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VIII. *On the Relation of the Physical Properties of Aqueous Solutions to their state of Ionization.* By Prof. J. G. MAC-GREGOR, *Dalhousie College, Halifax, N.S.**

IT has often been pointed out that, according to the dissociation or ionization conception of the constitution of a solution of an electrolyte, the difference between the physical properties of one in which ionization is complete and those of the solvent must be compounded additively of the differences produced by the two ions. It would seem to be equally obvious that, in the case of solutions in which the ionization is not complete, the differences referred to must be similarly compounded of those produced by the undissociated molecules and by the free ions; and if so, it should be possible to express the numerical values of the various properties in terms of the state of ionization. Such an expression would take its simplest form in the case of solutions so dilute that the molecules, dissociated or undissociated, might be regarded as sufficiently far apart to render mutual action between them impossible, and in these circumstances the change produced in the properties of the solvent by the undissociated and the dissociated molecules respectively might be expected to be simply proportional to their respective numbers per unit of volume. It is the object of this paper to test the applicability to sufficiently dilute solutions of such an expression, viz.,

$$P = P_w + k(1 - \alpha)n + l\alpha n, \quad . \quad . \quad . \quad (1)$$

where P is the numerical value of any property (density &c.), P_w that of the same property for water under the same physical conditions, n the molecular concentration of the solution, *i. e.*, the number of gramme-equivalents of the dissolved substance per unit volume of the solution, α the ionization-coefficient, αn and $(1 - \alpha)n$ consequently the numbers of dissociated and undissociated gramme-equivalents per unit of volume respectively, and k and l constants, which may be spoken of as ionization-constants, which will vary with the solvent, the substance dissolved, the property to which they apply, the temperature, and the pressure, but not with the concentration of the solution.

The formula can obviously apply only to properties for which P_w has a finite value. Thus it is inapplicable to electrical resistance, for which P_w would have a practically infinite value.

* Abstract of a paper read before the Nova Scotian Institute of Science. Communicated by the Author.

Simple Solutions.

In order to test the applicability of the above expression I have determined the ionization-constants for the density, thermal expansion, viscosity, surface-tension, and refractive index of solutions of Sodium and Potassium Chlorides, by the aid of observations made by Bender*, Brückner†, and Rother‡. I selected these observations as a first instalment not because of their precision (for in one or two cases more exact observations are available), but because these observers, in all cases but one, determined the values of the above properties for mixtures of solutions as well as for simple solutions. I selected the above chlorides partly because I thought it well to begin with salts of simple molecular structure, but largely also because, for the purpose of calculating the conductivity of mixtures of them (as described in my paper on this subject§), I had already obtained interpolation formulæ and curves which, judged by the results of that paper, gave with considerable accuracy the ionization-coefficients of the simple solutions of these salts in terms of their molecular concentration. To save space I may tabulate here the values of the ionization-coefficients used in the calculations for simple solutions. They are as follows:—

Sodium Chloride.		Potassium Chloride.	
Grm.-mols. per litre.	Ionization- coefficient at 18° C.	Grm.-mols. per litre.	Ionization- coefficient at 18° C.
·25	·792	·1875	·8267
·5	·736	·3402	·811
·8928	·6866	·375	·796
1·0	·676	·5	·788
1·5	·633	·6856	·769
1·8353	·601	·75	·768
2·0	·5866	1·0	·756
2·5	·5504	1·0467	·755
2·8373	·5255	1·4292	·731
3·0	·514	1·5	·731
3·9375	·4516	2·0	·712
		2·185	·7048
		2·5	·695
		2·986	·681
		3·0	·680

* Wied. Ann. vol. xxii. (1884) p. 184, and vol. xxxix. (1890) p. 89.

† Ibid. vol. xlii. (1891) p. 293.

‡ Ibid. vol. xxi. (1884) p. 576.

§ Phil. Mag. [5] xli. p. 276 (1896); and Trans. N.S. Inst. Sci. ix. (1896) p. 101.

These coefficients were obtained from Kohlrausch and Grottrian's and Kohlrausch's observations of conductivity at $18^{\circ}\text{C}.$ * In obtaining them I took the specific molecular conductivity (referred to mercury) at infinite dilution to be 1216×10^{-8} for KCl, and 1028×10^{-8} for NaCl, not being aware at the time that Kohlrausch had given 1220 and 1030 respectively as more exact values. Nevertheless, to save labour I have used the above values of α in the calculations of this paper, having satisfied myself by a re-calculation in one case that no appreciable difference in the results would be produced by the employment of more exact values. It will be noticed that in one or two cases the above values of α are obviously a little out; but they would seem to be sufficiently accurate for my purpose. I did not foresee the extent of the calculations, or I should have determined all the values of α required at the outset, and checked them by comparison with one another.

I have determined the ionization-constants (k and l) in all cases in which more than two observations of a property on solutions of sufficient dilution were available by the method of least squares. The constants thus determined and used in the calculations are tabulated below. In all cases the available observations had been made on solutions of such great concentration that the values of the constants obtained cannot be regarded as exact; but the calculations may serve as a test of the general applicability of the expression referred to above. The only available observations, so far as I know, on solutions of sufficient dilution for the determination of the ionization-constants and the limits of concentration within which the above expression is applicable, are those by Kohlrausch and Hallwachs† on the specific gravity of dilute solutions, from which two of my students have undertaken to determine the density-constants for the salts and acids examined.

With regard to the observations which I used in determining the various ionization-constants, the following statements should be made:—

Bender's determinations of density (*i. e.* specific gravity referred to water at $4^{\circ}\text{C}.$) were made at $15^{\circ}\text{C}.$, but were readily reduced to 18° by the aid of his observations on the thermal expansion between 15° and 20° of the same solutions. According to his statement, the fourth place of decimals in his values may be in error by ± 2 or ± 3 . The density of water was taken to be 0.99863.

* Wied. *Ann.* vi. (1879) p. 37, and xxvi. (1885) p. 195.

† Wied. *Ann.* liii. (1894) p. 14.

Bender's determinations of thermal expansion are for the interval between 15° and 20° C.; and will therefore be sufficiently nearly proportional to the coefficients of expansion at 18° for my purpose. He considers that they may be in error by ± 2 in the sixth place of decimals. On plotting his observations, however, it becomes obvious that they do not all attain this degree of accuracy. The expansion of water was taken, according to his observations, to be 0.03878 for the same interval.

Brückner's observations of viscosity were made at 15° C.; but he gives an interpolation formula, applicable between 15° and 20° , by means of which at least approximate values for 18° were obtained. His values for water at 15° and 20° do not agree well with those given by Landolt and Börnstein. I have therefore taken 0.010613 as the viscosity at 18° of the water used by him, a value which has to his value at 15° the same ratio as Landolt and Börnstein's for the same temperatures. The actual concentrations of Brückner's solutions differed from those given in the tables below by about 0.1 per cent.; but so small a difference could produce no appreciable error in the result. He gives as his "mean probable error of observation," ± 2.4 in the fifth place of decimals for sodium-chloride solutions, and ± 1.8 for those of potassium chloride.

Rother's observations of surface-tension were made at 15° , and are therefore not precisely comparable with calculated values based on the values of ionization-coefficients for 18° . From Kohlrausch's data*, however, it would appear that between 15° and 18° in the case of potassium-chloride solutions containing 0.5 and 3 gramme-molecules per litre, the ionization-coefficient changes only by about 0.13 and 1.3 per cent. respectively; and in the case of sodium-chloride solutions of the same concentrations only by about 0.4 and 0.6 per cent. respectively. For the more dilute solutions, therefore, my calculations will be practically comparable with Rother's observations. He seems to regard his determinations as possibly in error by ± 5 to 8 in the third place of decimals. The surface-tension of the water he used he found to be 7.357 .

Bender's observations of refractive index were made at 15° C., but were reduced to 18° by means of data provided in his paper, based on observations made by Fouqué†. The refractive index of the water he used he found to be 1.33310

* Wied. Ann. xxvi. (1885) p. 223.

† Compt. Rend. lxiv. (1867) p. 121.

Sodium Chloride Solutions.				Potassium Chloride Solutions.			
Grm.-mols. per litre.	Observed value.	Calc. value.	Difference.	Grm.-mols. per litre.	Observed value.	Calc. value.	Difference.
Density (Bender's observations).							
0.25	1.00898	1.00916	+0.018	0.1875	1.00752	1.00731	-0.021
0.5	1.01930	1.01929	- 01	0.375	1.01567	1.01586	+ 19
1.0	1.03925	1.03910	- 15	0.75	1.03317	1.03278	- 39
1.5	1.05834	1.05842	+ 08	1.0	1.04362	1.04401	+ 39
2.0	1.07772	1.07701	- 71	1.5	1.06630	1.06621	- 09
2.5	1.09633	1.09532	-0.0101	2.0	1.08767	1.08823	+ 56
				2.5	1.10755	1.11008	+0.0253
				3.0	1.13057	1.13177	+ 120
Thermal Expansion (Bender's observations).							
0.25	.001013	.001022	+0.09	0.1875	.000963	.000966	+0.003
0.5	.001141	.001141	$\pm$ 0	0.375	.001037	.001040	+ 03
1.0	.001357	.001349	- 8	0.75	.001183	.001173	- 10
1.5	.001522	.001526	+ 4	1.0	.001249	.001255	+ 06
2.0	.001663	.001657	- 6	1.5	.001395	.001395	$\pm$ 00
2.5	.001776	.001769	- 7	2.0	.001500	.001517	+ 17
3	.001876	.001848	-0.028	2.5	.001580	.001621	+ 41
Viscosity (Brückner's observations).							
0.5	.010988	.010978	-0.010	0.5	.010457	.010451	-0.006
1.0	.011480	.011475	- 05	1.0	.010395	.010379	- 16
1.5	.012048	.012047	- 01	1.5	.010351	.010366	+ 15
2.0	.012707	.012730	+ 23	2.0	.010394	.010393	- 01
2.5	.013472	.013458	- 14	2.5	.010444	.010457	+ 13
3.0	.014373	.014267	-0.0106	3.0	.010566	.010555	- 11
Surface-tension (Rother's observations).							
0.8928	7.482	7.482	$\pm$ 0.000	0.3402	7.411	7.408	-0.003
0.8353	7.629	7.629	$\pm$ 0	0.6856	7.460	7.462	+ 2
2.8373	7.780	7.798	+ 18	1.0467	7.518	7.519	+ 1
3.9375	7.954	7.997	+ 43	1.4292	7.584	7.583	- 1
				2.1851	7.705	7.709	+ 4
				2.9859	7.844	7.846	+ 2
Refractive Index, D line (Bender's observations).							
0.5	1.33824	1.33824	$\pm$ 0.000	0.5	1.33803	1.33806	+0.003
1.0	1.34307	1.34306	- 01	1.0	1.34278	1.34274	- 04
1.5	1.34770	1.34770	$\pm$ 00	1.5	1.34721	1.34722	+ 01
2.0	1.35213	1.35206	- 07	2.0	1.35179	1.35158	- 21
2.5	1.35673	1.35632	- 41	2.5	1.35623	1.35582	- 41

at 18° for the D line. He seems to regard his observations as possibly in error by ± 1 in the fourth decimal place.

The Tables on page 50 contain the results of the calculations of the values of the physical properties mentioned, with both the observed values on which the determination of the constants was based, and a few additional observed values for stronger solutions.

The following comments may be made on the above tables:—

Density.—NaCl. The first four observations were used in determining the constants; and up to a concentration of 1.5 the differences are within the limits of experimental error, and show a satisfactory alternation of sign.—KCl. The first five observations were used. The differences are large, but the alternation of sign shows that the expression is applicable. On plotting Bender's values they are readily seen not to lie on a smooth curve.

Thermal Expansion.—NaCl. The first four observations were used. The differences up to a concentration of 2.5 are probably within the limits of experimental error, and their alternation of sign is satisfactory.—KCl. The first five observations were used. The differences are not so satisfactory as in the case of the sodium salt either as to magnitude or sign; but on plotting the observations the third is seen to be somewhat out; and it is obviously to this observation that the defective agreement is due.

Viscosity.—NaCl. The first five observations were used. The differences are within the limits of error, but the signs are not satisfactory. The fourth observation, however, appears to be defective. Mützel*, in applying a formula for viscosity in terms of density and concentration to these observations, found also that this observation was out. It is worth noting, also, that Mützel found his formula, which expressed the increase of viscosity due to the salt in solution on the assumption that the only action occurring was between salt and water, was applicable to only the first five of the above observations. To represent the viscosity of stronger solutions he had to introduce a term expressing the effect due to the mutual action of the molecules of salt.—KCl. All six observations were used. The agreement in this case is quite satisfactory.

Surface-Tension.—NaCl. Only two observations on sufficiently dilute solutions were available, and the applicability of the formula cannot therefore be tested. The constants were found, for use in the calculation of the surface-tension of mixtures.—KCl. The first four observations were used,

* Wied. *Ann.* xliii. (1891) p. 35.

and the agreement is quite satisfactory up to a concentration of 3 grm.-mols. per litre.

Refractive Index.—In the case of both salts the first three observations were used, and in both the agreement is quite satisfactory up to a concentration of about 2 grm.-mols. per litre.

The above tables seem to be at any rate quite consistent with the possibility of expressing the values of at least five of the physical properties of moderately dilute solutions in terms of their state of ionization. I hope to find leisure at an early date to extend the investigation to solutions of salts and acids of a more complex character and to other properties.

The following are the ionization-constants used in the above calculations :—

	Sodium Chloride.		Potassium Chloride.	
	<i>k.</i>	<i>l.</i>	<i>k.</i>	<i>l.</i>
Density	+·030841	+·045079	+·03543	+·048591
Thermal Expansion	−·0001445	+·0007658	−·000614	+·00069625
Viscosity	+·002347	+·0001504	+·001904	−·0009247
Surface-Tension ...	+·20574	+·11001	+·24249	+·126806
Refractive Index...	+·006318	+·011713	+·0027853	+·011853

These constants are obtained from solutions of too great concentration to be regarded as exact values. Nevertheless it may be admissible so far as these two salts are concerned to draw the following conclusions :—Undissociated and dissociated molecules are nearly equally effective in increasing the density, those dissociated, however, being somewhat the more effective of the two. (2) Undissociated molecules diminish the thermal expansion, those dissociated increasing it to a greater extent. (3) In the case of viscosity it is the undissociated molecules which have the preponderating influence, those dissociated having but a slight effect, which may be an increasing or a diminishing effect. Thus Arrhenius's expectation that all dissociated ions would be found to diminish viscosity seems to be only partially realized, though possibly from observations on more dilute solutions, both *l*'s might be found to be negative. (4) In the increase of surface-tension the undissociated molecules have about twice as great an influence as the dissociated. (5) In increasing the refractive index it is the dissociated molecules which have the pre-

ponderating influence; and their superiority is greater in increasing the refractive power than in increasing the density.

Mixtures of Solutions.

For a solution containing several salts, 1, 2, &c., the value of a property, according to the conception under consideration, will be:—

$$P = P_w + k_1(1 - \alpha_1)n_1 + l_1\alpha_1n_1 + k_2(1 - \alpha_2)n_2 + l_2\alpha_2n_2 + \&c., \quad (2)$$

the n 's being numbers of gramme-equivalents per unit volume of the solution. If the solution have been formed by the mixture of the volumes v_1 and v_2 of two simple solutions of salts, having one ion in common, for which, before the mixing, the property had the values:—

$$\left. \begin{aligned} P_1 &= P_w + k_1(1 - \alpha_1)n_1 + l_1\alpha_1n_1, \\ P_2 &= P_w + k_2(1 - \alpha_2)n_2 + l_2\alpha_2n_2, \end{aligned} \right\} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

then, since, on mixing, the state of ionization will, in general, change, we shall have as the value of the property for the mixture, assuming no change of volume on mixing,

$$P = P_w + (k_1(1 - \alpha_1')n_1 + l_1\alpha_1'n_1) \frac{v_1}{v_1 + v_2} + (k_2(1 - \alpha_2')n_2 + l_2\alpha_2'n_2) \frac{v_2}{v_1 + v_2}, \quad (4)$$

the n 's being numbers of gramme-equivalents per unit volume of the original simple solutions, and α_1' and α_2' being the ionization-coefficients in the mixture. As the values of the k 's and l 's have been determined above for sodium and potassium chloride for a number of properties, and as I have shown in my paper on the "Conductivity of Mixtures," cited above, how the ionization-coefficients after mixing may be determined, it should be possible to predict the values of these properties for mixtures of solutions of these salts.

The following tables show that this can be done. The ionization-coefficients were determined in the way described in the paper referred to. The constants k and l employed in the calculations were those determined above. The observations were made by the authors whose determinations for simple solutions were used above; in fact in most cases it was the solutions of the tables given above which were mixed. The limits of experimental error are thus of about the magnitudes mentioned above in each case. All remarks made above with regard to the reduction of observations to 18° C., the values of the property for water, &c., apply also to the mixtures. In all cases, except that of surface-tension, the solutions mixed were mixed in equal volumes. Unfortunately, Bender made no observations on the refracting power of mixtures.

Constituent Solutions (gram.-mols. per litre).		Ionization Coefficients in Mixture.		Observed Value.	Calculated Value.	Difference.
NaCl.	KCl.	NaCl.	KCl.			
Density (Bender's observations).						
1.0	0.1875	.7268	.7720	1.02358	1.02350	-0.008
"	0.375	.714	.7625	1.02785	1.02766	- 19
"	0.75	.688	.7629	1.03641	1.03600	- 41
"	1.0	.6728	.7632	1.04139	1.04158	+ 19
"	1.5	.6494	.7478	1.05293	1.05263	-0.030
"	3.0	.6143	.7283	1.08580	1.08595	+ 15
Thermal Expansion (Bender's observations).						
1.0	0.1875	.7268	.7720	.001174	.001174	±0.000
"	0.375	.714	.7625	.001208	.001203	- 05
"	0.75	.688	.7629	.001275	.001264	- 11
"	1.0	.6728	.7632	.001297	.001305	+ 08
"	1.5	.6494	.7478	.001376	.001376	± 00
"	3	.6143	.7283	.001543	.001596	+ 53
Viscosity (Brückner's observations).						
1.0	0.5	.7059	.7635	.010940	.010947	+0.007
"	1.0	.6728	.7632	.010918	.010920	+ 02
"	1.5	.6494	.7478	.010876	.010915	+ 39
"	2.0	.6143	.7283	.010890	.010956	+ 66

Surface Tension (Rother's observations).

Constituent Solutions.				Ionization Coefficients in Mixture.		Observed Value.	Calculated Value.	Difference.
Concentration (grm.-mols. per litre).		Volume (litres).						
NaCl.	KCl.	NaCl.	KCl.	NaCl.	KCl.			
0.8862	0.6836	0.14487	0.14545	0.6906	0.7632	7.477	7.472	-0.005
1.8109	1.411	0.13993	0.14096	0.6087	0.7279	7.607	7.602	- 5
0.8824	2.1822	0.14489	0.13659	0.6123	0.7311	7.600	7.591	- 9
2.8406	0.6862	0.13511	0.14544	0.6027	0.7298	7.622	7.616	- 6
1.8155	2.9887	0.13996	0.13241	0.5185	0.7125	7.734	7.810	+ 76

It will be noticed that in the case of the third mixture of the density and thermal expansion series (the same mixture) the differences are comparatively large, but it is obvious from the data of the fourth column in these series that the ionization-coefficients have not been accurately determined for mixtures of about the concentration of the one referred to. With these exceptions the agreement between observed and calculated values is satisfactory, the differences being either well within or at worst on the limit of observational error, up to mean concentrations of about 1·5. The determination of the ionization-coefficients was especially difficult in the case of the surface-tension observations, because Rother mixed equal weights of his simple solutions, not equal volumes. Nevertheless, in all except the strongest of these mixtures, the differences are probably not beyond the limits of experimental error. Obviously, alternation of sign is not to be expected in these calculations.

[To be continued.]

IX. *On a complete Apparatus for the Study of the Properties of Electric Waves.* By JAGADIS CHUNDER BOSE, M.A. (Cantab.), D.Sc. (Lond.), Professor of Physical Science, Presidency College, Calcutta*.

THE work of Hertz and his eminent successors, both here † and on the Continent, has opened out for study a new region of æthereal vibration, bridging over the gap that hitherto existed between the comparatively slow æther vibrations and the quick oscillations which give rise to radiant heat. In the vast range of possible æther vibrations we recognize only a few octaves by our senses; the rest are beyond our perception. Many unexpected properties of

* Read before the British Association at Liverpool, 21st Sept., 1896. Communicated by Lord Kelvin, F.R.S.

[The apparatus described in this communication is founded on Prof. Oliver Lodge's and M. Branly's discovery of the "coherer" for detecting electric waves. The general design of the apparatus, both in respect to generator and receiver, was given originally by Prof. Lodge, and described in his book 'The Work of Hertz and some of his Successors, published by the Electrician Co. in 1894.—EDITORS.]

† By "here" is meant not only England, but Professor Lodge's laboratory especially, where the paper was read, and where, as is well known, some of the most important investigations on electric radiation have been carried out. For my interest in the subject I owe greatly to Prof. Lodge.