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THE EFFECT OF ONE SALT ON THE SOLUBILITY OF ANOTHER IN ETHYL ALCOHOL SOLUTION. PART I.

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Received 12th April, 1927.

The experiments described in the present communication are the first of a series made with the object of determining the effect of one salt on the solubility of another in ethyl alcohol solutions. The treatment will not be confined to very dilute solutions, nor to those which at the moment seem to be of theoretical interest. The study will include concentrated as well as dilute solutions. In the experiments now described the influence of lithium iodide, and of sodium thiocyanate, on the solubility of sodium iodide in ethyl alcohol at 25° has been investigated, and conductivities and viscosities of one set of solutions (sodium iodide and sodium thiocyanate) have been determined in addition to the solubility data.

No application of the conductivities has been made in the present paper since time did not permit the extension of the measurements to the solutions containing lithium iodide, nor the completion of the necessary calculations. So far as we are aware the present work is the first which has been made with the object of studying the solubility relations of electrolytes in nonaqueous solution, and we intend, as stated above, to extend this work in a number of directions.

Experimental.

Preparation of Materials.

(1) Sodium Iodide and Ethyl Alcohol.—The preparation and purification of these substances have been described in a short paper on the solubility of sodium iodide in ethyl alcohol.¹

(2) Sodium Thiocyanate.—Sodium thiocyanate was prepared by the decomposition of pure ammonium thiocyanate with caustic soda prepared from

¹ J. Chem. Soc., 128, 20, 1926.

sodium. A concentrated solution containing these substances was evaporated in a porcelain dish until all the ammonia had been driven off and crystallisation began. The sodium thiocyanate was then recrystallised from distilled water and 96 per cent. alcohol. A small amount of the salt was dried in an electric oven at 130° and was analysed by precipitation as silver thiocyanate, which was weighed. Two determinations gave the theoretical percentage of CNS, 71.64.

(3) Lithium Iodide.-The method of preparation of lithium iodide was identical with that of the sodium salt, with the exception that it was first necessary to free the lithium carbonate from traces of sodium salts by washing with boiling distilled water. By repeated crystallisation almost white crystals of LiI, 3H₂O were obtained which were partly dehydrated by phosphorous pentoxide in a vacuum desiccator. To dehydrate the iodide completely fairly strong heating is necessary,² and on account of the ease with which the compound oxidises, it is necessary to carry out this operation in an inert gas, or in a vacuum. The method finally adopted was that due to W. E. S. Turner and Bissett,³ in which the iodide is heated electrically in a vacuum desiccator over phosphorous pentoxide. Analysis by gravimetric silver estimations gave iodine 94.77 per cent. (Theory 94.83 per cent). The salt was free from iodate, which Simmons and Pickett,⁴ have shown to be the chief product of oxidation, and errors in weighing out the samples for analysis, due to the extreme deliquescence of the iodide, probably account for the slight difference between the observed and theoretical percentages of iodine.

Solubility Determinations.

The method of preparing the solutions of the sodium iodide-thiocyanate mixtures differed only slightly from that previously described for the pure iodide.¹ The materials were introduced into the larger tube (A, Fig. 1 in the paper quoted) of the solubility apparatus, and after immersion overnight in a thermostat at 25°, during the whole of which time the solution was stirred, the excess of solid was allowed to settle and the colourless saturated solution drawn off into the tube B as previously described.

On the addition of alcohol to mixtures of sodium and lithium iodides, however, the lithium salt was oxidised on account of the rise in temperature produced by its large heat of solution, and a dark brown solution containing free iodine resulted. A solution of the required amount of lithium iodide in alcohol was therefore prepared by placing the dehydrated salt in an empty desiccator, previously dried out by phosphorous pentoxide, together with a quantity of pure alcohol contained in a separate vessel. The desiccator was exhausted, and the alcohol vapour began to condense on the iodide, this process continuing until all the alcohol had been transferred. The solution thus produced was poured over an excess of sodium iodide in the solubility apparatus and the determination carried out as before.

In order to obtain the solubilities in terms of c.c. of solution from those in terms of grams of solvent, an accurate value for the density of the solution must be known. This could not be obtained by the use of the ordinary pipettes previously employed, and the filter tube was therefore ground to fit a pyknometer, shaped in the form of a V to facilitate filling. The rubber stopper was removed from the top of the filter tube, the pyknometer was attached and filled by suction. Caps were fitted on the pyknometer which was then placed in the thermostat. After adjustment

² Abegg, Handbuch der anorganischen Chemie, ii, 1, 130. ³ J. Chem. Soc., 29, 233, 1913. ⁴ J. Amer. Chem. Soc., 49, 701, 1927. to the correct volume the pyknometer was dried, suspended on the balance, and allowed to attain the temperature of the balance case. No precipitation of the salts resulted from this treatment and it was unnecessary to replace the pyknometer in the thermostat (although this precaution was generally taken) before going on with the solubility determinations.

The bulk of the solution in the pyknometer was run into an evaporating flask previously described, and its weight determined. The flask was then electrically heated with a current of pure dry hydrogen passing through it. This process was repeated with a second sample of the solution.

The weighed residues of approximately 2.5 to 3 gms. were then dissolved in water and made up to 200 c.c. for analysis. Although direct analysis of chloride or bromide in the presence of thiocyanate is possible. this method cannot be used with mixtures of iodide and thiocyanate, since the iodide is also decomposed by the methods used to remove the thio-The solutions were therefore analysed indirectly. Measured cyanate. volumes of the aqueous solution were precipitated with acidified silver nitrate solutions, the precipitated silver salts dried at 130°-135°, and weighed. This was afterwards replaced by the more convenient volumetric method. The results obtained by both methods when applied to the same solutions were in good agreement. At first an attempt was made to obtain both iodide and thiocyanate directly. The precipitation of the iodide occurs quantitatively first, and the end-points of the thiocyanate titrations are shown by the disappearance of the red colour due to ferric thiocyanate, produced by the addition of iron alum solution towards the end of the titrations. An external indicator of chlorine water and starch gave the end-points of the iodide titrations, but with solutions of known strength the amounts of iodide indicated by the observed end-points were appreciably lower than the correct values. It was found that the blue colour of starch iodide is destroyed by sodium thiocyanate and although at first there is sufficient soluble iodide to give a colour, the thiocyanate interferes with the titration as the iodide concentration becomes small, producing a false end-point Complete titration with silver nitrate solution, however, forms a good method for indirect estimation of a mixture of sodium iodide and sodium thiocyanate, when taken in conjunction with the weight of the mixed salts.

If x and y are the amounts of sodium iodide and sodium thiocyanate in the experimentally determined weight, w, of the residue obtained on the evaporation of a weighed amount of alcoholic solution saturated with the former salts, and if z is the total amount of silver required to titrate the x + y grams of residue, then

and
$$\begin{aligned} x + y &= w\\ \frac{Ag}{NaI} \cdot x + \frac{Ag}{NaCNS} \cdot y &= z, \quad i.e., \ 0.7195 \ x + 1.331 \ y &= z. \end{aligned}$$

From these equations the values of x and y are found from the experimentally determined values w and z.

The indirect method appears to be the most satisfactory for the mixed iodides of sodium and lithium and the determinations were carried out gravimetrically by precipitation of the aqueous solution with silver nitrate. The amounts, x', y', of each salt present in the mixture were determined by means of the equations,

$$x' + y' = w'$$

$$\frac{\text{AgI}}{\text{NaI}}x' + \frac{\text{AgI}}{\text{LiI}}y' = z', \quad i.e., \text{ 1.566 } x' + \text{ 1.754 } y' = z',$$

where z' is the total weight of silver iodide produced from w' grams of the mixed iodides.

Solubility Data.

TABLE I. -- Solubilities of Sodium Iodide in Presence of Sodium Thiocyanate.

Solution.	Total Solubility.	NaI.	NaCNS.	Density $D_4^{25^\circ}$.
NaI 1 2 3 4 5 NaCNS	42'85 (Mean) 42'98 43'11 43'18 43'16 43'26 20'99	41-81 39-18 36-70 36-25 35-65 —	 3'93 6'48 6'91 7'61 	1'04599 1'04223 1'03603 1'03089 1'03050 1'02994 0'882502

TABLE II.-Solubilities of Sodium Iodide in Presence of Lithium Iodide.

Solution.	Total Solubility.	NaI.	LiI.	Density $D_{40}^{25^{\circ}}$.
I 2 3 4 5 LiI	42'79 42'87 43'32 49'98 52'00 250'8 (T and B)	34'71 29'56 15'57 3'18 2'56 	8.08 13.31 27.75 46.80 49.44 —	1'04706 1'04763 1 05606 1'09753 1'10990

The solubilities of sodium iodide in the presence of five different concentrations of sodium thiocyanate, the solubilities of the separate salts, and the densities of these solutions, are given in Table I. All solubility results are expressed in grams of salt per 100 grams of solvent.

Table II. consists of the solubilities of sodium iodide in five different solutions of lithium iodide, together with the densities of the solutions of the mixtures. The value for the solubility of lithium iodide obtained by W. E. S. Turner and Bissett,⁵ is included.

In Fig. 1 the amounts of sodium iodide, in terms of grams/100 grams EtOH, in the mixtures have been plotted against the concentrations of the added salts in equivalents/100 grams EtOH. Although a mean value for the solubility of sodium iodide of 42.57 grams/100 grams EtOH has been found it will be seen that experiments 1, 5, 6, 7 and 10 (Solubility of NaI etc., *loc. cit.*), differ but slightly from a mean value of 42.85. If this value for the solubility is assumed, the points representing the solubilities in presence of sodium thiocyanate are in a perfectly straight line. For similar concentrations the curve illustrating the effect of lithium iodide is of the same type, but with higher concentrations the precipitating effect of the iodide is less pronounced.

In Fig. 2 the values of $\log s/s_0$ are plotted against c, where s_0 and s are the solubilities in grams/litre of saturated solution, of sodium iodide alone, and in the presence of an added salt of concentration c equivalents/litre.

⁵ J. Chem. Soc., 103, 1904, 1913.



Fig. 2 shows that the effect of sodium thiocyanate on the solubility of sodium iodide in these solutions is of the kind usually associated with the salting out effect.⁶

In the case of lithium iodide the effect due to small amounts is of the

⁶ K. Linderstrom-Lang, Compt.-rend. trav. lab. Carlsberg, 15, No. 4, 1, 1924.

same character, the curve being nearly a straight line, but at higher concentrations a pronounced curvature makes its appearance. It is clear that no simple equation such as $\log s/s_0 = kc$ can account for the salting out effect of lithium iodide over a wide range of concentration. This is to be expected because the equation applies strictly only to solutions of a non-electrolyte. It is, however, interesting that the results for sodium thiocyanate and part of those for lithium iodide can be represented by this equation. The precipitating power of the lithium salt is greater than that of the thiocyanate, and in this connection it is noteworthy that for *aqueous* solutions the lithium salts in general show the greatest precipitating power, while thiocyanates show the least.

Conductivity and Viscosity Determinations.

A cell, Fig. 3, was used in which the conductivity and viscosity of the same sample of solution could be determined. It consists of a glass tube, A, 18 cms. in length and $2\frac{1}{2}$ cms. in diameter,

sealed at the bottom to a capillary arm, B, near the top of which is a small bulb, C, of approximately 5 c.c. capacity. This is continued in a tube, D, of about $\frac{1}{2}$ cm. bore having a constriction at E about 2 cms. above the bulb. Two marks, one just below the bulb and the second at the narrowest part of the constriction, form the graduation marks of the viscometer. The top of the cell is closed by means of a glass stopper F, through which pass two tubes sealed to stout circular platinum electrodes at the bottom of the cell. The stopper is continued in a tube, G, of narrow bore which is bent at right angles about 5 cms. above the top of the cell. Just below the stopper is a vertical side arm, H, ground to fit the pyknometer, by means of which the solutions are run into the cell.

The viscosities were determined by means of the method due to Scarpa.⁷ By means of a siphon device the pressure on the liquid in the viscometer is reduced by a constant amount, and this constant negative pressure causes the liquid to rise. The time t_1 taken by the top of the liquid column to pass from the lower mark and reach the upper mark is noted, and then the time t_2 taken in falling under its own weight between the same marks. According to Scarpa the viscosity is proportional to $t_1 t_2/(t_1 + t_2)$, and is independent of the surface tension, density, and amount of liquid, provided that the negative pressure is constant. The apparatus was standardised by means of water, the viscosity of



which ⁸ at 25° was taken as 0.00012 dynes. cm. ⁻². Thorpe and Rodger's value ⁹ is 0.00801 dynes. cm. ⁻². The former value has been preferred. From this value the proportionality constant for a given negative pressure is obtained. Pure water was introduced from the pyknometer, and the viscometer arm was connected to a 2-way tap by means of which connection with the atmosphere, or the negative pressure apparatus and a water manometer, could be made. The times of ascent under negative pressures of

⁷ Gazz., 40, ii., 261, 1910. ⁹ Phil. Trans., 185, 397, 1894. approximately 15, 25, and 35 cms. of water less than atmospheric read off on the water manometer, and the times of fall, were determined. From the viscosity of water the constants for the three pressures were obtained.

The cell was thoroughly washed out with 96 per cent. EtOH until the conductivity of the alcohol appeared constant. It was then emptied, and dry dust-free air passed through until the cell was completely dried. The side arm was closed by a rubber stopper, the cell placed in the thermostat and the viscometer arm connected to the 2-way tap. To prevent the access of moisture to the alcoholic solutions tubes of phosphorous pentoxide and caustic potash were inserted between the tap and the negative pressure device, and similar tubes were connected to the second arm of the 2-way tap and to the tube from the stopper of the cell. The presence of these tubes made no difference whatever in the times of flow of the liquid in the viscometer.

The alcoholic solutions were withdrawn from the solubility apparatus by means of the pyknometer and run into the cell through the side arm, which was then closed. The solution was drawn up into the bulb to moisten the apparatus and to assure that the solution attained the temperature of the thermostat. A standardised circular bridge containing about 20 ft. of wire, calibrated resistance boxes, and the current from a small induction coil were used for the conductivity measurements. To obtain sharp minima the electrodes were lightly platinised. This did not cause any noticeable change in the readings, due to oxidation of the alcohol, the first reading being reproducible after a number of others had been taken.

The negative pressure was then adjusted to one of its constant values and the times of rise and fall of the liquid in the viscometer were taken.

In order to test the apparatus the viscosity of pure ethyl alcohol was determined. The conductivity was found to be too slight for accurate measurement with the existing apparatus, but it was of the order of 1×10^{-7} to 1×10^{-8} [ohms cm.]⁻¹. The viscosity was then determined. With the highest negative pressure (about 35 cms. water less than atmospheric) there was a pronounced turbulence in the alcohol, and even with the medium pressure (25 cms. less than the atmospheric) this was still visible. The same statement applies to the calibration liquid, water. It is not surprising therefore, that only the lowest negative pressure (15 cms. water less than atmospheric) gave results in fair agreement with the determinations of other workers. A value of 0.01065 dynes. cm. -2 for the viscosity of ethyl alcohol was found, which is somewhat lower than Thorpe and Rodger's value of 0.010933 dynes cm. -2 interpolated for the same temperature. With the higher negative pressures exceedingly low values were obtained, and these were rejected for reasons previously stated. It will be seen that taking only the times of fall, the instrument may be regarded as an Ostwald viscometer, since the volumes of liquid used were the same in all cases. The density of the alcohol had been determined, $(D_{4^{\circ}}^{25^{\circ}} = \circ 785\circ7)$, and using the formula $\eta_l = \eta_w \delta_l t_l / \delta_w t_w$, the viscosity is found to be 0.01071 dynes. cm. - 2 which is in fairly good agreement with the value obtained by the Scarpa method. However, the results obtained by this latter method should be accepted with caution; if we consider the values of η for the saturated solutions it is seen that they are consistently higher than those obtained by the Ostwald method. For the purpose of correcting conductivity measurements, extremely accurate values are unnecessary.

In determining the ionisation values of the mixtures, the conductivities of the separate salts are required. Dutoit and Rappeport ¹⁰ give the mole-

¹⁰ J. Chim. Phys., 6, 545, 1908.

cular conductivity at infinite dilution Λ_{∞} of sodium thiocyanate in alcohol at 18° as 41.6 (Siemens' units), while Dhar and Bhattacharyya¹¹ have determined the conductivities at several dilutions at temperatures of 0.2°, 5°, and 29.9°. No measurements at 25° appear to have been recorded and the conductivities at dilutions of approximately 10. V, 100. V, and 1000. V were therefore determined in a conductivity cell of ordinary design. The exact concentrations (moles/c.c.) and the conductivities ([ohms cm]⁻¹) of the three dilute solutions and those of the saturated solution are given in Table III. A. The cube-roots of the concentrations are plotted against Λ in Fig. 4, and it is obvious that the usual extrapolation formula, considered



adequate by Philip and Courtman¹² for solutions of potassium and tetraethylammonium iodides in various organic solvents, does not apply. Furthermore, the results of Völlmer¹³ show that the cube-root formula does not apply generally to electrolytes in ethyl alcohol. If Völlmer's formula, $\Lambda_{\infty} = \Lambda(I + Ac^{\dagger} + Bc^{\dagger})$ is employed a value for Λ_{∞} of sodium thiocyanate = 54.83 [ohms cm.]⁻¹, is obtained. Dhar's results for Λ at 29.9°, plotted in the same way, are included in

Dhar's results for Λ at 29.9°, plotted in the same way, are included in Fig. 4 for comparison. Extrapolation by means of the Völlmer formula, using the points marked r, 2 and 3, gave Λ_{∞} at 29.9°=68.37 [ohms cm.]⁻¹. When corrected by the temperature coefficient given by Dhar, Λ_{∞} at 25° = 63.54 [ohms cm.]⁻¹ is found. Dutoit and Rappeport's value, similarly corrected to 25°, is 49.60 [ohms cm.]⁻¹.

¹¹ Z. anorg. Chem., **82**, 257, 1913. ¹² J. Chem. Soc., **97**, 1261, 1910. ¹³ Ann. Phys. Chem., iii., **52**, 328, 1894.

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The viscosities and specific conductivities of the saturated solutions of sodium iodide and sodium thiocyanate, and of the solutions containing thiocyanate saturated with iodide, are given in Table III. B.

TAE	BLE	III.	а.—М	IOLECULAR	CONDUCTIVITIES	OF	NaCNS	IN	ALCOHOL.
IUT	i i i i	111.	A.—1	TOLECULAR	CONDUCTIVITIES	OF	nacino	IN	ALCOHOL,

Solution.			Concentration (Moles/c.c.).	Λ([ohms cm.]−1).	
Saturated 10.V 100.V 1000.V.	•	•	•	1.888×10^{-3} 1.0305×10^{-4} 1.0305×10^{-5} 1.0305×10^{-6}	9'50 21'59 32'33 41'59

TABLE III. B. — THE VISCOSITIES AND SPECIFIC CONDUCTIVITIES OF IODIDE-THIOCYANATE MIXTURES.

Solution	Specific Conductivity	Viscosities (Water = 0'00912 dynes cm. -2).				
Solution,	[ohms cm.]-1.	(a) Scarra Method.	(b) Ostwald Method.			
NaI	2.020×10^{-2}	0'02991	0.02878			
I	2.055×10^{-2}	0.03042	0.02834			
2	2.059×10^{-2}	0*03147	0.03030			
3	2.001×10^{-2}	0.03108	0.03048			
4	2.063×10^{-2}	0.03208	0.03092			
5	2.070×10^{-2}	0'03182	0.03035			
NaCNS	1.794×10^{-2}	0.02475	0.02378			

In the case of sodium iodide an excellent series of values for the conductivities has been determined by Robertson and Acree,14 and it was not considered necessary to do more than determine the value for the saturated solution ($c = 2.094 \times 10^{-3}$) in order to complete the series. The results are plotted against the cube roots of the concentrations in Fig. 5 and the value of 9.79 [ohms cm.]⁻¹ for the saturated solution is included. Robertson and Acree consider that complete dissociation is reached at a dilution of about 4000 V, corresponding to a value for Λ_{∞} of 41.51 $[ohms cm.]^{-1}.$

All the conductivity values in the present paper are uncorrected for viscosity. In connection with this point Robertson and Acree make the following remarks (p. 389, loc. cit.) :-

"No method is known at present, however, for doing this, namely correcting the conductivities for viscosity, with certainty. Noyes' method is to multiply the apparent per cent. of ionisation of the salt in a given solution by some power of the ratio of the viscosity of this solution to that of the pure solvent. The power chosen . . . as a first approximation was unity. We believe, however, that this correction is far too large . . . the relation of the viscosities and the conductivities of N/1, N/2 and of N/4 solutions of sodium iodide, . . . at 25° and 35°, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the per cent. of ionisation is practically the same for the N/I, N/2 and N/4solutions of each salt. Such a conclusion is, however, not in harmony with all of the known facts of physical chemistry and certainly is not borne out by our other experimental results. . . . We have therefore contented

14 7. physical Chem., 19, 413, 1915.

ourselves with the assumption that the ratio μ_v/μ_∞ gives a much closer approximation for a in our concentrated alcoholic solutions than does the expression $\mu_v Z_v/\mu_\infty Z_\infty$ used by Noyes, and we have made all our calculations accordingly."

If the viscosity correction η/η_0 is applied to the saturated solutions the values for Λ are more than doubled.

Thus Λ NaCNS uncorrected = 9.50 [ohms cm.]⁻¹ "corrected" = 21.1 [ohms cm.]⁻¹ Λ NaI uncorrected = 9.79 [ohms cm.]⁻¹ "corrected" = 26.3 [ohms cm.]⁻¹.

Conclusions.

The results obtained indicate that the mutual solubilities of salts in such concentrated solutions depend on more than one effect. Of these the Solubility Product effect is the most interesting, and this can be most easily examined in the case of sparingly soluble salts. We are proceeding with experiments of this nature. Experiments on the E.M.F.'s of concentration cells containing salts in ethyl alcohol solution are also in progress.

The cost of the materials used in this investigation has been defrayed by grants from the Chemical Society, and from the Dixon Fund of the University of London, for which the authors wish to express their thanks.

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PART II. QUANTITATIVE DISCUSSION OF THE SOLUBILITY OF SODIUM IODIDE IN THE PRE-SENCE OF SODIUM THIOCYANATE.

(Communicated after the Meeting on 23rd May, 1927.)

According to the theory of electrolytic dissociation the solubility of a salt is reduced by adding another salt with a common ion. Experiment has generally supported this solubility principle for aqueous solutions, while the work recorded in the first paper of this series has shown it to be true for sodium iodide in alcoholic solutions of lithium iodide and sodium thiocyanate. In discussing the mutual solubilities of salts from a quantitative point of view, it is necessary to assume a law governing the equilibrium of the electrolytes present in the solution, and on this law the values obtained for the concentrations of the un-ionised and ionised parts of the saturating salt will depend. Since the conductivity of a solution is determined by the concentrations of the various ions, a comparison between the observed and calculated conductivities will show to what extent the assumption with regard to the ionisation of the mixed electrolytes is justified.

The conductivities of the sodium iodide-sodium thiocyanate solutions have been calculated from the data for the separate salts by three different methods. Each of these methods is based on one of the three following assumptions:—

(I) The dissociation of each salt is unaffected by the presence of the second salt.

(2) The dissociation of each salt is equal to that which it has when present alone at a concentration equal to the total concentration of the mixture.1

(3) The dissociation of each salt is equal to that which it has when present alone in a solution in which its ions have a concentration equal to the concentration of the common ion in the mixture.²

It should be emphasised that some doubt exists as to the reliability of the values of the equivalent conductivities of the salts at infinite dilution used in calculating their degrees of ionisation. The curves obtained by plotting the values of Λ against the corresponding values of $\sqrt[3]{c}$ over the measured range of dilutions are nearly the same for the two salts (Figs. 4 and 5, Part I.), and hence a fairly close agreement between the respective conductivities at infinite dilution is to be expected. At dilutions greater than 1000V., however, the results of Robertson and Acree for sodium iodide, which in this range are not in good agreement with one another, indicate that Λ quickly approaches a limiting value in a finite concentration interval, which is quite different from that which has been calculated for the thiocyanate. If the equivalent conductivities 29.29, 32.25 and 35.07, and the corresponding concentrations are used to solve the Völlmer equation, the conductivity of sodium iodide at infinite dilution is found to be 52.98. The adoption of this value brings the curves for the two salts into nearly identical form throughout the whole range of dilutions, and the values 52.98 and 54.83 for the conductivities of sodium iodide and sodium thiocyanate at infinite dilution have therefore been employed. Nevertheless it must be pointed out that the curvature introduced by the adoption of these numbers is greater than that indicated by graphical methods. It is therefore very probable that the values of Λ_{∞} are somewhat too high, but in the absence of consistent data for the two salts more trustworthy figures cannot be obtained.

In calculating the specific conductivities of the solutions of the mixed salts by the first method the values of Λ for the separate salts were obtained from the curves shown in Figs. 4 and 5 (Part I.) drawn on a large As in the previous paper no corrections for the viscosities were scale. From the conductivities and the concentrations of the salts in applied. the mixtures the specific conductivities of the solutions were calculated. The results are presented in Table IV.

Solub	ilities.	Equiv. Co	Equiv. Conductivity.		Spec. Conductivity.	
NaI.	NaCNS.	NaI.	NaCNS.	K ₁ NaI.	K ₂ NaCNS.	Mixture.
20*33 18*91 17*62 17*41 17*01	1.052 3.509 5.754 6.136 6.748	9.89 10.18 10.47 10.52 10.59	21.50 15.95 13.75 13.48 13.15	2*010 1*924 1*845 1*831 1*801	0°226 0°560 0°791 0°822 0°887	2·236 2·484 2·636 2·653 2·688

TABLE IV.

The column headed Solubilities gives the solubilities of sodium iodide in equivalents \times 10⁴ per c.c. of solution in the presence of different concentrations of sodium thiocyanate expressed in the same units. K₁ and

¹ Barmwater, Z. physik. Chem., **28**, 424, 1899; **45**, 557, 1903; **56**, 225, 1906. ² Arrhenius, Z physik. Chem., **2**, 284, 1888; **31**, 218, 1899.

 K_2 are the separate conductivities $\times 10^2$ and $K_1 + K_2$ is the calculated specific conductivity ($\times 10^2$) of the mixture.

In applying the second and third assumptions to the calculation of $K_1 + K_2$, it is necessary to know the ionisations of the two electrolytes at concentrations greater than the saturation values in the pure solvent. Table V. shows that these can be extrapolated with fair accuracy from the existing data by means of the Storch dilution formula $(ca)^n/c(1 - a) = K$. The first two columns contain the concentrations $\times 10^4$ and the corresponding values of Λ for the respective salts, from which the values of 100a, and of the ion concentrations $\times 10^4$ given in columns 3 and 4 are derived.

	с.	Λ.	100a.	ΣCi.	к.	k.
Sodium Iodide n = 1.63 $\Lambda_{\infty} = 52.98$	10°00 17°01 17°41 17°62 18°91 20°33 20°34	12.50 10.59 10.52 10.47 10.18 9.89	23.59 19.98 19.85 19.75 19.20 18.66 18.48	2'359 3'398 3'455 3'481 3'632 3'794 2'868	16.0 16.3 16.4 16.3 16.4 16.1 16.1	0.728 0.849 0.856 0.857 0.864 0.871 0.877
	(22*49) (24*43) (26*60)	979	(18·00) (17·50) (17·00)	(4°048) (4°276) (4°523)	10.0 10.0 10.0	0.899 0.907 0.926
Sodium Thiocyanate n = 1.54 $\Lambda_{\infty} = 54.83$	1'052 3'509 5'754 6'136 6'748 18'88 (20'55) (22'28) (24'28) (24'28) (27'22) (30'20) (33'58) (37'50) (42'08)	21.50 15.95 13.75 13.48 13.15 9.50	39'21 29'10 25'08 24'59 23'98 17'33 (16'90) (16'50) (16'50) (15'50) (15'50) (15'50) (14'50) (14'50) (13'50)	0.413 1.021 1.443 1.506 1.619 3.272 (3.475) (3.945) (4.220) (4.530) (4.530) (4.869) (5.261) (5.680)	27.6 28.8 28.3 28.2 28.4 27.6 27.6 27.6 27.6 27.6 27.6 27.6 27.6	0.266 0.419 0.483 0.492 0.511 0.686 0.707 0.726 0.751 0.774 0.800 0.826 0.858 0.858 0.856

TABLE V.

By applying the Storch formula to the known values of c and 100a, and solving the equations in pairs the exponent n was found to be 1.63 for sodium iodide and 1.54 for sodium thiocyanate. At lower concentrations, however, the values of n increased considerably, and the expression cannot be said to represent the behaviour of these electrolytes over a wide range of concentrations with dependable accuracy. For this reason the extrapolation of Λ to infinite dilution by this method was not attempted. At very high concentrations, however, the constancy of K × 10⁴ in the last column but one justifies the adoption of the formula.

From the values of n and K the concentrations corresponding to various assumed values of 100*a* were calculated. For the sake of comparison the values of $k = (ca)^2/c(1 - a)$, *i.e.* the ordinary mass action equation $(\times 10^4)$, are included in the last columns of the two tables.

The values of $K_1 + K_2$ in Table VI. have been calculated by Barmwater's method. The concentrations of the two salts given in this table are equivalent to the total salt concentrations of the mixtures, and the values of 100*a* corresponding to these concentrations were obtained from the

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graph of c against a using the necessary extrapolated data from the Table V.

The results of the third method of calculation which are based on the isohydric principle are contained in Table VII.

Experiment	Equiv.	Concns.	100a	100a	K1	K ₂	K. I. K.
Experimenti	NaI.	NaCNS.	Nal.	NaCNS.	NaI.	NaCNS.	$\mathbf{x}_1 + \mathbf{x}_2.$
I 2 3 4 5	2*090 2*081 2*073 2*072 2*074	3.865 3.850 3.834 3.833 3.833 3.835	18*49 18*52 18*54 18*55 18*54	13*87 13*89 13*90 13*90 13*90	1'991 1'856 1'731 1'711 1'671	0'080 0'267 0'438 0'468 0'514	2.071 2.123 2.170 2.179 2.185

TABLE '	V	I.
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Experiment.	ΣCi.	100a NaI.	100a NaCNS.	K ₁ NaI.	K2 NaCNS.	$K_1 + K_2.$
1	3'901	18·36	16.05	1.977	0.093	2.070
2	3'988	18·13	15.93	1.817	0.306	2.123
3	4'065	17·98	15.57	1.689	0.491	2.170
4	4'078	17·95	15.55	1.656	0.523	2.179
5	4'093	17·91	15.51	1.614	0.573	2.188

In order to obtain the values for the degrees of dissociation of the salts in the mixtures, the ionisation values, a, were plotted against the ion concentrations, ca, of the separate salts. A value for ca was then chosen, and the corresponding ionisations of the two salts were obtained from the graph. This process was repeated until the sum of the values of ca for the two salts was identical with the assumed value of the ion concentration. The actual values of the total ion concentration, ΣCi , and of the corresponding ionisations, are presented in the columns 2, 3, and 4 of the table.

If the calculated specific conductivities are compared with the observed values (Table III.B, Part I.), it is obvious that the experimental results are quite opposed to the first assumption. The calculations of $K_1 + K_2$ are independent of the values of Λ_{∞} , and the alterations which a viscosity correction would introduce are comparatively small. It is evident, therefore, that the first supposition leads to results which are considerably higher than those determined experimentally.

The two remaining methods of calculation yield results which are practically identical, and the maximum deviation from the observed values is less than 6 per cent. The effect of a viscosity correction on the calculated figures would only serve to increase them slightly, and so it is concluded that neither Barmwater's method, nor that based on the isohydric principle, accurately represents the conditions existing in these concentrated solutions. The latter method is slightly more accurate, as the following considerations will show. The viscosity correction is greater for the lower values of a (*i.e.* higher concentrations) for a particular salt, and therefore the values of the specific conductivity due to thiocyanate, K_2 , will be increased to a greater extent in the case of Table VI. than in Table VII. This relative increase of K_2 will be greater than that of K_1 in Table VII. over K_1 in Table VI.

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and so the total increase of $K_1 + K_2$ will be greater in the results calculated by Barmwater's method.

From the values of a in the previous table and the solubility data the concentrations $(\times 10^4)$ of the ionised and un-ionised fractions in the mixture were calculated (Table VIII.). In the sixth and seventh columns are the concentrations of undissociated sodium iodide ($\times 10^4$) and the values of the solubility product ($\times 10^7$). Both of these quantities decrease markedly on the addition of increasing amounts of sodium thiocyanate although the concentration of the added salt is not large compared with the normal solubility of the iodide. The figures for $k = [Na^+][I']/[NaI]$ given in the last column show that the molecular solubility and the solubility product decrease at approximately the same rate.

Experiment.	[Na ⁺].	[CNS'].	[1′].	[NaCNS].	[NaI].	[Na ⁺][I'].	$k = [Na^+][I']$ [NaI].
NaI 1 2 3 4 5	3*869 3*901 3*988 4*055 4*078 4*093	0*169 0*559 0*896 0*954 1*047	3.869 3.732 3.429 3.169 3.124 3.046	0 ⁻⁸⁸³ 2·950 4·858 5·182 5·701	17.07 16.60 15.48 14.45 14.29 13.96	1°497 1°456 1°367 1°288 1°274 1°247	0*877 0*877 0*883 0*891 0*892 0*893

TABLE VIII.

It is interesting to compare these results with those obtained from similar studies of aqueous solutions. According to the principle of constant molecular solubility the total solubility of a salt in the presence of a second salt can never be less than the concentration of the undissociated part. Arrhenius³ was the first to show that this statement was untrue, and an examination of the data presented above will show that in the fifth experiment the solubility of sodium iodide has been depressed below the value of [NaI] for the saturated solution of the pure salt.

In addition to discrepancies of this kind Noyes and his co-workers,⁴ and Hill⁵, ⁶ have found variations in the values of the solubility product. The former have found that the solubility product increases on the addition of salts with or without common ions, while according to Hill's experiments on the mutual solubilities of electrolytes without common ions there is a Hill has shown, however, that the direction of decrease in this quantity. these changes in the solubility product depends on the dilution law employed in the calculations. The present work is based on assumptions similar to those used by Noyes, but a *decreasing* solubility product has been It must be borne in mind, however, that the values in the last table found. cannot be quantitatively exact, since the poor agreement between the calculated and observed conductivities proves that the underlying assumptions only approximately represent the dissociation equilibria of the salts present in the solutions.

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Ibid., 32, 1186, 1910; 6 Ibid., 39, 218, 1917.