In such a case, the activities of the two volatile components of the liquid solution are altered relative to each other in a manner which results in a change of composition of the equilibrium vapour phase, despite the fact that no salt is present in the vapour phase. Similar "salt effects" can also be achieved in solvents consisting of more than two components. Addition of a soluble salt to the liquid phase of a system undergoing fractional distillation is hence a possible technique of extractive distillation for the separation of "difficult" systems, such as systems of low relative volatility, or systems exhibiting azeotropic behaviour in composition regions critical to the separation. Phase equilibrium studies have shown that the magnitude of salt effect on vapour–liquid equilibrium relationships can be quite large in certain systems.

Extractive and azeotropic distillation operations using an added liquid "solvent" or "extractive agent" have been thoroughly investigated both theoretically and experimentally, and are in common industrial use for the separation of systems which would be uneconomical or impossible to separate by normal fractional distillation. However, relatively scant attention has been given to the possibility of using dissolved salts as extractive agents in distillation operations.

Applying salt effect to a system of volatile components undergoing fractional distillation would involve introducing the salt into the descending liquid phase near or at the top of the column, normally by dissolving in the entering reflux stream. Recovery of salt from the bottoms product would require a separate operation. The salt, being non-volatile, would appear *only in the liquid phase*, and hence would flow only downward within the fractionation column. Providing that reasonable precautions against entrainment were taken, a major advantage of this technique of extractive distillation would be

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that an overhead product completely free of the extractive agent would be obtained.

A substantial number of investigations, relating in one way or another to salt effect in distillation, have been undertaken by previous investigators. It is the purpose of this review to list and categorize references to previous work, and to review in some detail the more pertinent of these.

Literature relating to salt effect in distillation can be classified into three general categories:

(a) Salt effect in vapour-liquid equilibrium;
(b) Extractive distillation employing dissolved salts as extractive agents;
(c) Liquid-phase solution theory of electrolytes dissolved in mixed solvents.

This review will concern itself primarily with categories (a) and (b), since these are most closely related to salt effect in distillation. However, the more pertinent references in category (c), although concerned primarily with thermodynamic changes occurring in the liquid phase of non-boiling systems, and without direct reference to the vapour phase, are applicable and will also be reviewed.

2. SALT EFFECT IN VAPOUR–LIQUID EQUILIBRIUM

Many of the earlier investigators studied the effects of dissolved salts on the composition of the equilibrium vapour phase of mixed solvents by measuring vapour pressures under conditions of constant temperature in non-boiling systems. Others carried out simple laboratory distillations or laboratory fractionations at constant pressure, with the salt dissolved in the still.

More recently, investigators have employed various types of recirculation stills, most notably the improved Othmer type [1, 2], to measure salt effect on the vapour–liquid equilibrium relationships of boiling systems. Data from such investigations, most of them involving systems consisting of a salt and a two-component solvent, are presented normally in the form of an equilibrium curve in which vapour composition is plotted against liquid composition, the latter reported on a salt-free basis. Most investigators have tended to use saturated salt concentrations in order to achieve the largest possible salt effect in the systems under study. As a result, the equilibrium curve represents the effect of the salt at saturated concentration across the composition range of the binary solvent, rather than at a constant value of salt concentration such as would be found from tray to tray in a rectification column in which the assumption of constant molal overflow was valid.

2.1 *Vapour pressure measurements* (*at constant temperature*)

Kablukov [3, 4, 5] as early as 1891 reported results of observations of the effect of salt on the partial pressures exerted over aqueous ethanol. He observed that salts more soluble in water than in alcohol increased the vapour pressure of the alcohol and vice versa, variations in vapour pressure were proportional to salt concentration, and nonelectrolytes seemed to have less effect on vapour pressure than electrolytes. He observed that alkaline earth halides enriched the vapour in alcohol while mercuric chloride impoverished it, and that the degree of enrichment of the vapour was nearly proportional to salt concentration. Miller [6] in 1897 made similar observations, noting also that the magnitude of salt effect would depend on the difference in the solubility of the salt in pure water and in pure ethanol. He concluded that whether the total vapour pressure of a binary system was lowered or raised by salt addition depended merely on whether the partial pressure of one component was lowered by an amount more or less than that of the other was raised, this in turn depending on the solubility relationships of the components. Wright [7–9], and Butler [10, 11] also made similar observations, both attributing the effect to preference of salt ions for associating, or solvating, with the molecules of one component of the mixed solvent over those of the other.

Other investigators of salt effect on partial pressure relationships in aqueous ethanol were Nikol'skaya [12], Maizlish and Tverdovskii [13], Sergeeva and Mishchenko [14, 15], and Schulek *et al.* [16–18]. Both Sergeeva and Schulek observed a maximum to occur in the degree of salt effect caused by calcium chloride as ethanol concentration was increased, concluding that alcohol molecules took part in the solvation of the salt when insufficient water molecules were present. Schulek also observed this effect with zinc chloride.

Salt-effect studies in aqueous methanol were undertaken by Chernyak [19], Baron and Mishchenko [20], Storonkin and Simanavichus [21], and Sergeeva [22]. Sergeeva observed that lithium perchlorate, a salt quite soluble in methanol and almost insoluble in water, lowered the partial pressure of methanol but had little effect on that of water.

McBain and Kam [23], while investigating salt effect on the degree of dissociation of acetic acid in aqueous solution, observed that many dissolved salts raised the partial pressure of the acetic acid.

2.2 *Distillation techniques*

Another approach involved distilling binary mixtures first alone and then in the presence of salts, measuring either the distillation rate or enrichment of the overhead product. Quartaroli [24–26] fractionated various organic acid–water mixtures in the presence of common anhydrous salts. Kyrides *et al.* [27], and Samaddar and Nandi [28] performed similar experiments on the ethanol–water system.

Virtanen and Pulkki [29] studied the effects of various common salts on organic acid–water systems by measuring distillation rates, observing their salts to bear a similar order of effectiveness in increasing the separation ease of the system as in decreasing the solubility of the acids in water.

Craven [30], by dissolving sodium chloride in aqueous acetic acid, succeeded in creating an azeotrope where none had previously existed.

2.3 *Vapour-liquid equilibrium data in boiling systems (at constant pressure)*

Proszt and Kollar [31, 32] observed that dissolved salts in general tended to enrich the vapour in the component of lower dielectric constant. Fox [33] investigated the effect of sodium sulphate on the ethylene glycol–water system, observing that the relative volatility of the ethylene glycol–water system was already so high that vapour enrichment due to salt effect was difficult to detect experimentally. Fogg [34] also investigated the aqueous ethylene glycol system, saturated with each of sodium sulphate, potassium chloride, and potassium bromide. His observations agreed with those of Fox. Guyer, Guyer, and Johnsen [35] tested the effects of several salts on the formic acid–water system. Some salts were observed to increase relative volatility while others decreased it. There was some evidence of chemical reaction occurring between the salts and the acid. Googin and Smith [36] discovered that certain salts decreased the efficiency of distillation of light from heavy water. Simanivicius [37] studied the methanol–water–calcium chloride system.

Johnson, Ward, and Furter [38] found that sodium propionate greatly increased the proportion of *n*-octane in the equilibrium vapour of boiling mixtures of *n*-octane–propionic acid, and shifted the azeotrope considerably. Prausnitz and Targovnik [39] presented results of a study of the effects of sodium chloride, potassium benzoate, and sodium acetate on aqueous dioxane; of sodium chloride and potassium benzoate on aqueous isopropanol, and of sodium iodide and sodium sulphate on aqueous pyridine. Garwin and Hutchison [40] investigated the effect of various concentrations of calcium chloride on the acetic acid–water system, finding that the affinity of calcium chloride for water was sufficiently strong to reduce the low relative volatility of the system to reversal even at relatively low salt concentrations. At salt concentrations near saturation, the numerical value of the reversed relative volatility was observed to exceed that of the original salt-free binary system. Therefore, the net effect of a high concentration of this salt was to enhance ease of separation, at the same time reversing the overhead and bottoms products such that acetic acid was now obtained overhead instead of water. The system acetic acid–water was also studied by Ramalho *et al.* [41]. The salts used were calcium, strontium, magnesium, and barium chlorides, and the results agreed with those of Garwin and Craven. All salts introduced an azeotrope and reversed the volatility order of the two volatile components.

Jost [42] studied the effect of calcium chloride on aqueous ethanol. Yamamoto [43], investigating the same system, extended the study to include three other salts in addition to calcium chloride. All salts enriched the vapour in ethanol. Neither Jost's nor Yamamoto's data extended into the azeotrope region. Costa Novella and Moragues Tarraso [44] determined the effects of dissolved potassium acetate and cupric chloride on the ethanol–water system. Potassium acetate was observed to have a larger effect than cupric chloride, but both destroyed the azeotrope. They did not report salt concentrations. Meranda and Furter [45] studied the ethanol–water system saturated with potassium acetate, observing a salt effect larger than that reported by Costa Novella. Salt solubility data were measured. Ethanol–water relationships in the presence of dissolved salts have also been studied by Dobroserdov. Salts used were calcium chloride [46], potassium acetate [47], sodium chloride [48], sodium acetate [49], and zinc chloride [50]. He reported that sodium and potassium acetates and zinc chloride all destroyed the azeotrope, and that the use of dissolved salts for the dehydration of ethanol would be more economical than the present azeotropic distillation method which employs benzene [51]. In studying the effects of calcium chloride over a wide range of alcohol–water and salt concentrations [52], Dobroserdov observed that the activity coefficient of the ethanol increased in proportion to the concentration of salt up to about 60 mol per cent ethanol, but was inversely proportional to salt concentration at higher alcohol concentrations. Dobroserdov also investigated the effect of calcium chloride on the systems *n*-propanol–water and isopropanol–water [53, 54]. In both systems the azeotrope was destroyed. Data for the ethanol-rich region of the ethanol–water system in the presence of potassium acetate at various levels of concentration below saturation were published by Klar and Sliwka [55]. They also reported success in operating a small laboratory distillation column to produce absolute alcohol by dehydration with potassium acetate. Rieder and Thompson [56] studied the system ethanol–water saturated with potassium nitrate. Tursi and Thompson [57] extended this study to the salts sodium sulphate, sodium nitrate, and potassium sulphate. The results achieved were similar to those of Rieder, in that no marked effect on azeotropic composition was evident.

Johnson and Furter [58–61], employing an improved Othmer still modified for salt effect studies, measured vapour–liquid equilibrium data for a total of 24 systems, each consisting of an alcohol (methanol, ethanol, or *n*-propanol), water, and a salt. Twelve different salts were used with the ethanol–water system, and six each with methanol–water and *n*-propanol–water. By defining salt effect in terms of the difference in effect of the salt on the chemical potentials of the two volatile components, they derived from thermodynamic considerations an equation relating the magnitude of salt effect on vapour-phase composition to salt concentration in the liquid phase, the latter in turn related to the solubility properties of the pure components. They demonstrated that this equation could also be derived from Gilliland's relation [62] for liquid extractive agents, and from the "Gibbs characteristic" [63] as employed by Joseph [64]. Madonis [65] tested the relation with liquid extractive agents. Johnson and Furter observed their relation, which was derived *only for a specified ratio of volatile components* in a given system, also to hold as the relative proportions of the two volatile components were varied. This latter observation was unexpected, since salt effect is believed to be a complex function of interactions and self-interactions between all system components (each interaction being, furthermore, a function of liquid-phase composition and hence of degree of salt dissociation), and was attributed to an apparent tendency of various interaction mechanisms to balance each other insofar as salt effect of moderately soluble salt is concerned. When plotted as a function of alcohol–water ratio, the two individual salting parameters (of which the overall salt effect proportionality function is the algebraic sum), despite substantial variation in their individual values, were observed to demonstrate this balancing effect to a remarkable degree with the systems tested. Johnson and Furter extended the model proposed by Gross and Halpern [66, 67], in order to relate changes in vapour composition to reduction of mutual solubility of one volatile component in the other by the salt. They employed a derivation similar to that of Gordon [68] to prove that a salt will increase the chemical potential of the solvent component in which it is less soluble and vice versa. Ramalho and Edgett [69] proposed a graphical method, based on the Furter equation, for correlating salt effect at salt concentrations below saturation. Experimental verification of the correlation for the system propionic acid–water with various salts was presented. Yoshida *et al.* [70, 71] investigated the systems methanol–water and acetic acid–water, each with several salts. Each salt was studied at saturation, and also at a series of constant salt concentrations below saturation. They observed close agreement with the Furter equation for the methanol systems, but lesser agreement for those containing acetic acid.

Rozen [72] derived the same relationship as that of Johnson and Furter from equations for the evaluation of activity coefficients published by Krichevski [73]. Kogan [74, 75] demonstrated the consistency of this relation with the Redlich–Kister and Duhem–Margules equations, and tested it [76] with the aqueous systems of formic acid, pyridine, hydrochloric acid, acetic acid, and ethanol, each with several salts. He drew an analogy between this method of correlation and the original Setchenow [77, 78] equation relating the effect of salt concentration to the solubility of a nonelectrolyte in aqueous solution.

Rius [79–84] studied the effects of several salts on aqueous ethanol, *n*-propanol, and isopropanol. He attempted a thermodynamic correlation between fugacities and salt concentration which demonstrated a similarity to the Setchenow equation, and also applied modified Van Laar equations with some success. Lu [85] attempted to estimate salt effect by empirical methods, testing his proposed correlation with the data of Fogg. Baranov *et al.* [86–92] studied the nitric acid–water system in the presence of various nitrates, both singly and in pairs. They compared the effectiveness of these salts with that of sulphuric acid, the conventional agent for concentrating aqueous nitric acid, concluding that some were superior and some inferior. They observed that some of their systems exhibited the proportionality observed by Johnson and Furter, Kogan, and Rozen more closely than did others. Cigna *et al.* [93] also studied the effects of inorganic nitrates on the aqueous nitric acid system.

3. EXTRACTIVE DISTILLATION EMPLOYING DISSOLVED SALTS

Van Ruymbeke [94, 95] patented a process for extractive distillation of aqueous ethanol with glycerol, and later modified the process [96, 97] by adding salts such as calcium chloride, zinc chloride, and potassium carbonate to the glycerol. A concentrated feedstock was required to obtain absolute alcohol by this method.

Gorhan [98] patented a process for separation of acetic and formic acids by adding concentrated sulphuric acid to the still. Later, he proposed a method for concentrating dilute aliphatic acids by contacting the vapourized acid with fused sodium and potassium bisulphates [99, 100], and then modified this method to yield the acid directly by distilling a solution of acid and salt [101, 102]. Gorhan registered several patents [103–109] describing a process and apparatus for the production of absolute ethyl alcohol using salts such as acetates, chlorides, formates, propionates, and nitrates. The salts were added to the reflux stream of a fractionation column in fused condition, and were used both singly and in mixtures of two or three. Gorhan did not publish experimental data, but did describe in some detail [110] a plant producing up to 13200 gal/day of absolute alcohol by the HIAG process, which involved adding a molten salt to the reflux stream. Barbet [111, 112] patented a process for producing absolute alcohol in which the feedstream, containing a dissolved salt, was fed to the reboiler of a continuous still.

Mariller *et al.* studied the addition of salts to liquid extractive agents employed in the rectification of absolute alcohol from aqueous solution. Mariller [113–115]· and Mariller and Granger [116] tested the effects of glycerol containing dissolved salts, and described two commercial plants in operation with this process. Mariller [117, 118], and Mariller and Desse [119] proposed using various other organic liquids containing dissolved salts as extractive agents for ethanol rectification.

Mariller [115], Mariller and Coutant [120], Keyes [121], and Sunier [122] confirmed Kablukov's observation that a salt more soluble in ethanol than in water, such as mercuric chloride, would impoverish rather than enrich the vapor in ethanol.

Mariller [123], Burich [124], and Longinov and Dzirkal [125] described processes for production of absolute alcohol by extractive distillation, employing calcium chloride as the extractive agent.

Cook and Furter [126–129] developed a technique for dissolving salts into the reflux stream of a semiworks-scale column, involving the use of a fluidized bed principle to rapidly dissolve the salt. Using a potassium acetate concentration of only 0·06 mole fraction, they were successful in eliminating the ethanol–water azeotrope. Kelly [130] registered a patent for separating methanol from a mixture of saturated hydrocarbons by distillation with an inorganic salt soluble only in the alcohol. Othmer [131] developed a large-scale industrial process for distilling acetone from its azeotrope with methanol by passing a concentrated calcium chloride brine down the distillation column. Pure acetone was condensed overhead, and acetone-free methanol was recovered in a separate still from the brine, which was then recycled. Walker *et al.* [132] also referred to the use of salt effect to separate methyl alcohol from acetone. Suitable salts mentioned were sodium hydroxide, potassium carbonate, and sodium thiosulphate.

Suida [133, 134] described the dehydration of aliphatic alcohols with caustic alkali solutions. One method employed a hot reflux stream of extractive agent in a column through which the alcohol was distilled, and another involved bubbling the alcohol vapour through a bath of caustic alkali solution. Bogart and Brunjes [135, 136] recovered phenol from aqueous solution by extractive distillation with sodium chloride. The salt was present only in the reboiler. Dittmar [137] referred to a process in which aqueous solutions of nicotine were distilled using sodium chloride as the extractive agent. The salt addition was claimed to reduce the number of distillation trays, for the same degree of separation, from ten to two. Morrell and Gilliland [138] patented a process for separating two aliphatic water-soluble substances such as alcohols from each other by passing an aqueous salt solution down the distillation column. One alcohol and water would be obtained as the overhead product while the bottoms would consist of the other alcohol, water, and salt.

Extractive distillation of aqueous nitric acid with a salt instead of with concentrated sulphuric acid has also been investigated. The

Hercules Powder Company [139] patented a process in which magnesium nitrate is added to the reflux, and is recovered by evaporation. A somewhat similar process was patented by the Chemical Construction Corporation [140]. A 50 ton/day plant at Parlin, New Jersey, is operated by the Hercules Powder Company [141]. Sloan and Jamieson [142] described a plant operating on the same principle in Britain. The advantages claimed for the process are lower capital investment and operating costs, a higher yield at a higher quality (sulphates are eliminated), and less pollution of the atmosphere.

In summary, it is seen that some extractive distillation processes employing salt effect use a dissolved salt (or salts) as the extractive agent, while others use a liquid extractive agent with a salt (or salts) added to it.

4. SOLUTION THEORY OF ELECTROLYTES IN MIXED SOLVENTS

Such studies have tended to concentrate on thermodynamic changes occurring in the liquid phase without direct reference to the equilibrium vapour, and also have tended to be at temperatures below, rather than at, the boiling point. However, many of the electrolytic systems studied consist of a salt dissolved in a solution consisting of water and an organic nonelectrolyte. The theories and data of salting in and out in a mixed solvent are hence pertinent to salt effect in distillation.

It is important to note that the nomenclature commonly used by investigators of salt effect in vapour–liquid equilibrium and in extractive distillation refers to the salt as the solute and to the mixture of the two (or more) volatile liquid components as the solvent. However, because most of the investigators of the solution-phase effects of a dissolved salt in a mixed solvent have dealt with systems in which one of the volatile components was water, and because many common salts are more soluble in water than in other liquid compounds, these investigators have tended to use a nomenclature in which the dissolved salt is referred to as the *electrolyte*, the water is referred to as the *solvent*, and the other volatile liquid component is referred to as the *nonelectrolyte*. The latter nomenclature will be used in the following section, in conformity with the majority of the investigators in this related field.

The effect of the addition of charged particles to binary liquid solutions is a complex phenomenon. This complexity is not surprising when the variety of interactions that are involved is considered. These include interactions of ion–nonelectrolyte, ion–solvent, and nonelectrolyte–solvent, as well as self-interactions of all three components. Each of these interactions comprising salt effect is a function of the concentrations and properties of all three components. Hence the effects of different salts on a given two-component liquid solution are not the same, and even the order of effectiveness of salts in a series is found to vary widely with different nonelectrolytes in aqueous solution. The complexity is increased when the nonelectrolyte is polar.

Generally, the molecules of one liquid component are more strongly attracted into associations with the electrolyte than are those of the other. Usually, molecules of the more polar component are preferentially attracted by the electrostatic field of the salt ions. The molecules of the more-attracted component, according to the model proposed by Gross [66, 67], tend to congregate in the neighbourhood of the ions, in effect forcing the other component into the portions of the solution remote from the ion fields, raising the concentration of the less-attracted component in these latter regions. Hence, the volume in the solution accessible to the latter component has become diminished by the presence of the salt, the net result being a decreased solubility of this component in the solution. The effect of an electrolyte added to binary systems in which both volatile components are completely miscible is often sufficient to cause a reduction to partial miscibility. Butler [10, 11] indicated that the preferential attraction of the salt ions for one volatile component over the other removes molecules of the former component from their solution role, thus decreasing their activity in the solution. Molecules of the other volatile component are expelled from the ionic regions into a greater activity in the remainder of the solution. He indicated that the net result would be a reduction in the chemical potential of the former component and an increase in that of the latter. The term "salting out" is generally used to denote a decrease in the solubility of the nonelectrolyte in the solution, or, more rigorously, an increase in its activity coefficient, caused by the salt addition. "Salting in" refers to the opposite case.

Data and discussions of salt effect in liquid solutions are offered by many investigators, among them Swabb [143], Frejaques [144], Thompson and Molstad [145], Morrison [146], Frankforter [147–149], Zhdanov and Sarkazov [150], Gorin [151], Lebed [152] and Sergeeva [153–156]. Lescoeur [157] recorded that Lully in the 12th century found that potassium carbonate would salt out ethanol from aqueous solution. Jentoff [158], Fogg [34], and Bogart [135, 136] all discussed the use of liquid organic additives to precipitate salts from aqueous solutions. Tsvetkov and Yurzhenko [159], in studying the effect of added salts on the rate of emulsion polymerization of styrene, found that the rate was reduced because these salts salted out the emulsifying agent. Additional references to the effects of electrolytes include those of Falkenhagen [160], Robinson and Stokes [161], and Harned and Owen [162].

The literature on salting in and out in liquid solutions has been reviewed comprehensively by Long and McDevit [163]. Salt effect theories are generally concerned with the calculation of the ion–nonelectrolyte interaction parameter, which is known as the "salting-out parameter" and is used to indicate the magnitude of salt effect. Negative values indicate the occurrence of the opposite effect, salting in. Electrolyte dissociation must be considered when attempting to place salts in order of effectiveness. If molecular values are used for salt concentration, the salt parameter must then include consideration of ionic charges and the number of ions per salt molecule. Debye [164], and Randall and Failey [165, 166] have pointed out that in order to use this parameter as a measure of salt effectiveness, ionic strength rather than mole concentration of salt should be used in its evaluation. Long and McDevit [163] listed and categorized the large body of experimental salting-out data contained in the literature. From the literature on systems in which the nonelectrolyte was non-polar, they found a somewhat similar order of effectiveness of cations for any given anion, and also of anions for any given cation, to exist for various nonelectrolytes in aqueous solution. This series was only approximate, for it exhibited considerable variance from system to system. Johnson and Furter [59, 60] observed an order of effectiveness of various salt anions and cations which agreed with this series. The salting-out effectiveness of various ions was also investigated by Samoilov [167], Liu [168], and Yang [169]. Long and McDevit [170] and Morrison [171] noted a rough additivity of ionic contributions to the value of the salting-out parameter for certain systems. For the more complex case of polar nonelectrolytes, a similar salt order was noted, although this order exhibited much less uniformity with different nonelectrolytes than in the more ideal systems. Ciparis [172–178] investigated the order of effectiveness of a large variety of salts on salting in and out in aqueous solutions of various organic acids.

Because of the looseness of the ion order with various non-electrolytes, no definite relation has been found to correlate the properties of salt ions to their effects. However, a qualitative relation does appear to exist between the reciprocal of ion radius and ion effectiveness, as would be expected from electrostatic theory.

The causes and effects of the preferential attraction of a dissolved salt for one component of a water–nonelectrolyte solution over the other have been explained in various salt effect theories, some quantitative but most qualitative. These attempts can be classified under one of the following: hydration, electrostatic interaction, van der Waal forces, and internal pressure. They are discussed at length by Long and McDevit [163], and are briefly described below. In summary. it can be said that since no single theory has yet been able to represent the data on salt effect in liquid solutions satisfactorily except in restricted and limiting cases, previous investigators generally have agreed that salt effect is caused by a complexity of forces and interactions, no one of which is sufficiently significant in relation to the others that the others may be neglected.

4.1 *Hydration*

The simplest picture of salting out was proposed by Rothmund [179]. He postulated that salt ions become hydrated in aqueous nonelectrolyte solutions, each ion completely tying up a share of water molecules and thus removing them from their solvent role, but having no effect on the remaining water or on the nonelectrolyte. Long and McDevit found this model inadequate because it indicated that hydration numbers should be independent of the species of nonelectrolyte, which they are not. Also, the theory did not allow for the occurrence of salting in nor did it correspond to the observed ion order.

4.2 *Internal pressure*

This early concept of salt effect envisaged the solvent as being compressed by the force fields of the ions, thus squeezing the nonelectrolyte out of solution. Euler [180] noted experimentally that the degree of salting out was related to the observed volume contraction caused by the salt. Gibson [181, 182] defined the "effective pressure" of a salt as the external pressure that would have to be applied to the solution to cause a volume contraction equal to that caused by the salt. He found this parameter to correspond roughly to the magnitude of salt effect. Long and McDevit [170] showed that such a relation should hold only for strictly non-polar nonelectrolytes in dilute solution, and developed a theory for this case, relating volume contraction to salt effect. Bernal and Fowler [183] and Long and McDevit concluded that, since at ordinary temperatures a large fraction of liquid water is in an open-structured quasi-crystalline state, much of the compression caused by the ionic fields may come from a collapse of this ordered open form. Gibson, and Morrison [171, 184, 185] also discussed solvent structure in this context. Morrison concluded that the effective pressure theory was not valid with his data. Deno and Spink [186] presented evidence supporting the internal pressure concept.

4.3 *Electrostatic theories*

Electrostatic theory, originating in the early work of Debye and Huckel [187], gives the only really quantitative approach to salting out. The basic theory of salt effect in binary liquid mixtures, relating salt effect to the influence of the nonelectrolyte on the dielectric constant of the solvent, was proposed by Debye and McAuley [188]. It is based on a calculation of the amount of work necessary to discharge the ions in pure solvent (water) and to recharge them in a solution containing nonelectrolyte, thus yielding the electrical contribution to the free energy, and hence activity coefficient, of the nonelectrolyte. Debye [164] later extended this theory to take into account the heterogeneity of the water–nonelectrolyte mixture. Gross [189] further extended the theory to include the concept of ion atmosphere. Butler [190] derived a similar equation by a modified method, as did Belton [191], and Altshuller and Everson [192]. Baranowski [193], and Givon [194] further extended the Debye theories.

Kirkwood [195], taking into account the repulsion between the ionic charge and an image charge induced in the cavity created in the solvent by the nonelectrolyte molecule, calculated the ion–nonelectrolyte interaction energy. He derived an equation quite similar in form to that of Debye and McAuley.

These electrostatic theories treat the solvent only as a structureless continuum through which the electrostatic ion forces act, and whose interaction with the ions is determined solely by its macroscopic dielectric constant. They consider only departures from ideality arising from electrostatic interactions involving the ionic charges. The resulting equations are limiting laws since they assume infinite dilution. It would be expected, then, that at finite electrolyte concentrations, the electrostatic field of an ion would be weakened by ion interaction. Altshuller and Everson [192] stated that experimental measurements of dielectric constants of electrolytic solutions have been confusing and contradictory. They found that ionic radii obtained crystallographically did not apply with exactness in solution. Harned and Owen [162] stated that because of its limiting nature, the electrostatic theory cannot be expected to yield quantitative results in nondilute solutions. Gross and Kahn [196] studied the effects of various nonelectrolytes on the solubility of electrolytes in aqueous solution, relating the effects qualitatively to dielectric constant. They concluded that electrostatic theory failed to give a quantitative description of such effects. Attempts to calculate the salting out parameter from the electrostatic theories of Debye and Kirkwood made by Albright and Williams [197], Scatchard [198], Altshuller and Everson [192], Long and McDevit [199, 200], and Gross [66, 67, 196], were largely unsuccessful. At best, comparison with experimental values yielded agreement to within an order of magnitude. These theories did not predict the marked variations in either the effects of different salts or of different nonelectrolytes, and failed entirely for the case of salting in of the nonelectrolyte. They were unable to predict a series of effectiveness of salt ions which agreed with the experimentally-observed order. Previous investigators tended to conclude that their basic assumption of the only significant cause of non-ideal behaviour lying in electrostatic interaction was inadequate.

4.4 *van der Waal forces*

The fact that a given nonelectrolyte may be salted in by some electrolytes and salted out by others in the same solvent suggested that short range dispersion forces may also be appreciable in determining salt effect, especially at finite concentrations. However, Linderstrom-Lang [201] and Bockris *et al.* [202] had little success in correlating salt effect to dispersion forces.

Long and McDevit, in an attempt to allow for the trend toward salting in of the nonelectrolyte by large ions, proposed a modified version of the Kirkwood equation to account for dispersion and displacement forces. They concluded that the theory was inconclusive in establishing the role of dispersion forces, that at best these are not negligible, but are only secondary in determining the relative effects of a series of ions. Bergen and Long [203] discussed salting in and salting out in terms of the effect of the electrolyte on the degree of order in the solvent structure. Gross [66, 67] suggested that salting in indicates a preferential attraction of ions for the nonelectrolyte over the solvent. In the presence of large ions having weak electrostatic fields, or in the presence of relatively undissociated salts, the highly polar water molecules may tend to associate much more strongly with each other than with the salt, forcing the salt into the vicinity of the less polar nonelectrolyte molecules with which it then associates. Salting in has also been reviewed by Eck *et al.* [204], and by Bergen [205].

Once again, the conflict in nomenclature regarding the use of the term "solvent" should be emphasized. Investigators of salt effect in vapour–liquid equilibrium and in extractive distillation tend to designate the volatile components of the liquid phase collectively as the solvent, while investigators of the solution theory of electrolytes in two-component liquid mixtures of which one component is water usually refer to water as the solvent.

Sergeeva [206] has written a recent review of the literature on effects of electrolytes in mixed solvents.

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Résumé—Un sel dissous dans un solvant non pur est capable, grâce à une association préférentielle dans la phase liquide, d'altérer la composition de la phase vapeur à l'équilibre. L'effet du sel sur les relations d'équilibre vapeur–liquide fournit par là une technique possible d'extraction par distillation pour des systèmes difficiles ou impossibles à séparer par rectification normale.

La bibliographie correspondant à l'effet du sel sur l'équilibre vapeur–liquide et sur l'extraction par distillation est passée en revue.

Zusammenfassung—Ein in einem Lösungsmittel gelöstes Salz ist in der Lage durch bevorzugte Anlagerung in der flüssigen Phase die Zusammensetzung der Gleichgewichtsdampfphase zu verändern. Damit ermöglicht der Salzeinfluss auf das Verhältnis des Dampf–Flüssigkeitsgleichgewichts eine denkbare Methode der extraktiven Destillation für Systeme die schwer oder gar nicht durch normale Rektifikation zu trennen sind. Die den Salzeinfluss im Dampf–Flüssigkeitsgleichgewicht und in der extraktiven Destillation umfassende Literatur ist beschrieben.

Аннотация—Соль, растворенная в смешанном растворителе, способна изменить состав равновесной паровой фазы с помощью избирательной ассоциации в жидкой фазе. Следовательно, влияние соли на равновесные соотношения системы пар–жидкость обеспечивает потенциальный метод десорбции перегонкой для систем, которые трудно или невозможно разделит обычной ректификацией.

Проведен обзор литературы по влиянию соли при равновесии системы пар–жидкость и при десорбции перегонкой.