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I hereby recommend that the thesis prepared under my supervision by Aubrey Paul Altshuller *entitled* An Experimental Study of the Salt Effect in Aqueous Solutions.

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Approved by:

H. E. Everson

W. M. Burgess

E. F. Farrar

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AN EXPERIMENTAL STUDY OF THE SALT EFFECT IN AQUEOUS SOLUTIONS

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Aubrey Paul Altshuller

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I INTRODUCTION

One of the most important properties of a substance is its solubility. The truth of this statement may be seen if we consider briefly the wide applicability of solubility relationships. For convenience, some applications are listed below.

1. Qualitative inorganic analysis is based on differences in solubility due to variations in pH, complex ion formation, etc.

2. Gravimetric analysis depends on the insolubility of certain compounds which may be dried and/or ignited to constant weight to obtain composition.

3. Qualitative organic analysis has as one of its general procedures the solubility behavior of unknown compounds towards a group of solvents.

4. The separation and purification of materials depends on differential solubility relationships.

a. Separations of two or more electrolytes from each other may be obtained by means of differences in the rate of change of solubility with temperature.

b. Proteins and protein complexes are often separable because of differences in their solubilities in the presence of added electrolytes.

c. Organic substances may be separated from other organic or inorganic substances by extraction with another solvent.

d. The extraction procedure mentioned above may be aided by salting out with an added electrolyte into another solvent.

5. The solubility of protein preparations may be used as a measure of purity.

6. Solubility behavior may be used to study intermolecular forces.

7. Chemical reactions occurring in solution are influenced by the solubilities of reactants and of products; consequently, the proper choice of solvent is of considerable importance.

If solubility concepts are to be fully applied to the many practical problems in organic and inorganic chemistry in which they arise as important or determining factors, it is important that an understanding be had of the fundamental forces which give rise to the solubility differences we observe.

We are fortunate today in having some understanding of the nature of many of the intermolecular forces responsible for the variations in the solubility observed. These forces are the dispersion forces, ion-ion interactions, ion-dipole interactions, dipole

interactions, dipole-induced dipole interactions, and chemical interactions. We know that the interactions in non-polar media may be almost entirely considered as due to dispersion forces. We realize that when dealing with polar molecules dipole-dipole forces are of great importance, and that when hydrogen bonding occurs, its influence may be overwhelmingly significant in determining differences in solubility. We are cognizant of the fact that the solubilities of electrolytes are dependent upon the lattice energies, along with the heats and entropies of solutions of the ionic species. In many cases this knowledge has led us to quantitative expressions capable of relating solubility to molecular parameters or to macroscopic variables of a fundamental nature, but in many other cases the complexity of the problems involved is such that only semi-quantitative relationships may be indicated.

Applications of the Debye-Huckel theory (1,2,3) have made it possible to relate changes in solubility to the ionic strength, the dielectric constant, the valencies of the ions, and the temperature for slightly soluble substances upon addition of electrolytes by use of an expression of the form

$$\log S/S_0 = Az_+z_-(\mu_o^{\frac{1}{2}} - \mu^{\frac{1}{2}})/(DT)$$

where A is a constant, z_+ and z_-, the valencies of the

positive and negative ions, D the dielectric constant, T the absolute temperature, μ_0 the ionic strength due to the slightly soluble salt alone and μ the ionic strength due to the slightly soluble salt plus added electrolyte.

Kirkwood (4,5) has applied the Debye-Huckel theory to zwitter ions and has shown that the solubility of the zwitter ion varies with addition of electrolyte according to a relation of the form

$$\log S/S_0 = 0.125R^2D_0\mu/aD$$

where S_0 is the solubility of the zwitter ion in pure solvent and S its solubility in the presence of added electrolyte, R is the distance between charges on the zwitter ion, and a is the mean distance of approach of the other ions to the zwitter ions.

Both of the equations above give the limiting value for solubility changes. More complicated expressions may be derived which may hold for somewhat higher concentrations. These expressions, however, contain simplifying assumptions of considerable scope. Progress has been made here in relating solubility changes to fundamental parameters. It must be noted that only solubility differences are considered. The absolute solubility of simple or complex electrolytes in a solvent is not evaluated.

The difference between the absolute solubilities of electrolytes may be related, as has already been mentioned, to the lattice energies of the solid salts, the heats of solution of the ions, the entropies of vaporization of the ions and the entropies of solution of the gaseous ions. Thus, it is possible to trace the reason for the relative insolubility of lithium fluoride and the appreciable solubility of potassium bromide in water to the large negative value of the entropy of solution of the gaseous lithium and fluoride ions in water (6). On the other hand, the reason for the high solubility of silver fluoride and the relative insolubility of the other silver halides lies in the considerable contribution of covalent interactions to the lattice energies of the silver chloride, bromide and iodide (6).

The free energies of solution of electrolytes may be approximately evaluated by means of the Born expression (7). In the case of salts of appreciable solubility, such a limiting expression can hardly be expected to be valid. An empirical expression based on the fact that the activity coefficient in a saturated solution of electrolyte is practically constant and independent of dielectric constant has been used (8). The Debye-Huckel expression for the activity coefficient in two different media are equated and the solubility is

related to valence, temperature, and dielectric constant. No theoretical justification has been given for such a procedure.

Hildebrand and his coworkers along with many other investigators have considered the theoretical aspects of the solubility of non-electrolytes. (9,10) Where the molecules involved are non-polar or where the dipole moments are quite small, that is, where only the dispersion forces are of importance, quantitative expressions have been derived relating the solubility to the mole fraction of solute, the heats of vaporization, and the molar volumes of solute and solvent. It is now possible to classify solution types on the basis of enthalpy and entropy changes involved in transferring onemole of solute from its pure liquid to a solution. For an athermal,ideal and an athermal, non-ideal solution as well as for the general type of solution where no specific interactions are involved, the heat of mixing is zero. For regular solutions ($a_2 > x_2$, $v_1 = v_2$, $a_{12} = (a_{11}a_{22})^{\frac{1}{2}}$), the heat of mixing is given by

$$\bar{H}_2 - H_2^{\circ} = v_2 \phi_1 (\delta_1 - \delta_2)^2$$

where v_2 is the molar volume of component 2, ϕ_1 is the volume fraction of component 1, δ_1 and δ_2 are the solubility parameters equal to $(E^v/v)^{\frac{1}{2}}$ or the square roots of their

energies of vaporization per milliliter. For the case where one component is associated $\bar{H}_2 - H_2^o > 0$, while for solutions where solvation occurs $\bar{H}_2 - H_2^o < 0$.

The entropy of mixing is equal to $-R \ln x_2$, for athermal, ideal and regular solutions, $> -R \ln x_2$ for solutions with one component associated and $< -R \ln x_2$ for solvated solutions. For athermal, non-ideal and for general solutions, the entropy of mixing is given by

$$-R\left[\ln \phi_2 + \phi_1(1 - v_1/v_2)\right]$$

For regular solutions, we have, by combining entropy and enthalpy contributions, the expression

$$RT \ln a_2/x_2 = v_2 \phi_1 (\delta_1 - \delta_2)^2$$

This equation contains a large number of assumptions (10) which invalidate the equation for solutions where large dipole forces are present, where hydrogen bonding occurs, or where chemical reaction occurs. Since a radial force field is assumed, the equation can not be expected to hold for molecules such as paraffins which are in no way spherical. The equation above does appear to hold better, however, than would be expected considering the numerous assumptions involved.

From this brief discussion of the present state of solubility theory, it is evident that although significant progress has been made, much remains to be done in

almost every field of solubility study.

In a position between the fields dealing with the solubility of electrolytes and the solubility of non-electrolytes is that phenomenonassociated with the effect of electrolytes upon the solubility of non-electrolytes. Here again we are dealing with differential solubilities, for we wish to know what the solubility will be before and after a certain amount of electrolyte has been added. This phenomenon is often referred to as the salting-out effect, although salting-in may frequently occur. The theoretical background of this subject will be discussed in some detail later in this investigation.

Although a considerable amount of experimental work has been done in this field much of the work is both fragmentary and inaccurate. It was felt that a systematic solubility study over a range of temperatures using low concentrations of electrolytes and applying a reliable experimental method would be valuable. Furthermore, since the dielectric constants of the saturated solutions as well as a parameter depending on the difference between the dielectric constant of the pure solvent and the saturated solution is needed, for comparison with theory, dielectric constant measurements were made.

The non-electrolyte chosen was ethyl acetate. This substance is stable, easy to handle and of sufficiently

large solubility in water as to make differential solubility measurements not too difficult.

The electrolytes chosen were the alkali metal halides along with a few quaternary ammonium halides. These one-one valence type electrolytes were chosen to avoid problems arising due to hydrolysis, oxidation, incomplete ionization, and ion association which occur with other types of electrolytes. The quaternary ammonium salts were employed because, although salts containing large anions have been previously studied, salts containing large cations have been largely neglected. It was thought desirable to see if the salting-in effects obtained when large anions were present would also be obtained in the presence of large cations.

II REVIEW OF LITERATURE ON SOLUBILITY OF ETHYL ACETATE IN ELECTROLYTE SOLUTIONS*

The first studies of the effect of electrolytes upon the solubility of ethyl acetate in water were due to Hans von Euler (11,12). Euler employed the thermostatic method A(1).** Ethyl acetate and water were mixed together and brought to equilibrium for eight hours in a constant temperature bath at 18° and 28°C. The samples for analysis were removed by pipet from the aqueous layer, hydrolyzed with a known excess of alkali and back titrated with hydrochloric acid. An accuracy of one percent was claimed. The electrolytes employed included sodium chloride, potassium chloride, potassium nitrate, magnesium sulfate, zinc sulfate and sodium sulfate at concentrations of one quarter, one half, one and two molar. The results indicate the nitrates have much less of a salting out

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* For a general review of the literature on the "salting-out effect" see Altshuller, Master's Thesis, University of Cincinnati.

** See appendix for discussion of methods for the determination of liquid-liquid solubilities.

effect than do potassium or sodium chloride. The electrolytes with divalent ions cause more salting out than the uni-univalent electrolytes. Euler suggested that the addition of a salt to water increases the internal pressure and that this increased pressure is responsible for the salting out. No quantitative justification is given of this theory which resembles an approach which has been applied in the case of non-electrolyte solutions.

H. Lunden (13) has used the thermostatic method A(1) to study the solubility of ethyl acetate in electrolyte solutions. Lunden shook the two layers together for ten hours, removed the samples from the aqueous layer, saponified with excess of sodium hydroxide, and back titrated with hydrochloric acid. This investigator used sodium chloride, potassium chloride, sodium nitrate and potassium nitrate solutions at a temperature of 25°C. The concentrations of electrolyte ranged from two-tenths molar to four molar. The alkali nitrates employed salted out ethyl acetate much less than the alkali chlorides.

H. Euler and O. Svanberg (14) reported that ethyl acetate is more soluble in an aniline-nitrate solution than in water at 18°C.

E. Linde (15) employed an approximately thermostatic method (16-16.5°C) in which he used a series of

solutions containing increasing amounts of ethyl acetate. The solution in the series which was saturated with ethyl acetate was reported to show a sudden increase in the appearance of turbidity. The salts employed by Linde were sodium chloride and sodium nitrate. As with the results of Euler (11, 12) and Lunden (13), sodium nitrate showed considerably less of a salting out effect than did sodium chloride.

H. Euler and K. Rudberg (16) studied the effects of potassium nitrate solutions at 30.1°C and lithium nitrate solutions at 29.7°C upon the solubility of ethyl acetate. The method used was that of Euler (11,12).

S. Glasstone and A. Pound (17) investigated the solubility of ethyl acetate in aqueous electrolyte solutions by a thermostatic method. The electrolyte solution was shaken with a slight excess of ester at a temperature below 25°C or 50°C; the excess of ethyl acetate then separated out causing the solution to become cloudy. In the course of an hour or two the aqueous solution was clear again, and was of a saturated solution of the ester at the temperature of the thermostat. Care was always taken, according to the authors, so that the excess of ethyl acetate present was not so large that the amount of water or salt dissolved by it could not be neglected.

For analysis, a quantity of the saturated solution (3 to 8 grams) was transferred rapidly in a warmed pipet to a stoppered bottle and weighed. The weighed solution was then diluted with water, washed into a distilling flask, and the ethyl acetate, and some water were distilled over and collected in water. The residue in the flask was tested to make sure that no acetic acid, which might have resulted from the hydrolysis of the ester by boiling water, remained behind. The ester was then hydrolyzed with standard sodium hydroxide and estimated in the usual way. The electrolytes employed were the chlorides, bromides and iodides of the alkali metals and of ammonium, and also dextrose, laevulose,and sucrose. The solutions of electrolyte in water ranged in concentration from two-tenths molar to ten molar. Salting out was generally observed, but lithium bromide at the highest concentrations and lithium and ammonium iodides at all concentrations increased the solubility of the ethyl acetate in water. The authors believed that this increase was connected with compound formation between the salt and the ester. These investigators stated that concentrated solutions of the iodides containing ethyl acetate have a distinct yellow color which is not due to the presence of iodine but to complex formation.

The order of salting out for the alkali metal cations and the halides anions was observed to be as follows: $Li^+ > Na^+ > K^+ > NH_4^+ > Rb^+ > Cs^+$ and $Cl^- > Br^- > I^-$. The authors believe that hydration may be one of the factors responsible for the salting out effect.

Glasstone, Dimond and Jones (18) determined the solubility of ethyl acetate at 25 and 50 degrees centigrade in solutions of the nitrates of sodium, potassium, ammonium, lead, calcium, strontium and barium; and in solutions of the sulfates of nickel, potassium, magnesium, sodium, copper and zinc; ammonium acetate; potassium chromate, ferricyanide, ferrocyanide, chlorate and fluoride and in solutions of the chlorides of barium and copper at concentrations of two tenths molar and above. In general the results, according to the authors, revealed that the hydration effect of an ion was greater the greater its valence and the smaller its size. The authors believed that the hydration number represented a measure of the intensity of the electrostatic field surrounding an ion. The nitrate ions were observed to have a negligible salting out effect.

Glasstone, Dimond and Harris (19) observed the influence of mixtures of electrolytes and neutral molecules on the solubility of ethyl acetate in water at 25 degrees centigrade. The mixtures used were dextrose and sucrose,

laevulose and sucrose, sucrose and sodium chloride, sodium and potassium chloride, sodium and ammonium chloride, potassium and ammonium chloride, lithium and sodium chloride, barium and sodium chloride, potassium and cupric chloride and sodium and potassium nitrate. The salting out power of a mixture appeared equal to the sum of the salting out of the constituents, provided allowance was made for the electrical interactions of the ions. The nitrates again acted erratically.

It should be stated that the results reported for the solubility of ethyl acetate in water by Glasstone and Pound (17) were considerably lower than those reported by other investigators including the present ones. This might well indicate that an appreciable amount of ethyl acetate was lost in some stage of the procedure used. It should also be pointed out that although the investigations of Glasstone and his coworkers were quite extensive, most of the electrolyte concentrations used were above one molar. This fact makes comparison with the various theories, which held only at low electrolyte concentrations, quite difficult.

J. Traube, I. Schoning and L.J. Weber (20) made some rough solubility determinations to determine the solubility of ethyl acetate in ml. of ethyl acetate per 5ml of aqueous solvent. The salts used were sodium

butyrate, sodium benzoate and sodium salicylate. Salting in was observed.

Schlesinger and Kubasova (21) determined the solubility of ethyl acetate in water and in 0.1,0.25,0.5 and 1 molar solutions of sodium chloride, potassium bromide and potassium iodide at eighteen temperatures between 15 and 52 degrees centigrade. The determinations were made by the method of Alexejew, B (2). The temperature of formation and disappearance of turbidity did not vary more than 0.1 degree for any of the concentrations. The authors state that because of precipitation of iodine, no determinations were made for one molar potassium iodide solutions. Salting out was observed for the sodium chloride and potassium bromide. Potassium iodide showed a slight salting in effect at 0.1 molar and small salting out effects at higher concentrations of the potassium iodide. The investigators state that a preliminary determination of salting out by mixtures of two salts indicated additive effects only.

E. L. Smith (22) determined the solubility of ethyl acetate in a 0.4 normal sodium oleate solution at 20°C. Herz's method, A(2), was used. To a weighed quantity of 0.4 normal sodium oleate solution in a narrow necked flask, small quantities of the organic liquid were added until a slight excess was present. Small additions

of the sodium oleate solutions were then made until the solution was just saturated with the organic liquid at 20°C. Salting in was observed.

III EXPERIMENTAL PROCEDURE FOR THE SOLUBILITY DETERMINATIONS

The method used in this investigation was that of Alexejew (8).* Fifty milliliter volumetric flasks were used to hold the solutions. It was found that glass stoppers did not fit tightly enough (1), therefore, corks were used instead. The procedure was first to clean the flasks with soap solution, scrub the sides and necks of the flasks, rinse them with distilled water, and dry them in an electric oven for several hours at 120°C. The flasks with corks inserted were weighed on an analytical balance. Approximately 40.0 grams of salt solution as determined from its density was added from a buret and the flasks were reweighed. Ethyl acetate was then added from a buret in the appropriate amount and the flasks were again weighed. The flasks were then placed in rectangular glass baths and allowed to come to temperature equilibrium over a period of an hour or more. The temperature was then raised at a rate of approximately 0.1°C per minute by means of an electric light bulb partially immersed in the bath. The light bulb also served as a source of illumination for the observation of incipient

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*For primed references see appendix.

turbidity. The water baths were stirred during the determinations by stirring motors. The flasks were shaken by hand when the solutions they held were in the vicinity of their turbidity temperatures. Turbidity usually began over a range of 0.1 or 0.2 degrees centigrade. Duplicate determinations on the same solutions usually agreed within the experimental error in the determination of the turbidity temperature. Although the procedure used involves the observation of the separation of the second phase upon heating, when the solutions were gradually cooled it was found that the disappearance of turbidity occurred within the same range. Schlesinger and Kubasowa (21) studying the same system found that the temperatures of appearance and disappearance of tubidity agreed within 0.1 degrees. After each determination of the turbidity temperature the flasks were reweighed to determine any change in weight. Only in a few cases was the weight loss greater than a weight difference within the experimental error in the determination of the turbidity temperature. For example, if two solutions differed in ethyl acetate content by 0.1000 grams and if the difference in turbidity temperature of the two solutions was $3.0 \pm 0.1^{\circ}$, assuming linearity, a weight loss of five milligrams would be within the experimental error. It is assumed here that the loss in weight would be due

solely to volatilization of ethyl acetate.

After determining the solubility, the pH of each solution was measured with a pH meter in order to determine if any appreciable hydrolysis had occurred. A saturated solution of ethyl acetate is about one molar in ethyl acetate. Consequently, complete hydrolysis would produce a one molar acetic acid solution. In no case was a pH below 5 measured. A pH equal to 5, corresponds to an acetic acid concentration of approximately 5×10^{-6} molar. Thus no appreciable error resulted from hydrolysis.

In many cases the solubility measurements were remade after allowing the solutions to stand overnight. To prevent volatilization and hydrolysis of the ethyl acetate, the flasks were placed in a refrigerator. No weight change of any importance was found when the flasks were reweighed after standing overnight in the refrigerator.

Two thermometers, one graduated in one-twentieths of a degree and the other in tenths of a degree, were employed to measure the temperature. The thermometer graduated in twentieths of a degree was calibrated using the sodium sulfate transition point which fell about the middle of the temperature range employed. The temperature reading on the thermometer agreed to one one-hundredth of a degree with the transition temperature given in the

literature (23). The thermometer graduated in tenths of a degree was then calibrated against the other thermometer.

IV PURITY OF THE ETHYL ACETATE

The ethyl acetate used was Mallinckrodt analytical reagent grade ethyl acetate with maximum limits of impurities listed as follows:

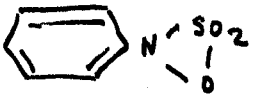
Free acid (CH_3COOH) 0.01%

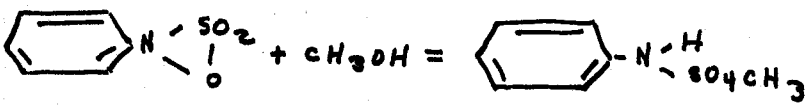
Non volatile matter 0.005%

Assay 99.5%

The ethyl acetate was distilled from a column of 24 theoretical plates and it was collected over a quarter of a degree temperature interval. When the refractive index was measured before and after distillation on an Abbe' Refractometer, no change in refractive index was detectable.

The ethyl acetate was analyzed for water by use of the Karl Fischer Reagent (24). The procedure consists of the direct titration of the wet material with a solution of iodine, sulfur dioxide and pyridine in methanol, the reagent serving as its own indicator. The reaction involved has been shown to procede as follows (25).

I. $I_2 + SO_2 + 3$  $+ H_2O = 2$  $+$ 

II 

It is found that the freshly prepared reagent is equivalent to 70% of theoretical water and after a month or two the reagent is equivalent to only about 40% of the theoretical water. Consequently, the number of grams of water equivalent to a milliliter of reagent must be determined each time the reagent is used. The side reactions have been found to involve reduction of iodine to the iodide ion and the formation of quaternary methyl pyridinium salts.

While other bases may be substituted for pyridine, in general the reagent formed has poor stability. Most organic solvents when incorporated in the reagent fail to dissolve the amine salts produced by the action of water. Methanol, dimethyl formamide and pyridine are satisfactory.

The reagent may be used to analyze a wide variety of substances for water. These include alcohols, hydrocarbons, carboxylic acids and esters as well as inorganic substances. On titration of aldehydes and ketones with the reagent unsatisfactory results occur due to the formation of acetals and ketals and the attendent liberation of water. The reagent may be readily modified so that satisfactory results are achieved.

Preparation

One liter quantities may be prepared (25) by dissolving 84.7g (0.33 mole) of iodine in a mixture of

269ml (3.3 mole) of pyridine and 667 ml of methanol. The above solution is cooled in a slurry of ice and 64 g of liquid sulfur dioxide is cautiously added. The final solution is dark brown. For ketones and aldehydes 860 ml of pyridine and 90 ml of methanol are used.

The water equivalent of the reagent at the time of analysis was determined by titration of methanol to remove its water content and the addition of a weighed amount of water (a few drops), and retitration to the end point (yellow to red). The material to be analyzed can be determined then by addition to methanol from which water has already been removed by a former titration. It was found that if the reagent (modified reagent for ketones) was added directly to the ethyl acetate a yellow crystalline solid precipitated (probably pyridine hydriodide and pyridine hydrogen sulfate) which dissolved upon addition of methanol. To test for water absorbence from the atmosphere, the ethyl acetate was allowed to stand for several hours in contact with the atmosphere. No appreciable difference was found.

TABLE I

Karl Fischer equivalent = 0.00268 g/ml

Titration	Percentage water
I	0.07
II	0.06
III	0.06
IV	0.07 after exposure to atmosphere

V PURITY OF SALTS

The sodium, potassium and lithium salts were C.P. salts of tested purity. The impurities listed were not large enough to affect the results. In the case of the rubidium and cesium salts no analyses were available. With the exception of the rubidium and cesium chloride it was found that these salts contained insoluble impurities which were probably aluminum and iron oxides. As a result, it was necessary to dissolve these salts in water, filter the resulting solutions, evaporate down the solutions and recrystallize the salts. All of the salts were dried in a vacuum desiccator over phosphorus pentoxide before use.

The rubidium and cesium salts were analyzed for soluble impurities by means of a Weichselbaum-Varney Universal Spectro-photometer-Model No. M4. In such a one cell instrument it is necessary to keep the characteristics of the flame source constant through each series of measurements. This is accomplished by careful regulation of the air, gas and oxygen pressures and rates of flow. The rate of addition of the sample to the flame is also controlled by the above regulation.

This type of flame photometer employs filters to cut off all but the line of interest. Since some contributions from other lines gets through the filter, a set of solutions containing a small amount of the interfering element or elements is used to calibrate the instrument before each set of determinations. Thus a set of standards for the determination of potassium contains a small amount of a sodium salt, thereby compensating for the sodium in the sample to be analyzed. In the samples analyzed for sodium and potassium, the intensities due to cesium and/or rubidium ions which managed to pass through the filters was not compensated for in the standardizing solutions. The results, consequently, give the upper limits of the sodium and potassium impurities.

Referring to Table II one sees that the results are in qualitative agreement with what one would expect. The amount of sodium and potassium in pollucite ore is not high (26), consequently, purification should result in very low sodium and potassium impurities. Rubidium is generally found in low concentrations in sodium and potassium deposits, therefore, while sodium, due to differences in chemical properties, should be rather readily removable, potassium is too much like rubidium to be easily separated. Hence, one finds rather high potassium impurities in the rubidium salts.

TABLE II

ANALYSIS OF CESIUM AND RUBIDIUM SALTS FOR SODIUM AND POTASSIUM IMPURITIES BY MEANS OF THE WEICHSELBAUM-VARNEY UNIVERSAL SPECTROPHOTOMETER-MODEL NO. M4

Salt	mg/liter		% cation impurity in the salt (dry basis)	
	Na	K	Na	K
RbF	<0.2	3	<0.04	0.6
RbCl	<0.2	23	<0.04	4.6
RbBr	<0.2	1	<0.04	0.2
RbI	<0.2	1	<0.04	0.2
CsCl	<0.2	~0.08	<0.04	~0.016
CsBr	<0.2	~0.08	<0.04	~0.016
CsI	<0.2	~0.02	<0.04	~0.004

VI Experimental Results

The experimental solubility results on the system ethyl acetate - water are given in Table III. The experimental solubility results for the systems ethyl acetate - water - electrolyte are given in Table IV. The experimental data are treated by the least squares method and the linear equations relating solubility and temperature are given in Table V. The solubilities at 20, 25, 30, 35, 40 degrees centigrade are given in Table VI. Where it was felt that undue extrapolation would be necessary to apply an equation at an extremity of the temperature range, the value was omitted.

Table III

Solubility of Ethyl Acetate in Water

Turbidity Temperature(t) in degrees centigrade	Solubility (s) in grams of Ethyl Acetate per 100 grams of water
21.3	8.26
22.0	8.22
22.6	8.14
22.7	8.12
23.0	8.11
23.4	8.10
24.7	8.05
25.1	8.03
25.4	8.02
25.4	8.00
25.9	7.93
26.0	7.93
26.3	7.94
27.0	7.89
28.0	7.80
28.1	7.81
28.4	7.82
28.7	7.81
29.7	7.71
30.0	7.72
30.0	7.69
30.1	7.69
31.2	7.60
31.8	7.58
31.9	7.58
31.9	7.57
32.0	7.51
32.8	7.49
33.0	7.46
34.0	7.45
34.0	7.38
35.0	7.39

Table IV

Solubility of Ethyl Acetate in Various Aqueous Electrolyte Solutions

Salt	c Conc. in moles/l	t Turbidity Temp. °C	s Sol. of E.A. in g/100g of water
LiF	0.0250	22.9	8.05
	"	24.8	7.96
	"	25.9	7.81
	"	27.6	7.75
	"	28.7	7.64
	"	30.9	7.49
	"	31.9	7.37
	"	34.0	7.27
LiCl	0.1000	26.9	7.56
	"	30.2	7.33
	"	33.8	7.13
	"	38.5	6.91
	0.2000	25.6	7.47
	"	28.3	7.26
	"	31.5	7.04
	"	36.7	6.77
	0.3000	23.2	7.38
	"	26.0	7.14
	"	30.0	6.88
	"	33.6	6.69
	0.4000	22.1	7.17
	"	24.6	7.03
	"	28.2	6.78
	"	31.8	6.55
LiBr	0.1000	24.5	7.91
	"	27.8	7.67
	"	31.3	7.46
	"	34.6	7.23
	0.2000	25.1	7.75
	"	27.4	7.57
	"	31.2	7.33
	"	34.4	7.11

Table IV (con't)

Salt	Conc. in moles/l.	Turbidity Temp. °C	Sol. of E.A. in g./100 g. of H_2O
LiBr	0.3000	24.3	7.69
	"	27.1	7.47
	"	30.8	7.23
	"	34.5	7.00
	0.4000	23.9	7.58
	"	27.3	7.35
	"	30.5	7.11
	"	33.8	6.91
NaF	0.1000	25.3	7.49
	"	28.6	7.26
	"	32.2	7.02
	"	36.3	6.80
	0.2000	23.0	7.12
	"	27.0	6.87
	"	30.3	6.65
	"	33.2	6.48
	0.3000	20.4	6.87
	"	22.0	6.70
	"	26.1	6.45
	"	30.7	6.16
	0.4000	20.9	6.34
	"	23.1	6.18
	"	26.6	5.96
	"	30.4	5.75
NaCl	0.1000	26.1	7.63
	"	29.6	7.37
	"	32.4	7.15
	"	37.8	6.91
	0.2000	23.6	7.50
	"	27.1	7.23
	"	30.0	7.02
	"	33.8	6.80

Table IV (con't)

Salt	c Conc. in moles/l.	t Turbidity Temp. °C	s Sol. of E.A. in g/100g H_2O
NaCl	0.3000	21.4	7.26
	"	24.7	7.03
	"	28.0	6.82
	"	32.1	6.56
	0.4000	18.4	7.24
	"	23.1	6.88
	"	26.0	6.56
	"	29.5	6.46
NaBr	0.1000	24.9	7.79
	"	27.6	7.62
	"	31.1	7.38
	0.2000	23.8	7.68
	"	26.8	7.46
	"	29.9	7.23
	"	33.2	7.03
	0.3000	22.2	7.59
	"	24.6	7.38
	"	28.2	7.14
	"	31.2	6.93
	0.4000	20.5	7.52
	"	23.8	7.28
	"	26.3	7.06
	"	29.7	6.84
NaI	0.1000	22.8	8.14
	"	25.9	7.94
	"	28.7	7.69
	"	32.5	7.47
	0.2000	24.2	8.05
	"	26.5	7.85
	"	29.8	7.59
	"	36.9	7.17

Table IV (con't)

Salt	Conc. in moles/l.	Turbidity Temp. °C	Sol. of E.A. in g/100g of water
NaI	0.3000	24.7	7.95
	"	27.2	7.74
	"	30.2	7.52
	"	34.0	7.27
	0.4000	24.5	7.87
	"	27.7	7.64
	"	30.7	7.42
	"	34.8	7.19
KCl	0.1000	26.8	7.54
	"	29.3	7.34
	"	34.0	7.09
	"	36.6	6.89
	0.2000	24.8	7.42
	"	28.3	7.19
	"	31.0	6.99
	"	35.2	6.77
	0.3000	22.5	7.29
	"	25.3	7.06
	"	27.2	6 .89
	"	31.8	6.65
	0.4000	19.8	7.23
	"	22.7	6.99
	"	25.9	6.75
	"	28.5	6.54
KBr	0.1000	29.3	7.47
	"	34.2	7.22
	"	37.6	7.01
	0.2000	28.5	7.34
	"	32.0	7.14
	"	36.1	6.90
	"	41.0	6.69
	0.3000	28.0	7.22
	"	30.8	7.02
	"	35.0	6.78
	"	39.0	6.58
	0.4000	26.5	7.14
	"	30.2	6 .87
	"	33.6	6.67
	"	37.8	6.46

Table IV (con't)

Salt	conc. in moles/l.	Turbidity Temp. °C	Sol. of E.A. in g/100g of water
KI	0.1000	22.8	8.13
	"	26.4	7.87
	"	29.0	7.68
	"	33.2	7.45
	0.2000	23.2	7.99
	"	26.6	7.77
	"	31.0	7.55
	"	34.3	7.33
	0.3000	26.5	7.82
	"	29.2	7.62
	"	31.8	7.39
	"	37.0	7.17
	0.4000	28.2	7.65
	"	31.3	7.46
	"	35.7	7.22
	"	39.2	7.03
KI	0.1000	22.4	8.01
	"	25.5	7.79
	"	28.6	7.55
	"	31.1	7.36
	0.2000	23.1	7.92
	"	26.7	7.67
	"	30.0	7.44
	"	32.8	7.22
	0.3000	24.8	7.80
	"	26.9	7.57
	"	30.9	7.35
	"	35.0	7.13
	0.4000	25.2	7.74
	"	28.5	7.49
	"	31.5	7.29
	"	35.3	7.09
RbF	0.1000	24.2	7.57
	"	27.3	7.36
	"	30.4	7.16
	"	32.6	7.03

Table (con't)

Salt	c Conc. in moles/l.	t Turbidity Temp. °C	Sol. of E.A. in g/100g. of water
RbF	0.2000	23.6	7.18
	"	27.3	6.91
	"	31.4	6.68
	"	32.4	6.63
	0.3000	23.7	6.77
	"	25.5	6.64
	"	30.4	6.35
	"	33.9	6.14
	0.4000	24.0	6.37
	"	27.3	6.16
	"	31.9	5.92
	"	34.3	5.78
RbCl	0.1000	25.0	7.71
	"	28.0	7.49
	"	31.8	7.23
	"	34.9	7.05
	0.2000	22.8	7.58
	"	25.4	7.37
	"	28.5	7.15
	"	31.8	6.95
	0.3000	21.2	7.44
	"	23.2	7.27
	"	26.0	7.03
	"	29.8	6.82
	0.4000	18.5	7.42
	"	21.2	7.14
	"	23.8	6.96
	"	25.8	6.76
RbBr	0.097*	27.6	7.56
	"	31.0	7.36
	"	35.1	7.09
	"	39.5	6.91

* corrected for insoluble residue

Table IV (con't)

Salt	c Conc. in moles/l.	t Turbidity Temp. °C	Sol. of E.A. in g./100g of H_2O
RbBr	0.194*	24.9	7.55
	"	28.7	7.29
	"	31.6	7.06
	"	36.0	6.80
	0.296*	25.0	7.39
	"	28.0	7.19
	"	35.6	6.76
RbI	0.099*	21.5	8.29
	"	24.1	8.07
	"	26.8	7.84
	"	30.0	7.58
	0.189*	23.0	8.18
	"	25.8	7.93
	"	28.7	7.69
	"	31.1	7.52
	0.248*	23.6	8.07
	"	26.9	7.80
CsCl	0.1000	27.3	7.62
	"	30.6	7.37
	"	34.1	7.16
	"	38.2	6.93
	0.2000	23.6	7.62
	"	26.3	7.41
	"	29.0	7.20
	"	33.1	6.94
	0.3000	23.0	7.40
	"	26.1	7.18
	"	29.0	6.95
CsBr	0.1000	25.2	7.81
	"	28.0	7.60
	"	31.4	7.37
	"	35.2	7.15

* corrected for insoluble residue

Table IV (con't)

Salt	Conc. in moles/l.	Turbidity Temp. °C	Sol. of E.A. in g/100 g. water
CsBr	0.2000	24.4	7.69
	"	26.2	7.48
	"	29.4	7.28
	"	33.7	7.05
	0.3000	23.8	7.61
	"	26.4	7.40
CsI	0.1000	25.0	8.07
	"	28.2	7.81
	"	30.3	7.66
	0.2000	24.2	8.16
	"	25.8	7.98
	"	29.8	7.71
	"	32.9	7.50
	0.3000	24.7	8.09
	"	29.7	7.68
$(CH_3)_4NI$	0.1000	20.7	8.54
	"	22.4	8.40
	"	23.0	8.31
	"	24.5	8.18
	"	26.3	8.06
	"	27.4	7.95
	"	28.7	7.87
	"	30.7	7.73
$(CH_3)_3(C_6H_5)NI$			
	0.1000	28.9	8.23
	"	30.9	8.12
	"	31.3	8.11
	"	35.0	7.90
	"	37.0	7.77
	"	38.2	7.72
	"	41.4	7.56

Table V

Least Square Equations Calculated from Solubility Data in Tables III and IV

Salt	Conc. in moles/l.	Equation
___*		s = -0.0647t + 9.628
LiF	0.025	s = -0.0730t + 9.735
LiCl	0.1000	s = -0.0556t + 9.030
	0.2000	s = -0.0626t + 9.045
	0.3000	s = -0.0658t + 8.880
	0.4000	s = -0.0647t + 8.608
LiBr	0.1000	s = -0.0665t + 9.535
	0.2000	s = -0.0679t + 9.445
	0.3000	s = -0.0671t + 9.305
	0.4000	s = -0.0684t + 9.213
NaF	0.1000	s = -0.0629t + 9.068
	0.2000	s = -0.0632t + 8.598
	0.3000	s = -0.0669t + 8.203
	0.4000	s = -0.0618t + 7.618
NaCl	0.1000	s = -0.0616t + 9.205
	0.2000	s = -0.0688t + 9.108
	0.3000	s = -0.0652t + 8.648
	0.4000	s = -0.0736t + 8.570
NaBr	0.1000	s = -0.0663t + 9.443
	0.2000	s = -0.0696t + 9.328
	0.3000	s = -0.0723t + 9.180
	0.4000	s = -0.0749t + 9.053
NaI		
	0.1000	s = -0.0705t + 9.748
	0.2000	s = -0.0684t + 9.673
	0.3000	s = -0.0728t + 9.733
	0.4000	s = -0.0664t + 9.483
KCl	0.1000	s = -0.0639t + 9.238
	0.2000	s = -0.0631t + 8.973
	0.3000	s = -0.0684t + 8.800
	0.4000	s = -0.0788t + 8.788

* ethyl acetate - water

Table V (Continued)

Salt	Conc. in moles/l.	Equation
KBr	0.1000	s = -0.0551t + 9.090
	0.2000	s = -0.0524t + 8.820
	0.3000	s = -0.0578t + 8.818
	0.4000	s = -0.0599t + 8.703
KI*	0.1000	s = -0.0657t + 9.610
	0.1000	s = -0.0750t + 9.695
	0.2000	s = -0.0558t + 9.265
	0.2000	s = -0.0718t + 9.583
	0.3000	s = -0.0620t + 9.430
	0.3000	s = -0.0631t + 9.318
	0.4000	s = -0.0561t + 9.225
	0.4000	s = -0.0644t + 9.343
RbF	0.1000	s = -0.0644t + 9.125
	0.2000	s = -0.0621t + 8.630
	0.3000	s = -0.0611t + 8.210
	0.4000	s = -0.0565t + 7.718
RbCl	0.1000	s = -0.0669t + 9.370
	0.2000	s = -0.0699t + 9.158
	0.3000	s = -0.0724t + 8.953
	0.4000	s = -0.0881t + 9.038
RbBr	0.097	s = -0.0556t + 9.080
	0.194	s = -0.0682t + 9.243
RbI	0.099	s = -0.0836t + 10.09
	0.189	s = -0.0818t + 10.05
CsCl	0.1000	s = -0.0628t + 9.313
	0.2000	s = -0.0717t + 9.300
	0.3000	s = -0.0750t + 9.127
CsBr	0.1000	s = -0.0659t + 9.458
	0.2000	s = -0.0663t + 9.258
CsI	0.1000	s = -0.0777t + 10.01
	0.2000	s = -0.0737t + 9.915
$(CH_3)_4NI$	0.1000	s = -0.0813t + 10.20
$(CH_3)_3C_6H_5NI$	0.1000	s = -0.0546t + 9.809

* two complete solubility determinations were made on this system and the results were averaged

Table VI

Percentage Salting Out or In Calculated from Least Square Equations in Table IV

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	0.6	1.3	1.8	2.5	-
LiCl	0.1000	-	4.6	4.3	3.4	3.3
	0.2000	-	6.6	6.8	6.9	7.1
	0.3000	-	9.7	10.1	10.6	11.2
	0.4000	-	12.7	13.3	13.9	14.5
LiBr	0.1000	-	1.7	1.9	2.0	-
	0.2000	-	3.3	3.6	3.9	-
	0.3000	-	4.7	5.2	5.4	-
	0.4000	-	6.4	6.9	7.3	-
NaF	0.1000	6.2	6.4	6.6	6.8	-
	0.2000	11.9	12.4	12.9	13.2	-
	0.3000	17.5	18.5	19.4	20.4	-
	0.4000	23.4	24.2	25.1	25.8	-
NaCl	0.1000	4.2	4.2	4.3	4.2	4.3
	0.2000	7.2	7.7	8.3	8.8	9.5
	0.3000	11.9	12.4	13.0	13.5	14.2
	0.4000	14.8	16.0	17.3	18.6	20.0
NaBr	0.1000	2.5	2.7	3.0	3.3	-
	0.2000	4.7	5.2	5.9	6.4	-
	0.3000	7.2	8.0	8.8	9.7	-
	0.4000	9.2	10.4	11.4	12.6	-
NaI	0.1000	- 0.1	0.2	0.8	1.1	-
	0.2000	0.2	0.6	0.9	1.1	-
	0.3000	0.7	1.3	1.8	2.3	-
	0.4000	2.0	2.4	2.6	2.7	-
KCl	0.1000	4.4	4.6	4.8	4.9	-
	0.2000	7.4	7.7	7.9	8.2	-
	0.3000	10.8	11.5	12.2	12.9	-
	0.4000	13.4	14.9	16.5	18.1	-

Table VI (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KBr	0.1000	-	-	3.2	2.7	2.1
	0.2000	-	-	5.7	5.0	4.4
	0.3000	-	-	7.8	7.6	7.5
	0.4000	-	-	10.1	10.2	10.4
KI	0.1000	1.0	1.4	1.8	2.3	-
	0.2000	2.2	2.1	2.3	2.3	-
	0.3000	2.5	2.5	2.6	2.4	-
	0.4000	3.0	3.0	2.9	2.6	-
RbF	0.1000	5.9	6.2	6.5	6.7	-
	0.2000	11.3	11.6	12.0	12.2	-
	0.3000	16.1	16.6	17.0	17.5	-
	0.4000	20.9	21.4	21.7	22.0	-
RbCl	0.1000	3.6	3.9	4.3	4.5	-
	0.2000	6.8	7.5	8.2	8.2	-
	0.3000	9.8	10.9	11.8	12.8	-
	0.4000	12.6	14.6	16.9	19.2	-
RbBr	0.1000	-	4.0	3.6	3.1	-
	0.2000	-	5.9	6.4	6.8	-
RbI	0.1000	- 1.0	0.2	1.4	-	-
	0.2000	- 1.1	0.0	1.2	-	-
CsCl	0.1000	3.2	3.4	3.4	3.3	-
	0.2000	5.5	6.2	7.0	7.7	-
	0.3000	8.4	9.4	10.5	11.7	-
CsBr	0.1000	-	2.5	2.7	2.9	-
	0.2000	-	5.1	5.5	5.7	-
CsI	0.1000	-	- 0.8	0.1	1.0	-
	0.2000	-	- 0.8	- 0.1	0.4	-
$(CH_3)_4NI$		- 3.0	- 2.0	- 0.9	-	-
$(C_6H_5)(CH_3)_3NI$		-	-	- 6.2	- 7.3	- 8.4

Figure 11

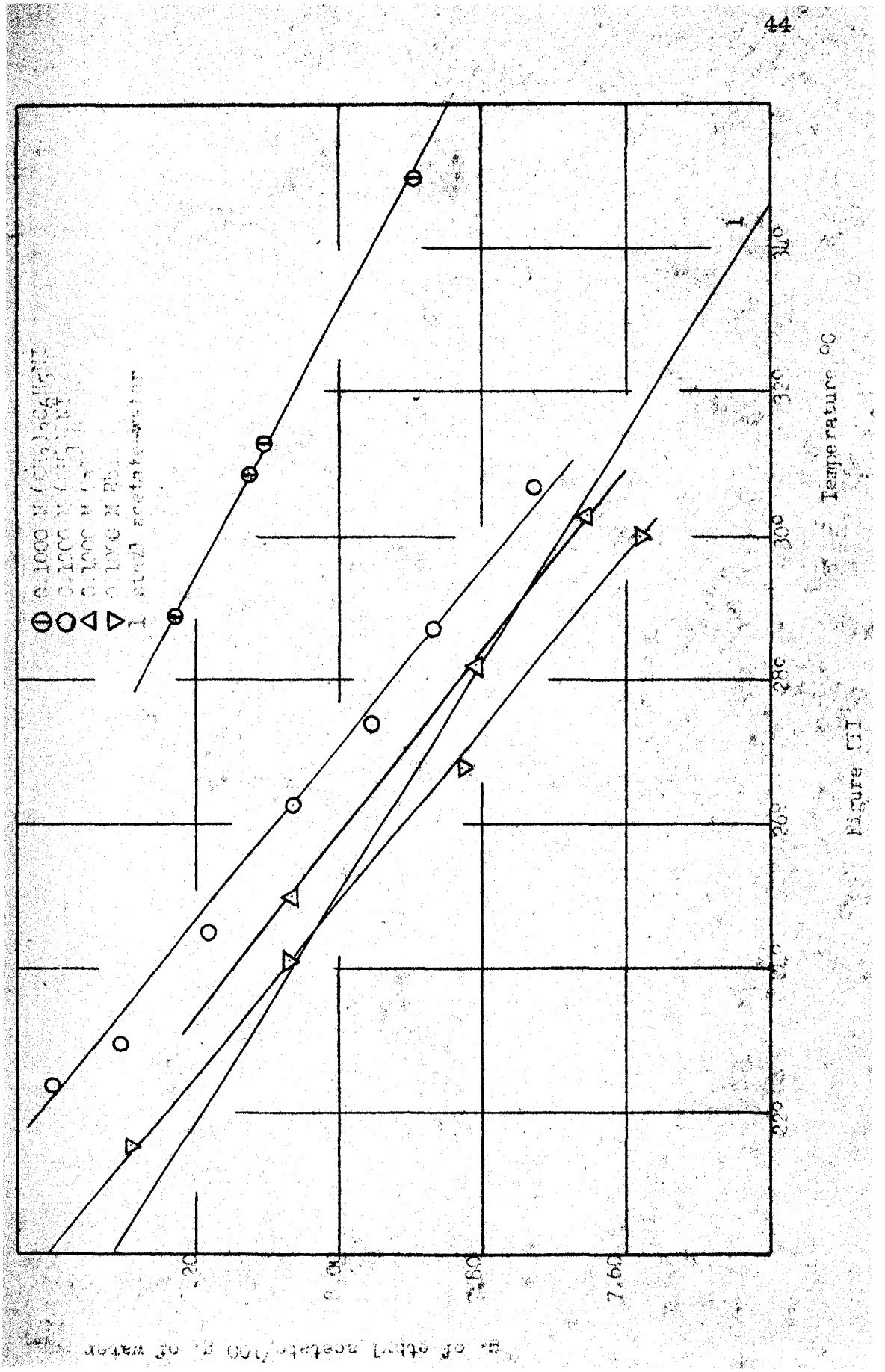
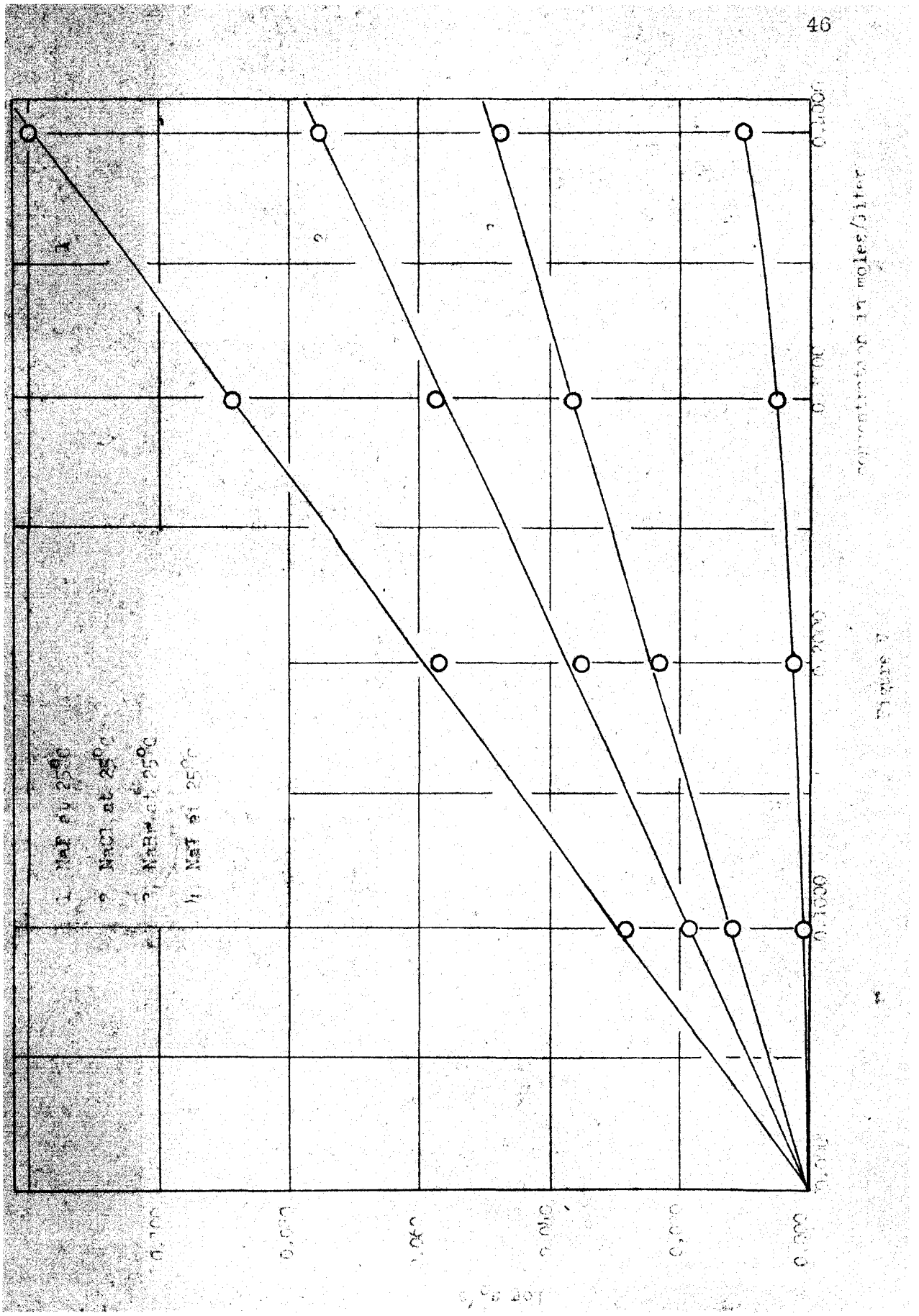


Figure III



VII Experimental Procedure for the Determination of Dielectric Constants of Ethyl Acetate-Water Mixtures

The dielectric constants were determined with a resonance-type instrument. In a circuit consisting of inductance L, capacity C, and resistance R in series, the effective current is

$$I = \frac{E}{[R^2 - (L\omega - 1/\omega C)^2]^{\frac{1}{2}}}$$

where E is the electromotive force with $\omega = 2\pi f$, f being the frequency of oscillation. I has a maximum value when $\omega L = 1/\omega C$, the condition referred to as resonance. At a given frequency, resonance may be brought about by the proper value of inductance or capacitance.

The method used may be described in general terms in the following manner. Oscillations are excited in a primary circuit which is coupled to a secondary or resonance circuit containing both capacitance and inductance. The capacity of this circuit is adjusted by means of a condenser until the current reaches a maximum as shown by a detector circuit coupled to it. The cell to be measured is connected in parallel with the condenser which is again adjusted to resonance. The difference between the two condenser readings gives the capacity of the cell. The resonance method is particularly useful in the case of conducting liquids.

With the particular resonance apparatus available it was found that when solutions having any appreciable conductance were measured, it was impossible to detect the point of resonance due to a flattening of the resonance maximum. Therefore, instead of detecting a maximum, the point of zero phase angle was determined. The phase angle in the vicinity of resonance is undergoing a maximum rate of change making it a sensitive means of detecting resonance. An oscilloscope was employed to detect changes in phase angle as the capacity was changed. The pattern for two equal frequencies with different phase angles being applied to the vertical and horizontal plates is an ellipse which collapses to a line at resonance. Actually, due to some higher harmonics being present, the pattern at resonance consisted of a thin figure eight. It was found that this fact did not affect the results, but instead made detection of resonance simpler. It was found that a general purpose oscilloscope was not satisfactory, because of the fact that the amplification dropped off drastically at the frequency employed, 4×10^5 cycles/sec. However, a Du Mont model 224A oscilloscope which maintains peak amplification on the vertical plates up to about one megacycle proved quite satisfactory. The connections to the horizontal plates bypassed the horizontal amplifiers which were not capable of handling

the frequency employed without overloading. A phase-shifting network was connected to the vertical plates to make it possible to adjust conditions so that the current (voltage) maximum (which also could be detected on the oscilloscope) would occur at the same place as zero phase angle. A variable resistance was connected in parallel with the precision condenser to compensate for resistance changes when the measuring cell was connected and disconnected.

The dielectric constant measuring cell was purchased. Its capacity empty is 9 $\mu\mu$f. The cell is of the fixed capacity type. The plates are concentric cylinders of nickel attached through glass seals by heavy wire leads to an inner glass cylinder. The leads run through metal prongs which run outside the cylinder. The glass cylinder fits into an outer glass tube. The connection between the two glass pieces of the cell is by means of a ground glass joint.

The lead capacity was determined for the equations (27)

$$C_1 = C_a + C_r$$

$$C_2 = 2.28C_a + C_r$$

The capacity was measured in air and benzene. The residue capacity was less than 1 $\mu\mu$f.

The water used for the dielectric constant measurements was distilled water which was passed through a

cation-anion exchange column. This procedure has several advantages over the customary practice of distilling the water from permanganate. The amount of water which can be purified over a given period of time is much greater when an ion exchange column is employed. An ion exchange column may be run overnight unattended, while a distillation apparatus must be flushed out for a considerable length of time before water of conductivity grade can be obtained. On the other hand, it is only necessary to wash an ion exchange column with a liter or two of water to insure washing out of any decomposition products resulting from the instability of the anion resin. The water obtained had a specific conductance of from 1.3 - 2.0 x 10^{-6}ohm^{-1}. The dielectric constant measuring cell was allowed to stand overnight filled with this water before it was used.

The ethyl acetate employed was of the batch used for the solubility measurements.

Due to the high dielectric constant of the aqueous solutions to be measured, it was decided that calculations could be made most accurately by using pure water as a standard. The dielectric constants of the ethyl acetate - water mixture could then be calculated from the values for water. The measurements given by Wyman (28) for the dielectric constant of water were used. The empirical

equation representing his results is as follows,

$$D_o = 78.54 \left[1 - 0.00460(t - 25) + 0.0000088(t - 25)^2\right]$$

At any given temperature the dielectric constant of the saturated solution of ethyl acetate in water was determined by treating the experimental results by least squares to obtain an equation relating concentration in grams of ethyl acetate per 100 grams of water to the capacity in the measuring cell of that solution in $\mu\mu$f. The relationship between capacity and concentration was found to be linear. The concentration value at saturation was substituted in the least squares equation and the corresponding capacity was found. The dielectric constant was then found from the relationship

$$D_x = \frac{D_o C_x}{C_o}$$

where D_o = dielectric constant of water at a given temperature

D_x = dielectric constant of the ethyl acetate - water mixture at the same temperature

C_o = capacity in $\mu\mu$f of the measuring cell with water in it

C_x = capacity in $\mu\mu$f of the measuring cell with the saturated solution of ethyl acetate in water in it.

VIII Experimental Results of Dielectric Constant Measurements

Table VIa

Experimental Values of Capacity versus Concentration of Ethyl Acetate at Various Temperatures

Temperature	g. of Ethyl Acetate per 100 g. of water (g)	Capacity in μμf (C)
25°C	0	759
	1.98	745
	4.43	731
	6.91	718
	7.35	714
30°C	0	746
	2.23	727
	4.50	714
	6.50	706
	6.97	699
35°C	0	716
	2.20	710
	4.48	702
	6.46	684
	6.97	669
40°C	0	711
	2.21	697
	4.47	683
	5.62	677

Table VIb

Least Squares Equations for Capacity (C) versus Concentration of Ethyl Acetate

Temperature	Equation
25°C	$C = -5.94g + 758$
30°C	$C = -6.28g + 744$
35°C	$C = -6.18g + 721$
40°C	$C = -6.09g + 668$

Table VIc

Dielectric Constants and Dielectric Constant Lowering of Saturated Ethyl Acetate - Water Solutions at Various Temperatures

Temperature	Dielectric Constants	Dielectric Constant Lowerings
20°C*	75.2	5.1
25°C	73.5	5.0
30°C	71.8	4.9
35°C	70.3	4.7
40°C	68.8	4.4

* No experimental measurement was made at this temperature, the value given is believed to be a reasonable estimate.

IX Theoretical Discussion

One would like to be able to represent the change in solubility of a non-electrolyte in a solvent upon the addition of electrolyte in terms of a detailed structural model of the three component system involved. Unfortunately, the complexity of such a model is so great as to discourage such an approach. The approach to the problem generally used is to represent the ions as spheres characterized by a charge e and a radius r and to consider the bulk of the solution as a structureless continuum characterized by a dielectric constant D. Such a model may be treated mathematically. We may then discuss qualitatively, but with an indication of sign and magnitude, certain other forces which arise from a more detailed consideration of structure. The discussion to follow will be based on this viewpoint.

Although several types of treatment may be used to relate the solubility change to fundamental parameters, the first step generally is to evaluate the reversible work or free energy of a hypothetical process similar to the physical change in conditions taking place in solution. This process may involve the discharging of a spherical particle of charge e and radius r in a pure solvent of dielectric constant D_o and the recharging of the ion in a medium consisting of solvent plus non-electrolyte of

dielectric constant D. Another process would involve the calculation of the work involved in the removal of a molecule of solvent from the vicinity of the ion and its replacement with a molecule of non-electrolyte. It is also possible to calculate the energy of the field of the ion in two media and to set the difference equal to the free energy. A somewhat different approach is to set up an integral expression for the free energy and to minimize the integral by a variation method. This latter method leads to a distribution function relating concentration of the components to the distance from the ion. If the free energy of the process is directly evaluated, it is then possible to find the partial molar free energy, the chemical potential, of either the non-electrolyte, electrolyte or solvent. The logarithm of the activity coefficient may then be readily evaluated. If a distribution is evaluated, it too may be related to the solubility change. A detailed consideration of these various processes has already been given (29).

Any of the first three processes mentioned may be employed to derive an expression originally obtained by Debye and MacAulay (30) of the form

$$\ln f = \frac{w\epsilon^2 N}{2000 D_o kT} \sum_i \frac{c_i z_i}{b_i} \qquad (1)$$

where f is the activity coefficient of the non-electrolyte which may be shown to be equal to s_o/s (31, 32), ϵ is the electronic charge, N is Avogadro's number, T is the absolute temperature, k is the Boltzmann constant, D_o is the dielectric constant of the solvent, c_i is the concentration in moles per liter of the i th species of ion, z_i is its valence, b_i the ionic radius of the i th species of ion, and w is a quantity given by the expression

$$D = D_o(1 - wn - rn') \qquad (2)$$

where n is the number of molecules of non-electrolyte per milliliter and n' is the number of ions per milliliter. w and n are related to the dielectric constant change caused by the addition of non-electrolyte and electrolyte to the pure solvent. If the variation in dielectric constant with n and the effects of the ionic atmosphere are also considered, the following equation may be derived (29)

$$\ln f = \frac{wD_o\epsilon^2N}{2000D^2kT}\sum_i \frac{c_iz_i^2}{b_i} - \frac{wD_o\epsilon^2N\kappa}{2000D^2kT}\sum_i c_iz_i^2 \qquad (3)$$

The last process mentioned above involving the variation method was developed by Debye (33) and has the following form

$$1/f = 1 - 4\pi N/1000\sum_i J_ic_i \qquad (4)$$

where $$J_i = \int_{b_i}^{\infty} (1 - e^{-(R_i/r)^4}) r^2 dr \qquad (5)$$

for $R_i > b_i$

$$J_i = \bar{R}_i^3 \left[1.21 - 1/3(R_i/b_i)^3 - \ldots\ldots\ldots \right] \qquad (6)$$

for $\bar{R}_i < b_i$

$$J_i = \bar{R}_i^4/b_i \left[1 - 1/25(\bar{R}_i/b_i)^4 \ \ldots\ldots\ldots \right] \qquad (6')$$

and

$$\bar{R}_i^4 = \frac{e_i^2 w'}{8\pi RTD} \qquad (7)$$

where w' is given by

$$D = D_o(1 - w'\bar{c}) \qquad (8)$$

here $\bar{c}$ is equal to the mole fraction of solute divided by the molar volume of solvent, N_2/V_1.

All of these expressions predict salting out if the dielectric constant of the non-electrolyte is less than the dielectric constant of the solvent and salting in if the dielectric constant of the solvent is less than that of the non-electrolyte. None of these equations are valid at high concentrations of the electrolyte, since the energy of the ion is taken to be that of an isolated point charge in equations (1) and (4); in (3) the energy of the ion takes into consideration the effects of the ionic atmosphere only at lower concentrations (below 1 molar). The effects of electrostriction have been ignored. The free energy of solution receives

only a small contribution from electrostriction (34, 35).

The ionic radius in solution is not, in general, equal to the crystallographic radius of the ion. The crystallographic radius does provide us with a first approximation. Most cations, excepting possibly large monovalent cations, are generally considered to be hydrated in solution, as are a few anions such as the fluoride and hydroxide ions. This hydration may be due to chemical or physical interactions in solution (36). In general it is probably due to both. It is often difficult to make a distinction, because it is not easy to say whether a combination resulting from ion-dipole interaction results in a weak homonuclear interaction or an electrostatic one. Whatever may be the case, a certain increment should be added to the crystallographic radius to compensate for hydration of the ion. It is hard to say just what the "effective" radius of an ion should be. Latimer, Pitzer, and Slansky (37) have found that if they added 0.85 A to the crystallographic radii of cations and 0.1 A to the crystallographic radii of anions, the free energies of hydration of ions follow the Born equation (7). We have here a second approximation which is certainly better to use for small monovalent ions and any multivalent ions. It is evident, however, that the amount

of hydration is not constant but for constant charge will decrease with increasing ionic radius. Bernal and Fowler (38) using results based on the densities of ionic solutions have concluded that rubidium and cesium ions are not hydrated in solution.

Evidence from transference experiments (36) indicates that lithium ion is from 1.5 - 2.0 times as hydrated as the sodium ion and the sodium ion in turn is about twice as hydrated as the potassium ion. The hydration of potassium, rubidium, and cesium ions appears to be about the same. It should be noted that the correction for electro-osmosis through the membranes used is uncertain. A difficulty in such experiments is that water is carried along hydronamically.

The hydration of ions would be expected to decrease with increasing concentration due to more competition among the ions for the water molecules. Hydration should decrease with increasing temperature due to the increased thermal energy of the water molecules.

It should be mentioned also that the presence of non-electrolyte molecules in the solvation layer should also be considered. Since the water is present in large excess and is generally more polarizable than the non-electrolyte, not much non-electrolyte is to be expected in the solvation layer around the ion.

The dielectric constant of a solution measured by instrumental methods is the macroscopic dielectric constant, that is, the dielectric constant of the bulk of the solution, and it is possible that the dielectric constant in the vicinity of an ion is not equal to the macroscopic value. This question will be discussed presently.

The macroscopic value of the dielectric constant for a three component system depends upon the nature of the solvent and the natures and concentrations of the non-electrolyte and electrolyte added. If water is the solvent, most non-electrolytes when added will lower the dielectric constant. Exceptions are such substances as hydrogen peroxide, hydrogen cyanide, formamide as well as zwitter-ions and proteins. The change of dielectric constant with addition of non-electrolyte is usually a linear function of the concentration of the non-electrolyte at moderately low concentrations. Addition of electrolytes in small amounts to a solvent has an unknown effect, the claims made being highly contradictory (39). For ionic concentrations from 0.5 to 2.0 molar, Hasted, Ritson and Collie (40) have found by application of microwave methods that the dielectric constant of aqueous electrolyte solutions is considerably lower than that of

pure water. The lowering of dielectric constant ranges from 10 to 15 units at one molar depending upon the electrolyte present. The change in dielectric constant up to two molar is a linear function of the electrolyte concentration.

Debye (41) used the Sack theory which employs the Mosotti hypothesis, in calculating that dielectric saturation should begin at about 11 Å from a monovalent ion and at greater distances from multivalent ions. Debye notes, however, that experimentally Malsch (42) did not find as large an effect of dielectric saturation as the Mosotti hypothesis would lead one to expect. More recently Hasted, Ritson, and Collie (40) have used a model obeying the Onsager equation (43) and another model which is a modification of Kirkwood's formula (44) for small fields so as to extend itto large fields. They calculated the variation of dielectric constant with distance from an ion and have found for monovalent ions that no appreciable dielectric saturation occurs until about 4 Å. Grahame (45) has applied the experimental data of Malsch (42) and has constructed plots of D vs. r. He finds no appreciable dielectric saturation at distances greater than 4 Å from a monovalent ion. The curves given by Hasted, Ritson and Collie and those of Grahame agree very

well. Both sets of curves indicate an onset of dielectric saturation at about 4 Å and a very rapid drop in dielectric constant between 2 and 3 Å. Grahame has recalculated the free energy of hydration by the Born equation (7) taking into account the variation of dielectric constant with field strength and has found that the results are almost identical with those calculated by the simple Born equation. These results seem to indicate that dielectric saturation is not a factor of major importance.

Justification for the use of equations such as the Debye-MacAulay equation is related to the validity of the ion-dipole interaction equations. To be specific the equation

$$u = -\frac{e\mu\cos\theta}{r^2} \tag{9}$$

where θ is the angle of inclination of the dipole to the ion, holds for $e/r^2 \gg kT$. If on the other hand, $e/r^2 \ll kT$, Boltzmann averaging gives

$$\bar{u} = -1/3\,\frac{e^2\mu^2}{kTr^4} \tag{10}$$

If equation (10) were correct everywhere within the solution then the Born equation would be correct everywhere within the solution. Near the ions, however, where $e\mu/r^2 \gg kT$, equation (9) holds. The application of equation (9) is closely equivalent to considering

dielectric saturation as having set in. This problem has already been discussed. We may say that since dielectric saturation does not seem to set in until 3 - 4 Å from the ion, if a monolayer of solvent molecules has been considered as present, dielectric saturation effects have been largely accounted for. Thus, the use of effective radii in the equations applied is probably equivalent to a separate calculation using equation (9) in the vicinity of the ion.

Thus far all of the equations discussed have included Coulombic terms only. That is to say, only charge-molecule and charge-charge interactions have been considered. If we were to remove the charge from an ion in solution, say a sodium ion, we would produce a neon atom. Such a neutral particle would also have an effect on the other two components of the system. Its interaction would be due to molecular attraction forces generally termed Van der Waals forces. To gain an understanding of the exact nature of such forces and their importance, let us briefly consider the general theory of intermolecular forces (46).

Two molecules of the same or of different kinds may have unsymmetrical charge distributions which give rise to permanent dipoles μ. Such dipoles will interact in such a way as to give interaction energies as

follows,

$$\bar{u} = -\frac{2\mu_I\mu_{II}}{r^3} \tag{11}$$

which holds for the most favorable orientation of the two molecules and when $\mu_I\mu_{II}/r^3 \gg kT$. Boltzmann statistics yields

$$\bar{u} = -\frac{2/3\mu_I^2\mu_{II}^2}{r^6kT} \tag{12}$$

for $\mu_I\mu_{II}/r^3 \ll kT$.

However, Van der Waals forces do not drop off with temperature as rapidly as predicted by equation (12). The consideratiom of interactions of quadrupole and higher moments will not help, since the expressions for their interaction energies will have the same temperature dependency as the dipole-dipole interaction energy in equation (12).

Molecules are not characterized by their permanent moments μ alone, but also by their tendency to be deformed so as to produce induced moments. This tendency is represented by their polarizability α. Two dipoles may interact to produce additional induced moments in each other. The energy of such an interaction is given by

$$\bar{u} = -1/r^6(\alpha_I\mu_{II}^2 - \alpha_{II}\mu_I^2) \tag{13}$$

or if only one of the molecules has a permanent moment then

$$\bar{u} = -\alpha_I \mu_{II}^2 / r^6 \qquad (14)$$

Molecules having no permanent dipoles, nevertheless, show phenomena due to Van der Waals forces. Such molecules do have quadrupole moments in some cases (N_2, H_2 etc.)
and may consequently induce dipoles in each other giving rise to the energy

$$\bar{u} = -3/2 \alpha \Theta^2 / r^8 \qquad (15)$$

where Θ is the quadrupole moment.

Quantum mechanical calculations on H_2 have shown, however, that the interaction energy resulting from quadrupole-quadrupole interaction is only one-one hundredth of the Van der Waals forces observed.

Rare gas atoms have been shown by quantum mechanics to be fully symmetrical, that is, they have no dipole, quadrupole or higher multipole moments. How is the condensation of the inert gas to be accounted for? Before answering this question, let us consider more closely what the situation in the liquid state would be.

It does not necessarily follow that the orientation (dipole-dipole interactions) and induction (induced dipole-induced dipole) effects will be the same

in the gaseous state where the molecules may interact in pairs without perturbation by other particles, and in the liquid state where the dipoles and the polarization fields of many molecules will be interacting. Indeed, if two interacting dipoles are so oriented as to be attracted by a third dipole the resulting perturbation effect on the original dipole-dipole interaction will be such as to produce large repulsive forces. If the polarization fields of many molecules interact the result will be a net lowering of the interaction. Thus, in condensed phases the orientation and induction interactions may be expected to be very considerably lowered.

How then is the condensation of molecules to be explained? To what are the molecular interactions of the components of liquid solutions to be attributed?

As a consequence of the uncertainty principle, the nuclei and the electrons of all atoms and molecules at all temperatures are in constant oscillation. The oscillations cause these particles to have instantaneous dipoles of varying magnitude and direction. These moments average out vectorially over even a short period of time to zero. The instantaneous dipole possessed by a given particle acts upon the polarizability of other particles and thus produces dipoles which are

in phase with and in interaction with the dipole producing them. Thus as London has pointed out, "the zero point energy is accompanied by a synchronized electric alternating energy field, but not by a radiation field". The existence of a radiation field which would dissipate the zero point energy of the oscillator is forbidden by the uncertainty principle. The London effect unlike the orientation and induction effects previously considered is additive in the liquid and solid states. Dipoles which are not in phase give rise only to periodic interactions which when averaged over all the possible phases available are equal to zero. We have available then an explanation for the condensation of the inert gases as well as gases such as N_2 and H_2, whose quadrupole interactions are insufficient to account for their condensation and other Van der Waals effects. In non-electrolyte solutions consisting of all but the most highly polar molecules, dispersion forces contribute the major portion of the Van der Waals forces.

For homonuclear diatomic molecules the dispersion forces are almost 100 per cent of the Van der Waals forces acting. For HCl the dispersion forces contribute 80 per cent of the total interaction. In ammonia, dispersion forces constitute 50 per cent of the Van

der Waals forces. Even for H_2O, a highly polar molecule with a high contribution from hydrogen bonding, the dispersion effect still contributes 20 per cent of the total effect.

The formula for the dispersion energy of two oscillating dipoles is given by

$$\bar{u} = - 3/4\ h\nu\alpha^2/r^6 \qquad (16)$$

The total interaction energy of the "periodic" dipoles of two molecules, one in state k, and the other in state m which have periodic dipoles, μ_{kl} and μ_{mn}, with frequencies, ν_{kl} and ν_{mn}, is given by

$$\bar{u} = - 2/3hr^6 \sum_{ln} \frac{\mu_{kl}^2 \mu_{mn}^2}{\nu_{kl} + \nu_{mn}} \qquad (17)$$

For the inert gases and other simple molecules whose dispersion formula consists only of one term, the characteristic frequency may be approximated, when multiplied by h, by the ionization energy. Even for the inert gases where values are available for both $h\nu$ and I, the agreement is only fair. Thus for neon I = 21.5 electron volts, while $h\nu$ = 25.7 electron volts. For complex organic molecules there is no assurance that the characteristic frequencies are even approximately equal to the ionization energies. It is possible that they may be equal instead to some non-ionizing electronic transition (47). It has been pointed out

by Born and Mayer (48) that for simple rare-gas like ions, the ionization potential to be used for positive ions is the second ionization potential and for negative ions the electron affinity should be employed.

The dispersion forces due to dipole-quadrupole and quadrupole-quadrupole interactions, which vary with r^{-8} and r^{-10} may also be calculated. In general they are not important. However, at close distances they must be considered for H_2 and He.

We are now in a position to again consider the specific problem at hand -- interactions in three component systems. Let us consider a process whereby an ion is transferred from pure solvent to a solution of solvent plus non-electrolyte. We may see firstly, that the ion will perturb such orientation and induction interactions as there may be between solvent and non-electrolyte. The net result here will probably be to lower the interaction. Secondly, since we have replaced a portion of the solvent with non-electrolyte, the interaction of the ion with the medium will be different. Principally, the replacement of solvent with non-electrolyte will result in a difference in the dispersion forces between the ion and its medium. These dispersion interactions will have an opposite effect compared to the coulombic interactions. They will consequently

increase the tendency towards salting-in. Not only will there be a difference in dispersion effects, but there also will be differences resulting from differing dipole interactions of the medium with the ion to produce an induced dipole in the ion. Furthermore, the ion will interact only with the solvent to produce induced moments in the first medium, but with both solvent and non-electrolyte in the second medium. Since ion-dipole forces will tend to favor the presence of water over non-electrolyte in the immediate vicinity of the ion, the differences in the energy of interaction for the orientation and induction forces in the two media will not be very great. Furthermore, since the orientation and induction effects are not additive, but tend to cancel out, they should be quite small. Whatever residue orientation and induction effects there are will act in the same direction as the dispersion effect.

Since the dispersion interaction is proportional to the polarizability of the ions, large ions, and especially large anions, will interact to give rise to considerable dispersion effects. These may result in diminished salting-out or even salting-in of the non-electrolyte.

Recently Bockris, Bowler-Reed, and Kitchener (49)

have introduced dispersion forces into a derivation of a salt effect equation which is derived in a very similar manner to a salt effect equation derived by Butler (50). This derivation is rather weak in a number of details. After the reversible work is calculated in the derivation, the Maxwell Boltzmann distribution law is used. To avoid integration of an expression with a rather complicated exponential factor in it, the exponential is expanded and only the first two terms are retained. This practice which is rather widely used, is in general not justified. In this case it is not justified when W, the reversible work, is greater than kT. The approximation, $\log \left(1 - \frac{s_o - s}{s}\right) = \frac{s_o - s}{s}$ is made in the following step. This approximation introduces a five per cent error for a ten per cent change in solubility, a ten per cent error for a twenty per cent change in solubility, and almost a twenty per cent error for a thirty per cent change in solubility. The ionization potentials are used to represent $h\nu$ without justification. The quaternary ammonium iodides are used as electrolytes in the experimental investigation described. Since experimental values of even the ionization potentials of the quaternary ammonium ions are not available, the values of I were found by an extrapolation from the ionization potentials of the alkali metal ions. The

authors do not say whether or not they used the second ionization potentials, and no mention is made of what values were used to represent $h\nu$ for the anions. The ionization potential of benzoic acid, the non-electrolyte employed, is calculated, according to the authors, from "structural relationships" deduced by Walsh (51). No such structural relationships could be found in this article. It is true that the value given, 10.0 e.v., is close to the values of the first ionization potentials tabulated for some other molecules such as acetaldehyde and acetone, but these values do not justify the use of 10.0 e.v. for benzoic acid. As has been pointed out previously, the use of the ionization potential for a molecule such as benzoic acid may be grossly in error. The authors fail to discuss this problem. To calculate the molecular polarization needed, these investigators use the formula $P = (D_s - 1)M/(4\pi dN)$. How this equation may be used for a calculation of molecular polarization is not clear. Ordinarily P is given by $P = (D_s - 1)M/(D_s - 2)dN$, if $D_s \cong 1$, then $P = (D_s - 1)M/3dN$ for gases. Where the 4π given by the authors comes from is not at all clear. Of course, even the relationship $P = (D_s - 1)M/(D_s - 2)dN$ holds only for non-polar substances and $P = (D_s - 1)M/3dN$ holds only for non-polar gases. A consideration of the

experimental results will shed further light upon the inadequacy of the theoretical treatment. Although salting-in is found experimentally and predicted theoretically from their equation, large differences between the experimental and theoretical results are to be noted. For Me_4NI, the theoretical result is about twenty per cent higher than the experimental result. For Et_4NI, the experimental result is about three hundred per cent higher than the theoretical result. When Pr_4NI was used, the theoretical prediction was about eight hundred per cent low. When Bu_4NI was employed, the theoretical prediction was two hundred per cent low. Thus the experimental results indicate increasing salting-in with increasing ion size at a much greater rate than the theoretical results predict, except that the discrepancy seems to decrease again for the solution containing Bu_4NI.

It may be said, in summary, that while the authors are making a step in the right direction in considering dispersion forces, the theoretical approach is probably more complicated than they indicate. As has already been pointed out, however, the salting-in effects due to dispersion should be expected to be indicated qualitatively for large ions, especially large organic ions. This is in agreement with many experimental results.

X Theoretical Calculations

Theoretical calculations were made for ethyl acetate water - electrolyte solutions using equations (1), (2), and (3) in section X. Four variations of a Debye-MacAulay type equation (1) were used. The calculations based on these equations are to be found in Tables VII through X. Calculations using equation (2) are included in Table XI. Calculations based on the Debye equation are included in Table XII. The theoretical results given at 30°C in Tables VI through XII are compiled in Table XIII.

Table	Equation	
VII	$\ln f = Sb^{-1}c$	(1)
	where $S = \frac{N\epsilon^2\omega}{2000kTD_o}$	
	and $\frac{1}{b} = \frac{1}{b_+} + \frac{1}{b_-}$	
VIII	$\ln f = Sb'^{-1}c$	(1a)
	where $\frac{1}{b'} = \frac{1}{b_+ + K_+} + \frac{1}{b_- + K_-}$	
IX	$\ln f = S'b^{-1}c$	(1b)
	where $S' = \frac{N\epsilon^2 D_o\omega}{2000kTD^2}$	
X	$\ln f = S'b'^{-1}c$	(1c)

Table	Equation	
XI	$\ln f = S'b^{-1}c - 2S'\varkappa c$	(2)
XII	$\% \text{ S.E.} = 1 - \frac{1}{f} = \frac{4\pi N}{1000}\sum_i J_i c_i$	(3)
	$\% \text{ S.E.} = 1 - \frac{1}{f} = \frac{4\pi N}{1000}\sum_i \bar{R}_i^3 \left[1.21 - \frac{1}{3}\left(\frac{b_i}{R_i}\right)^3\right] c_i$	
	$\% \text{ S.E.} = [1.83\text{x}10^{24}\bar{R}^3 - 0.252\text{x}10^{24}(b_+^3 + b_-^3)]\,c$	
	$\% \text{ S.E.} = [A + B(b_+^3 + b_-^3)]\,c$	

The procedure used was to first calculate the constants (at a given temperature) S, S', $\bar{R}^3$ and 1/b, 1/b', $(b_+^3 + b_-^3)$. The log f was immediately found from the produce (except for the Debye equation in Table VII). The value of the antilog of -log f was found and this value 1/f was subtracted from 1 and multiplied by 100. Thus we have $(1 - \frac{1}{f})100$. Since $f = S_o/S$, we obtain $(1 - \frac{S}{S_o})100 = \frac{S_o - S}{S_o} \times 100$ which is the per cent change in solubility. Values of $\frac{1}{b}$, $\frac{1}{b'}$, $b_+^3 + b_-^3$ are to be found elsewhere (29). The values of S, S', $\bar{R}^3$ are given below

Temperature	S	S'	$\bar{R}^3$
20°C	2.59×10^{-9}	2.95×10^{-9}	14.2×10^{-24}
25°C	2.71×10^{-9}	3.09×10^{-9}	14.7×10^{-24}
30°C	2.83×10^{-9}	3.23×10^{-9}	15.3×10^{-24}
35°C	2.92×10^{-9}	3.32×10^{-9}	15.6×10^{-24}
40°C	2.94×10^{-9}	3.33×10^{-9}	15.8×10^{-24}

Table VII

Calculation of the % Salt Effect by the Debye-MacAulay Equation Using Crystallographic Radii

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	1.4	1.5	1.5	1.6	-
LiCl	0.1000	-	5.2	5.5	5.6	5.7
	0.2000	-	10.2	10.6	10.9	11.0
	0.3000	-	14.9	15.5	15.9	16.0
	0.4000	-	19.4	20.1	20.6	20.8
LiBr	0.1000	4.9	5.1	5.3	5.5	-
	0.2000	9.5	10.0	10.4	10.7	-
	0.3000	13.9	14.6	15.2	15.6	-
	0.4000	18.1	19.0	19.8	20.3	-
NaF	0.1000	4.4	4.6	4.8	5.0	-
	0.2000	8.6	9.1	9.4	9.7	-
	0.3000	12.7	13.3	13.8	14.2	-
	0.4000	16.5	17.4	18.0	18.5	-
NaCl	0.1000	3.9	4.1	4.3	4.5	4.5
	0.2000	7.7	8.1	8.5	8.7	8.8
	0.3000	11.4	11.9	12.4	12.8	12.9
	0.4000	14.9	15.4	16.2	16.7	16.8
NaBr	0.1000	3.8	4.0	4.2	4.3	-
	0.2000	7.5	7.9	8.2	8.5	-
	0.3000	11.0	11.6	12.1	12.4	-
	0.4000	14.2	15.1	15.7	16.2	-
NaI	0.1000	3.7	3.9	4.1	4.2	-
	0.2000	7.3	7.6	8.0	8.2	-
	0.3000	10.7	11.2	11.7	12.0	-
	0.4000	14.0	14.7	15.3	15.7	-
KCl	0.1000	3.3	3.5	3.6	3.8	-
	0.2000	6.3	6.9	7.1	7.4	-
	0.3000	9.7	10.2	10.5	10.8	-
	0.4000	12.7	13.3	13.8	14.2	-

Table VII (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KBr	0.1000	-	-	3.5	3.6	3.6
	0.2000	-	-	6.9	7.1	7.1
	0.3000	-	-	10.2	10.5	10.5
	0.4000	-	-	13.3	13.7	13.8
KI	0.1000	3.1	3.2	3.4	3.5	-
	0.2000	6.1	6.4	6.6	6.8	-
	0.3000	9.0	9.4	9.8	10.1	-
	0.4000	11.8	12.3	12.8	13.2	-
RbF	0.1000	3.6	3.8	3.9	4.0	-
	0.2000	7.0	7.4	7.7	7.9	-
	0.3000	10.3	10.8	11.3	11.6	-
	0.4000	13.5	14.2	14.7	15.2	-
RbCl	0.1000	3.1	3.2	3.4	3.5	-
	0.2000	6.1	6.4	6.6	6.8	-
	0.3000	9.0	9.4	9.8	10.1	-
	0.4000	11.8	12.3	12.8	13.2	-
RbBr	0.097	-	3.0	3.2	3.3	-
	0.194	-	6.0	6.2	6.4	-
RbI	0.099	2.8	3.0	3.1	3.2	-
	0.189	5.3	5.6	5.8	5.9	-
CsCl	0.1000	2.9	3.1	3.2	3.3	-
	0.2000	5.7	6.0	6.2	6.5	-
	0.3000	8.5	8.9	9.2	9.5	-
CsBr	0.1000	-	3.0	3.1	3.2	-
	0.2000	-	5.8	6.0	6.2	-
CsI	0.1000	-	2.8	2.9	3.0	-
	0.2000	-	5.5	5.7	5.9	-
$(CH_3)_4NI$	0.1000	2.2	2.3	2.4	-	-

Table VIII

Calculation of the % Salt Effect by the Debye-MacAulay Equation Using "Effective" Radii

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	0.9	0.9	0.9	1.0	-
LiCl	0.1000	-	3.1	3.3	3.4	3.4
	0.2000	-	6.2	6.4	6.6	6.7
	0.3000	-	9.1	9.5	9.8	9.9
	0.4000	-	11.9	12.4	12.8	12.9
LiBr	0.1000	2.9	3.0	3.1	3.3	-
	0.2000	5.7	5.9	6.2	6.4	-
	0.3000	8.4	8.8	9.2	9.5	-
	0.4000	11.0	11.5	12.0	12.4	-
NaF	0.1000	3.2	3.3	3.5	3.6	-
	0.2000	6.2	6.5	6.8	7.0	-
	0.3000	9.2	9.6	10.0	10.3	-
	0.4000	12.0	12.6	13.1	13.3	-
NaCl	0.1000	2.7	2.9	3.0	3.1	3.1
	0.2000	5.4	5.6	5.9	6.1	6.1
	0.3000	8.0	8.3	8.7	9.0	9.0
	0.4000	10.5	11.0	11.4	11.8	11.9
NaBr	0.1000	2.6	2.8	2.9	3.0	-
	0.2000	5.2	5.5	5.7	5.9	-
	0.3000	7.6	8.1	8.4	8.7	-
	0.4000	10.0	10.6	11.0	11.4	-
NaI	0.1000	2.5	2.6	2.7	2.8	-
	0.2000	4.9	5.1	5.3	5.5	-
	0.3000	7.2	7.6	7.9	8.1	-
	0.4000	9.6	10.0	10.4	10.7	-
KCl	0.1000	2.5	2.7	2.8	2.9	-
	0.2000	5.0	5.2	5.5	5.6	-
	0.3000	7.4	7.8	8.1	8.3	-
	0.4000	9.7	10.2	10.6	11.0	-
KBr	0.1000	-	-	2.6	2.7	2.7
	0.2000	-	-	5.2	5.3	5.4
	0.3000	-	-	7.7	7.9	8.0
	0.4000	-	-	10.1	10.4	10.5

Table VIII (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KI	0.1000	2.3	2.4	2.5	2.6	-
	0.2000	4.5	4.7	4.9	5.1	-
	0.3000	6.7	7.0	7.3	7.5	-
	0.4000	8.8	9.2	9.6	9.9	-
RbF	0.1000	2.9	3.0	3.1	3.3	-
	0.2000	5.7	5.9	6.2	6.4	-
	0.3000	8.4	8.8	9.2	9.5	-
	0.4000	11.0	11.5	12.0	12.4	-
RbCl	0.1000	2.4	2.6	2.7	2.8	-
	0.2000	4.8	5.0	5.2	5.4	-
	0.3000	7.1	7.4	7.8	8.0	-
	0.4000	9.3	9.8	10.2	10.5	-
RbBr	0.097	-	2.4	2.5	2.6	-
	0.194	-	4.7	4.9	5.0	-
RbI	0.099	2.2	2.3	2.4	2.5	-
	0.189	4.1	4.3	4.5	4.6	-
CsCl	0.1000	2.3	2.5	2.6	2.7	-
	0.2000	4.6	4.9	5.1	5.3	-
	0.3000	6.9	7.2	7.5	7.8	-
CsBr	0.1000	-	2.4	2.5	2.6	-
	0.2000	-	4.7	4.9	5.0	-
CsI	0.1000	-	2.2	2.3	2.4	-
	0.2000	-	4.4	4.6	4.7	-
$(CH_3)_4NI$	0.1000	1.9	2.0	2.1	-	-

Table IX

Calculation of % Salt Effect Using Equation 1c

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	1.6	1.7	1.7	1.8	-
LiCl	0.1000	-	5.9	6.2	6.3	6.4
	0.2000	-	11.5	12.0	12.3	12.4
	0.3000	-	16.7	17.4	17.9	18.0
	0.4000	-	21.7	22.5	23.1	23.2
LiBr	0.1000	5.5	5.8	6.1	6.2	-
	0.2000	10.8	11.3	11.8	12.1	-
	0.3000	15.7	16.4	17.1	17.5	-
	0.4000	20.4	21.3	22.2	22.7	-
NaF	0.1000	5.0	5.3	5.5	5.6	-
	0.2000	9.8	10.3	10.7	11.0	-
	0.3000	14.3	15.0	15.6	16.0	-
	0.4000	18.6	19.5	20.2	20.7	-
NaCl	0.1000	4.5	4.7	4.9	5.1	5.1
	0.2000	8.8	9.2	9.6	9.8	9.9
	0.3000	12.9	13.4	14.0	14.4	14.5
	0.4000	16.8	17.5	18.2	18.7	18.8
NaBr	0.1000	4.3	4.5	4.7	4.9	-
	0.2000	8.5	8.9	9.3	9.5	-
	0.3000	12.5	13.0	13.6	13.9	-
	0.4000	16.3	17.0	17.7	18.1	-
NaI	0.1000	4.2	4.4	4.6	4.7	-
	0.2000	8.2	8.6	9.0	9.2	-
	0.3000	12.1	12.7	13.1	13.5	-
	0.4000	15.8	16.5	17.1	17.6	-
KCl	0.1000	3.8	4.0	4.1	4.3	-
	0.2000	7.4	7.8	8.1	8.3	-
	0.3000	11.0	11.4	11.9	12.2	-
	0.4000	14.3	15.0	15.5	16.0	-

Table IX (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KBr	0.1000	-	-	4.0	4.1	4.1
	0.2000	-	-	7.8	8.0	8.1
	0.3000	-	-	11.4	11.8	11.9
	0.4000	-	-	15.0	15.4	15.5
KI	0.1000	3.5	3.7	3.8	3.9	-
	0.2000	6.9	7.2	7.5	7.7	-
	0.3000	10.2	10.6	11.0	11.3	-
	0.4000	13.3	13.9	14.4	14.8	-
RbF	0.1000	4.1	4.3	4.4	4.6	-
	0.2000	8.0	8.3	8.7	8.9	-
	0.3000	11.7	12.2	12.7	13.1	-
	0.4000	15.3	16.0	15.6	17.1	-
RbCl	0.1000	3.5	3.7	3.8	3.9	-
	0.2000	6.9	7.2	7.5	7.7	-
	0.3000	10.2	10.6	11.0	11.3	-
	0.4000	13.3	13.9	14.4	14.8	-
RbBr	0.1000	-	3.4	3.6	3.7	-
	0.2000	-	6.8	7.1	7.2	-
RbI	0.1000	3.2	3.3	3.5	3.6	-
	0.2000	6.0	6.3	6.5	6.7	-
CsCl	0.1000	3.3	3.5	3.6	3.7	-
	0.2000	6.5	6.8	7.1	7.3	-
	0.3000	9.6	10.0	10.5	10.7	-
CsBr	0.1000	-	3.3	3.5	3.6	-
	0.2000	-	6.5	6.8	7.0	-
CsI	0.1000	-	3.1	3.3	3.4	-
	0.2000	-	6.2	6.5	6.7	-
$(CH_3)_4NI$	0.1000	2.5	2.7	2.8	-	-

Table X

Calculation of Percentage Salt Effect by Equation 1d

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	1.0	1.0	1.1	1.1	-
LiCl	0.1000	-	3.5	3.7	3.8	3.8
	0.2000	-	7.0	7.3	7.4	7.5
	0.3000	-	10.3	10.7	11.0	11.1
	0.4000	-	13.5	14.0	14.3	14.5
LiBr	0.1000	3.3	3.4	3.6	3.7	-
	0.2000	6.5	6.7	7.0	7.2	-
	0.3000	9.5	9.9	10.3	10.7	-
	0.4000	12.5	13.0	13.5	13.9	-
NaF	0.1000	3.6	3.8	3.9	4.0	-
	0.2000	7.1	7.4	7.7	7.9	-
	0.3000	10.4	10.8	11.3	11.6	-
	0.4000	13.6	14.2	14.8	15.2	-
NaCl	0.1000	3.1	3.2	3.4	3.5	3.5
	0.2000	6.1	6.4	6.7	6.8	6.9
	0.3000	9.0	9.4	9.8	10.1	10.2
	0.4000	11.9	12.3	12.9	13.2	13.3
NaBr	0.1000	3.0	3.1	3.3	3.4	-
	0.2000	5.9	6.2	6.4	6.6	-
	0.3000	8.7	9.1	9.5	9.7	-
	0.4000	11.4	11.9	12.4	12.7	-
NaI	0.1000	2.8	3.0	3.1	3.2	-
	0.2000	5.5	5.8	6.1	6.2	-
	0.3000	8.2	8.6	9.0	10.2	-
	0.4000	10.8	11.3	11.8	12.1	-
KCl	0.1000	2.9	3.0	3.1	3.2	-
	0.2000	5.7	5.9	6.2	6.4	-
	0.3000	8.4	8.8	9.2	9.4	-
	0.4000	11.0	11.5	12.0	12.3	-

Table X (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KBr	0.1000	-	-	3.0	3.1	3.1
	0.2000	-	-	5.9	6.0	6.1
	0.3000	-	-	8.7	8.9	9.0
	0.4000	-	-	11.4	11.7	11.8
KI	0.1000	2.6	2.7	2.8	2.9	-
	0.2000	5.1	5.3	5.6	5.7	-
	0.3000	7.6	7.9	8.3	8.5	-
	0.4000	10.0	10.4	10.9	11.1	-
RbF	0.1000	3.3	3.4	3.6	3.7	-
	0.2000	6.5	6.7	7.0	7.2	-
	0.3000	9.5	9.9	10.1	10.4	-
	0.4000	12.5	13.0	13.5	13.9	-
RbCl	0.1000	2.8	2.9	3.0	3.1	-
	0.2000	5.5	5.7	5.9	6.1	-
	0.3000	8.1	8.4	8.8	9.0	-
	0.4000	10.6	11.0	11.5	11.9	-
RbBr	0.097	-	2.7	2.8	2.9	-
	0.194	-	5.3	5.5	5.7	-
RbI	0.099	2.5	2.6	2.7	2.8	-
	0.189	4.7	4.9	5.1	5.2	-
CsCl	0.1000	2.7	2.8	2.9	3.0	-
	0.2000	5.3	5.5	5.8	5.9	-
	0.3000	7.8	8.1	8.5	8.8	-
CsBr	0.1000	-	2.7	2.8	2.9	-
	0.2000	-	5.3	5.5	5.7	-
CsI	0.1000	-	2.5	2.6	2.7	-
	0.2000	-	5.0	5.2	5.4	-
$(CH_3)_4NI$		2.2	2.3	2.4	-	-

Table XI

Calculation of Percentage Salt Effect by Equation 2

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	1.0	1.0	1.1	1.1	-
LiCl	0.1000	-	3.4	3.5	3.6	3.7
	0.2000	-	6.6	6.9	7.0	7.1
	0.3000	-	9.6	10.0	10.2	10.3
	0.4000	-	12.4	12.9	13.2	13.4
LiBr	0.1000	3.1	3.3	3.4	3.5	-
	0.2000	6.1	6.3	6.6	6.8	-
	0.3000	8.9	9.2	9.6	9.9	-
	0.4000	11.5	11.9	12.5	12.8	-
NaF	0.1000	3.5	3.6	3.8	3.9	-
	0.2000	6.7	6.9	7.3	7.5	-
	0.3000	9.7	10.1	10.6	10.9	-
	0.4000	12.6	13.1	13.7	14.1	-
NaCl	0.1000	3.0	3.1	3.2	3.3	3.4
	0.2000	5.7	6.0	6.3	6.4	6.5
	0.3000	8.4	8.7	9.1	9.3	9.4
	0.4000	10.9	11.3	11.8	12.1	12.2
NaBr	0.1000	2.9	3.0	3.1	3.2	-
	0.2000	5.5	5.8	6.0	6.2	-
	0.3000	8.0	8.4	8.7	9.0	-
	0.4000	10.4	10.9	11.3	11.6	-
NaI	0.1000	2.7	2.8	2.9	3.0	-
	0.2000	5.2	5.4	5.7	5.8	-
	0.3000	7.5	7.9	8.2	8.5	-
	0.4000	9.8	10.2	10.7	11.0	-
KCl	0.1000	3.7	3.9	4.0	4.1	-
	0.2000	5.3	5.5	5.8	5.9	-
	0.3000	7.7	8.1	8.4	8.7	-
	0.4000	10.0	10.5	10.9	11.2	-
KBr	0.1000	-	-	2.8	2.9	2.9
	0.2000	-	-	5.5	5.6	5.6
	0.3000	-	-	8.0	8.1	8.2
	0.4000	-	-	10.3	10.5	10.6

Table XI (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KI	0.1000	2.5	2.6	2.7	2.8	-
	0.2000	4.7	4.9	5.2	5.3	-
	0.3000	6.9	7.2	7.5	7.7	-
	0.4000	8.9	9.3	9.8	10.0	-
RbF	0.1000	3.1	3.3	3.4	3.5	-
	0.2000	6.1	6.3	6.6	6.8	-
	0.3000	8.9	9.2	9.4	9.9	-
	0.4000	11.5	11.9	12.5	12.8	-
RbCl	0.1000	2.6	2.8	2.9	3.0	-
	0.2000	5.1	5.3	5.5	5.7	-
	0.3000	7.4	7.7	8.0	8.3	-
	0.4000	9.6	10.0	10.4	10.7	-
RbBr	0.097	-	2.6	2.7	2.8	-
	0.194	-	5.0	5.2	5.3	-
RbI	0.099	2.3	2.5	2.6	2.6	-
	0.189	4.4	4.5	4.7	4.9	-
CsCl	0.1000	2.5	2.7	2.8	2.8	-
	0.2000	4.9	5.1	5.3	5.5	-
	0.3000	7.1	7.4	7.8	8.0	-
CsBr	0.1000	-	2.5	2.6	2.7	-
	0.2000	-	4.9	5.1	5.2	-
CsI	0.1000	-	2.4	2.5	2.6	-
	0.2000	-	4.6	4.8	4.9	-
$(CH_3)_4NI$	0.1000	2.0	2.1	2.2	-	-

Table XII

Calculation of Percentage Salt Effect by Debye Equation

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
LiF	0.025	0.6	0.7	0.7	0.7	-
LiCl	0.1000	-	2.5	2.6	2.7	2.7
	0.2000	-	5.1	5.3	5.4	5.5
	0.3000	-	7.6	7.9	8.1	8.2
	0.4000	-	10.1	10.5	10.8	10.9
LiBr	0.1000	2.4	2.5	2.6	2.7	-
	0.2000	4.8	5.0	5.2	3.3	-
	0.3000	7.2	7.5	7.8	8.0	-
	0.4000	9.6	10.0	10.4	10.6	-
NaF	0.1000	2.5	2.6	2.7	2.8	-
	0.2000	5.0	5.2	5.4	5.5	-
	0.3000	7.6	7.8	8.2	8.3	-
	0.4000	10.1	10.4	10.9	11.1	-
NaCl	0.1000	2.4	2.5	2.6	2.7	2.7
	0.2000	4.9	5.0	5.3	5.4	5.4
	0.3000	7.9	7.6	7.9	8.0	8.2
	0.4000	9.7	10.1	10.5	10.7	10.9
NaBr	0.1000	2.4	2.5	2.6	2.6	-
	0.2000	4.8	4.9	5.2	5.3	-
	0.3000	7.1	7.4	7.7	7.9	-
	0.4000	9.5	9.9	10.3	10.5	-
NaI	0.1000	2.3	2.4	2.5	2.6	-
	0.2000	4.6	4.8	5.0	5.1	-
	0.3000	6.9	7.2	7.5	7.7	-
	0.4000	9.2	9.6	10.0	10.2	-
KCl	0.1000	2.4	2.5	2.6	2.6	-
	0.2000	4.8	5.0	5.2	5.3	-
	0.3000	7.2	7.4	7.8	7.9	-
	0.4000	9.6	9.9	10.4	10.6	-

Table XII (Continued)

Salt	Conc. in moles/l.	% Change in Solubility 20°C	25°C	30°C	35°C	40°C
KBr	0.1000	-	-	2.6	2.6	2.7
	0.2000	-	-	5.1	5.2	5.4
	0.3000	-	-	7.7	7.8	8.0
	0.4000	-	-	10.2	10.4	10.7
KI	0.1000	2.3	2.4	2.5	2.5	-
	0.2000	4.5	4.7	4.9	5.0	-
	0.3000	6.8	5.1	7.4	7.6	-
	0.4000	10.1	10.4	9.9	10.1	-
RbF	0.1000	2.5	2.5	2.7	2.7	-
	0.2000	4.9	5.1	5.3	5.4	-
	0.3000	7.4	7.6	8.0	8.1	-
	0.4000	9.8	10.2	10.6	10.8	-
RbCl	0.1000	2.4	2.5	2.6	2.6	-
	0.2000	4.7	4.9	5.1	5.2	-
	0.3000	7.1	7.4	7.7	7.8	-
	0.4000	10.4	9.8	10.2	10.4	-
RbBr	0.097	2.3	2.3	2.4	2.5	-
	0.194	4.5	4.7	4.9	5.0	-
RbI	0.099	2.2	2.3	2.4	2.5	-
	0.189	4.2	4.4	4.6	4.7	-
CsCl	0.1000	2.3	2.4	2.5	2.6	-
	0.2000	4.7	4.8	5.1	5.2	-
	0.3000	7.0	7.3	7.6	7.7	-
CsBr	0.1000	-	2.4	2.5	2.5	-
	0.2000	-	4.8	5.0	5.1	-
CsI	0.1000	-	2.3	2.4	2.5	-
	0.2000	-	4.6	4.8	4.9	-
$(CH_3)_4NI$	0.1000	2.0	2.1	2.2	-	-

Table XIII Comparison of the Experimental Salt Effect with the Results of the Theoretical Equations at 30°C. Compiled from Table VI - XII

Salt	Conc. in moles/l.	% Change in Solubility VI	VII	VIII	IX	X	XI	XII
LiF	0.025	1.8	1.5	0.9	1.7	1.1	1.1	0.7
LiCl	0.1000	4.3	5.5	3.3	6.2	3.7	3.5	2.6
	0.2000	6.8	10.6	6.4	12.0	7.3	6.9	5.3
	0.3000	10.1	15.5	9.5	17.4	10.7	10.0	7.9
	0.4000	13.3	20.1	12.4	22.5	14.0	12.9	10.5
LiBr	0.1000	1.9	5.3	3.1	6.1	3.6	3.4	2.6
	0.2000	3.6	10.4	6.2	11.8	7.0	6.6	5.2
	0.3000	5.2	15.2	9.2	17.1	10.3	9.6	7.8
	0.4000	6.9	19.8	12.0	22.2	13.5	12.5	10.4
NaF	0.1000	6.6	4.8	3.5	5.5	3.9	3.8	2.7
	0.2000	12.9	9.4	6.8	10.7	7.7	7.3	5.4
	0.3000	19.4	13.8	10.0	15.6	11.3	10.6	8.2
	0.4000	25.1	18.0	13.1	20.2	14.8	13.7	10.9
NaCl	0.1000	4.3	4.3	3.0	4.9	3.4	3.2	2.6
	0.2000	8.3	8.5	5.9	9.6	6.7	6.3	5.3
	0.3000	13.0	12.4	8.7	14.0	9.8	9.1	7.9
	0.4000	17.3	16.2	11.4	18.2	12.9	11.8	10.5
NaBr	0.1000	3.0	4.2	2.9	4.7	3.3	3.1	2.6
	0.2000	5.9	8.2	5.7	9.3	6.4	6.0	5.0
	0.3000	8.8	12.1	8.4	13.6	9.5	8.7	7.7
	0.4000	11.4	15.7	11.0	17.7	12.4	11.3	10.3

Table XIII (Continued)

Salt	Conc. in moles/l.	% Change in Solubility VI	VII	VIII	IX	X	XI	XII
NaI	0.1000	0.8	4.1	2.7	4.6	3.1	2.9	2.5
	0.2000	0.9	8.0	5.3	9.0	6.1	5.7	5.0
	0.3000	1.8	11.7	7.9	13.1	9.0	8.2	7.5
	0.4000	2.6	15.3	10.4	17.1	11.8	10.7	10.0
KCl	0.1000	4.8	3.6	2.8	4.1	3.1	4.0	2.6
	0.2000	7.9	7.1	5.5	8.1	6.2	5.8	5.2
	0.3000	12.2	10.5	8.1	11.9	9.2	8.4	7.8
	0.4000	16.5	13.8	10.6	15.5	12.0	10.9	10.4
KBr	0.1000	3.2	3.5	2.6	4.0	3.0	2.8	2.6
	0.2000	5.7	6.9	5.2	7.8	5.9	5.5	5.1
	0.3000	7.8	10.2	7.7	11.4	8.7	8.0	7.7
	0.4000	10.1	13.3	10.1	15.0	11.4	10.3	10.2
KI	0.1000	1.8	3.4	2.5	3.8	2.8	2.7	2.5
	0.2000	2.3	6.6	4.9	7.5	5.6	5.2	4.9
	0.3000	2.6	9.8	7.3	11.0	8.3	7.5	7.4
	0.4000	2.9	12.8	9.6	14.4	10.9	9.8	9.9
RbF	0.1000	6.5	3.9	3.1	4.4	3.6	3.4	2.7
	0.2000	12.0	7.7	6.2	8.7	7.0	6.6	5.3
	0.3000	17.0	11.3	9.2	12.7	10.1	9.4	8.0
	0.4000	21.7	14.7	12.0	15.6	13.5	12.5	10.6
RbCl	0.1000	4.3	3.4	2.7	3.8	3.0	2.9	2.6
	0.2000	8.2	6.6	5.2	7.5	5.9	5.5	5.1
	0.3000	11.8	9.8	7.8	11.0	8.8	8.0	7.7
	0.4000	16.9	12.8	10.2	14.4	11.5	10.4	10.2

Table XIII (Continued)

Salt	Conc. in moles/l.	% Change in Solubility VI	VII	VIII	IX	X	XI	XII
RbBr	0.1000	3.6	3.2	2.5	3.6	2.8	2.7	2.4
	0.2000	6.4	6.2	4.9	7.1	5.5	5.2	4.9
RbI	0.1000	1.4	3.1	2.4	3.5	2.7	2.6	2.4
	0.2000	1.2	5.8	4.5	6.5	5.1	4.7	4.6
CsCl	0.1000	3.4	3.2	2.6	3.6	2.9	2.8	2.5
	0.2000	7.0	6.2	5.1	7.1	5.8	5.3	5.1
	0.3000	10.5	9.2	7.5	10.5	8.5	7.8	7.6
CsBr	0.1000	2.7	3.1	2.5	3.5	2.8	2.6	2.5
	0.2000	5.5	6.0	4.9	6.8	5.5	5.1	5.0
CsI	0.1000	0.1	2.9	2.3	3.3	2.6	2.5	2.4
	0.2000	- 0.1	5.7	4.6	6.5	5.2	4.8	4.8
$(CH_3)_4NI$	0.1000	- 0.9	2.4	2.1	2.8	2.4	2.2	2.2
$(C_6H_5)CH_3NI$	0.1000	- 6.2	-	-	-	-	-	-

XI Discussion of Results

The results obtained for the solubility of ethyl acetate in water in this investigation are compared with other results given in the literature in the table below.

Investigator	20°	25°	30°	35°	40°	45°	50°
A.P.A.	8.33	8.01	7.69	7.36	7.04	-	-
Schles.&Kub (21)	8.42	8.03	7.69	7.41	7.18	7.00	6.88
Merriman (52)	8.53	8.08	7.70	7.38	7.10	-	-
Seidel (53)	9.02	8.58	8.24	7.98	7.72	7.53	7.31
Gl. and P. (19)	-	7.39	-	-	-	-	6.04

It may be seen that large differences exist. The data of A.P.A. (present investigation) and Schlesinger and Kubasowa (21) were obtained by the same method -- the Alexjew method. The method used by Merriman (52) was a thermostatic one. A bulb of 75 milliliter capacity was sealed on to a tube divided into tenths of a milliliter. Known weights of water and ethyl acetate were introduced into the apparatus and the tube was sealed. The apparatus was placed in a thermostat and shaken until the two layers of liquid were thoroughly saturated. This point is reached according to Merriman, when the volume of each layer, after it has completely separated out, has a constant value. The thermostatic, analytical method used by Glasstone and Pound has already been described

(Review of the Literature). The agreement of this investigation, Schlesinger and Kubasowa and Merriman at 25, 30 and 35 degrees centigrade is quite good. At 40 degrees centigrade the agreement between the three values is only fair. The solubilities of Seidel (53) are much higher at all the temperatures given than in the three investigations just discussed. The results given by Glasstone and Pound are much lower. As has already been mentioned, the results of Glasstone and Pound would lead one to believe that a considerable amount of ethyl acetate was lost during their procedure. The high solubility results of Seidel might be explained by the use of impure ethyl acetate. If the ethyl acetate used contained much water or alcohol the results obtained would be higher than the true solubilities.

The experimental results indicate that the solubility of ethyl acetate in both water and electrolyte solutions is a linear function of the temperature in the range between 20 and 40 degrees centigrade. The solubility of ethyl acetate in electrolyte solutions appears to be almost a linear function of concentration. The salting out order for anions is clearly $F^- > Cl^- > Br^- > I^-$. The salting out ability of cations decreases with increasing radius except that lithium ion is out of order, which is not an unexpected result. The alkali

iodides salt out ethyl acetate to a small or negligible extent or salt it in to a negligible extent. The quaternary ammonium iodides salt in the ethyl acetate to an appreciable extent. The salting in effect of the trimethyl phenyl ammonium iodide is especially pronounced. The rubidium and cesium iodides seem to cause slightly less salting out with an increase in concentration from one to two tenths molar. In general, the salting out effect appears to increase with increasing temperature in the temperature range studied.

The experimental results on the dielectric constants of ethyl acetate - water mixtures indicate that ethyl acetate lowers the dielectric constant of water. The dielectric constant lowering appears to decrease with increasing temperature. Albright (54) found a dielectric constant lowering of 5.2 units for ethyl acetate compared with a lowering of 5.0 units reported in this investigation. Devotto (55) found a dielectric constant lowering of 5 units when water is saturated with methyl acetate at 25 degrees centigrade.

A comparison of the results in Tables VII to XII, which are calculated from equations 1, 1a, 1b, 1c, 2, and 3, with the experimental results indicates that none of these equations represents the experimental effect of iodides upon ethyl acetate. This may well be

due to the fact that the dispersion forces discussed previously have not been considered in the equations used. The iodide ion is highly polarizable and consequently, would be expected to show considerable dispersion interaction with the medium. Apparently the dispersion effect is nearly as large as the coulombic effect in the case of the sodium, potassium and rubidium iodides, while in the case of cesium iodide the addition contribution from cation polarizability is sufficient to result in the two effects balancing each other. In the quaternary ammonium iodides both cation and anion are highly polarizable, consequently, appreciable salting-in is observed. The possibility of chemical interaction should not be excluded from discussion. Glasstone and Pound (17) stated that in concentrated solutions of iodides containing ethyl acetate, the yellow color found is not due to iodine, but to the presence of some complex compound in solution. Schlesinger and Kubasowa (21) report that a considerable amount of iodine is formed when a five-tenths molar potassium iodide solution was exposed to the light during the determination of solubility of ethyl acetate. In the present investigation, it was found that after four or five hours even the 0.4000 molar iodide solutions were only faintly yellow. The iodine formed appeared

by comparison with a prepared iodine-iodide solution to have an iodine concentration of less than 10^{-5} molar. It was found that after several hours of standing a one molar potassium iodide solution saturated with ethyl acetate could be decolorized with one drop of 0.1 normal sodium thiosulfate. Even after two days of standing in the light only 0.10 milliliters of thiosulfate were needed to decolorize this solution. It may be however, that some complex is formed in dilute solutions which does not absorb in the visible.

The experimental salting out of ethyl acetate by bromides (except lithium bromide) appears to be well represented within a difference of 5-10 per cent by equation (2), (see Table XI). Results calculated from equations (2b) and (2d) also agree with the experimental results for bromides to 10 per cent (see Tables VIII and X). The experimental salting out of ethyl acetate by lithium bromide is unusually low, being best represented by equation (3) although this equation still gives results about 50 per cent higher than those observed experimentally. Equation (2) gives agreement to 5 per cent with the experimental salting out of ethyl acetate by lithium chloride. Equations (1b), (1d) and (2) employ "effective" radii in solution.

The calculated results from equation (1b) give

excellent agreement (5 - 10 percent) with the experimental results for salting out of ethyl acetate by sodium, potassium, rubidium and cesium chlorides (see Table IX). This equation is corrected for dielectric constant lowering but the crystallographic radii are used in the equation.

The experimental salting out results measured when fluorides are used, is higher than those predicted theoretically. The calculated results which give the best agreement come from equation (1b) again. The experimental results are still 25 per cent higher than those calculated from equation (1b).

One further refinement might have been made in the calculations and that would have been to consider the dielectric constant lowering due to the electrolyte (40). This correction for even a 0.4000 molar chloride solution would amount to a little less than five per cent increase in the salting out percentage. No information is available on the dielectric lowering due to alkali fluorides.

The temperature coefficient of salting out is found theoretically to be positive, that is, increasing salting out is predicted with increasing temperature. This is in agreement with the experimental findings.

XII Conclusion

A. Summary

1. The solubility of ethyl acetate in water, 17 aqueous alkali halide solutions and two aqueous quaternary ammonium iodide solutions has been investigated. The concentrations of electrolyte used ranged from 0.025 to 0.4000 molar. The variation of solubility of ethyl acetate in electrolyte solutions with temperature was studied in the temperature range from 20 to 40 degrees centigrade. The turbidimetric method was used to determine the solubility limit.

2. The experimental data were treated by the method of least squares. The solubility of ethyl acetate in water and electrolyte solutions was calculated from the least squares equations at 20, 25, 30, 35 and 40 degrees centigrade as a function of electrolyte concentration.

3. The percentage water in the ethyl acetate was determined by means of Karl Fischer reagent. The sodium and potassium impurities in the rubidium and cesium salts were determined by use of a flame photometer.

4. The dielectric constants of ethyl acetate - water mixtures at 25, 30, 35, and 40 degrees centigrade were determined by use of a resonance type apparatus at 400,000 cycles. An oscilloscope was used to determine resonance by means of the detection of zero phase change at resonance.

5. The capacity data weretreated by the method of least squares and the capacities of saturated solutions of ethyl acetate-water were determined. The dielectric constants of the ethyl acetate mixtures were calculated using Wyman's data for water as a standard.

6. Several types of theoretical equations which allow for coulombic interactions in solution were discussed. The importance of the effective radii in solution was considered. The macroscopic and microscopic dielectric constants in solution were discussed. The qualitative effects of dispersion, orientation and induction effects were considered.

7. Calculations were made using the dielectric constant data obtained by six types of theoretical equations of the salting out percentage.

8. Comparison is made of the data obtained for the solubility of ethyl acetate in water with other determinations in the literature. Agreement is found to be satisfactory. The dielectric constant lowering found at 25 degrees centigrade agrees favorably with data found in the literature. The salting out order is found to be $F^- > Cl^- > Br^- > I^-$ for anions and the salting out of cations, with the exception of lithium ion, is found to decrease with increasing radius. The quaternary ammonium salts are found to increase the solubility of

ethyl acetate in water. The per cent salting out is found experimentally to increase with increasing temperature. A temperature coefficient of the same sign is found theoretically. In accord with theory, the salt effect is found to be almost a linear function of concentration. The theoretical salting out percentages from various of the equations employed are found to agree within 5-10 per cent with the experimental salting out percentages for chlorides and bromides. The small salting out effect of alkali iodides and the salting in of quaternary ammonium halides is considered to be largely due to Van der Waals forces. The possibility of chemical interactions is discussed.

B. Suggestions for Further Investigation

Before anything like a complete understanding of the effect of electrolytes upon the solubility of non-electrolytes can be achieved, a number of non-electrolytes must be investigated systematically over a range of temperatures and at fairly low electrolyte concentrations. Much more work is needed on the dielectric constants of water - non-electrolyte solutions. The experimental work should be extended to non-aqueous solvents. A comprehensive theoretical attack should be made on the effect of non-coulombic interactions on the salt effect.

The possibilities of chemical interaction should be investigated by means of ultra-violet, infra-red, and Raman spectroscopy.

APPENDIX

METHODS FOR DETERMINING LIQUID-LIQUID SOLUBILITIES

By an application of the phase rule Hill (1) has devised a scheme of classification of methods for the determination of the solubility of one liquid in another. The phase rule states that $F = C - P + 2$, thus, for a system of two components consisting of two liquid phases and one vapor phase $F = 1$, that is, the system is univariant. If we fix the temperature of the system, the composition of the liquid phases and the pressure are also determined. Methods based on constant temperature may be referred to as thermostatic methods. If we fix composition and then vary temperature until the liquid has that composition, we are dealing with a method which may be termed plethostatic. If we should operate at fixed pressure, the method then be spoken of as barostatic. It may be seen that the method of determining composition whether it be analytical or synthetic has no bearing on this fundamental classification of methods.

A. Thermostatic

(1) Analysis of the final composition of liquid phases

In this method two steps are essential: equilibrium must be secured between the two liquid phases with the precaution of approaching the final state from

both the high and low temperature side; and samples of each layer at the temperature of the experiment must be obtained for analysis. Any applicable chemical or physical method may be used for analysis. If calibrations have been obtained, the determination of density or refractive index is very convenient.

(2) Herz's method

One of the liquids may be added to the other slowly until saturation is reached. This method was used originally by Herz (2) and saturation was detected by the turbidity present. This procedure has been modified by the introduction of the use of dyes. Kloppie (3) added ponceau de xylidine, a dye insoluble in ether and soluble in water, to dry ether and then added water. As soon as the ether was saturated with water, the formation of water droplets changed the appearance of the hitherto dry dye particles. Sobotka and Kahn (4) used essentially the same method to determine the solubility of esters in water. These investigators added Sudan IV dye to the water. The ester is run into the water drop by drop. The dilute solution, shaken frequently assumes a pink color. When saturation is reached the floating jagged dye particles were converted into dark transparent droplets. Although the original method of Herz (2) was quite inaccurate, considerable accuracy is claimed for the modified methods.

It should be noted, however, that a procedure involving the drop by drop addition of the solute would be quite tedious and, furthermore, unless a closed system were employed considerable loss might result from volatility. On the other hand, if rather large additions of solute are made, there is no assurance of the attainment of equilibrium.

(3) Hill's Method

Hill (1) has devised a thermostatic method in which the volumes of the two layers of liquid are accurately determined in specially designed flasks. From two experiments with different initial weights of the two liquids, it is possible to calculate the composition and density of each phase. If m_{I_a}, m_{I_b}, m_{II_a}, m_{II_b} are the weights of components I and II in experiments a and b, x_1, x_2, y_1, y_2 represent the concentration in grams per ml in the upper and lower liquid phases of components I and II, and a_1, a_2, b_1, b_2, c_1, c_2, d_1, d_2, represent the volumes of the upper and lower phases in the two experiments for the two components then we have the two sets of equations-

$$a_1x_1 + a_2x_2 = m_{Ia} \qquad c_1y_1 + c_2y_2 = m_{IIa}$$

$$b_1x_1 + b_2x_2 = m_{Ib} \qquad d_1y_1 + d_2y_2 = m_{IIb}$$

Solving for x_1 and x_2 in the first set of equations and y_1 and y_2 in the second will give the concentration of each component in the two phases. By adding together the

weights of each component present in 1 ml of a given phase, the densities and the percent compositions by weight may be determined.

This method is highly accurate. The weight error in Hill's work was 0.01%, the volume error 0.02%. Under saturation was avoided by one-half hour of rotation and one-half hour of standing. The principle error was due to retention of a thin layer of a phases on the glass surface of the bulb containing the second phase. Hill asserts that this error was also small.

(4) Residue volume extrapolation method (5 , 6)

After a solvent has been saturated with a solute, further additions of the solute cause a proportional amount of undissolved residue, which can then be measured by volumetric means. A straight line plot of grams of solute vs volume of undissolved residue can then be extrapolated to zero volume of undissolved solute.

(5) Measured excess volume method (6 , 7)

A known excess volume of solute is added. After equilibrium is attained by shaking, the volume of undissolved solute is determined. Either Goetz or Babcock tubes are used depending on whether the specific gravity of the solute is greater or less than that of the solvent. This method is obviously only an approximate one for rapid determinations, since both water and salt may dissolve in the solute layer.

B. Plethostatic Method

(1) Analysis of contents of tubes after experiment

This procedure is evident. The synthetic procedure is usually employed when the plethostatic method is used.

(2) Alexejew's Method

This method first employed by Alexejew (8) has been termed the most generally reliable method yet devised (1). The procedure consists of either heating or cooling an initially isotropic one phase system until small liquid droplets of the second phase begin to appear throughout what was formerly a homogeneous system giving the solution a turbid appearance or of either heating or cooling a two phase system until it is transformed into a homogeneous one phase system. In many instances the point of turbidity may be determined to 0.1°C, making the method one of considerable accuracy. If, however, the tendency towards emulsification is not present the method fails. The applicability of the method to any system of interest must be determined experimentally. The temperatures at which incipient appearance and disappearance of the second phase occur often agree within an experimental error of 0.1°C, although this is not always the case. Davis (19) has found that in the system nitrobenzene-water, the phenomena of supersaturation occurs.

Differences of as much as 3° were observed at higher temperatures, smaller differences in the neighborhood of 1° were observed at room temperatures. This is an unusual case. Supersaturation in liquid-liquid systems is ordinarily rather difficult to obtain; furthermore, shaking or jarring will tend to destroy the metastable state.

C. Barostatic Method

This method does not seem to have been employed in liquid liquid solubility determinations.

In the present investigation, a third electrolytic component is present. If the effect of a given concentration of electrolyte upon solubility of one of the components in the other is desired, any method employing two liquid phases in equilibrium would not be desirable. If the electrolyte should show appreciable solubility in both liquid phases (both being of considerable volume), a separate partition experiment would be necessary to determine the distribution of electrolyte between the two phases. Where a third component is employed, Alexejew's method would seem to be the most accurate.

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