LXXXIX.—*Density and Electrostriction of Dilute Manganese Salt Solutions.*

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IT has been pointed out by Valson (*Compt. rend.*, 1870, **73**, 441) and by Bender (*Wied. Ann.*, 1883, **20**, 560) that the densities of salt solutions can be calculated with fair accuracy from the equation

$$d_\mu = d_{(\mu)\sigma} + \mu(m_a + m_b)$$

where d_μ is the density of a solution of the substance in question, containing μ equivs. per litre, $d_{(\mu)\sigma}$ the density of an ammonium chloride solution of the same normality and m_a and m_b are moduli for the ions of the salt in question. In this paper, the modulus for manganese is evaluated from three salts in dilute solution.

Valson also pointed out that the molecular solution volume of a substance is never equal to its molecular volume in the solid state, but always less. This contraction is designated " electrostriction," and attributed to a contraction of the solvent (Drude and Nernst, *Z. physikal. Chem.*, 1894, **15**, 79). According to Nernst and also Polowzow (*Z. physikal. Chem.*, 1911, **75**, 513), the electrostriction should increase with dilution to a practically constant value, and this is usually the case, as shown by Kohlrausch (*Wied. Ann.*, 1895, **56**, 185) and by Lamb and Lee (*J. Amer. Chem. Soc.*, 1913, **35**, 1667). The latter workers obtain one exceptional electrostriction curve, resembling to some extent that of manganese nitrate now described. Again, according to Baxter and Wallace (*ibid.*, 1916, **38**, 91), the electrostriction curves of the alkali halides are normal; they point out that " at least two important influences must be at work, one producing expansion, the other contraction," and the same conclusion is obvious from the graphs in this paper.

None of the above investigators draws attention to the fact that the value of the molecular volume in the solid state, which determines the electrostriction, has no absolute value : it is obviously much greater than the true, incompressible volume of the molecules. There must therefore be a contraction of the solid on dissolving, and only when this is allowed for is it possible to determine whether the solvent contracts or not. The expression $M(n^2 - 1)/d(n^2 + 2)$, where n is the refractive index for light of infinite wave-length, is supposed to represent the true molecular volume. The refractive indices of the dilute manganese salt solutions used were therefore determined, and hence, by the mixture rule, the molecular refractivities of the solid salts. From these figures the amended electrostriction was calculated.

EXPERIMENTAL.

The method used for the determination of density was that of Kohlrausch and Hallwachs (*Wied. Ann.*, 1894, **53**, 14). The density determinations given are each the mean of several differing only in the fifth decimal place; moreover, the results for very dilute solutions were checked on solutions made anew. The solutions investigated were in all cases 0·5, 0·3, 0·2, 0·1, 0·05, 0·02, 0·01 equivalent-normal. As the densities of ammonium chloride solutions had not previously been determined below 1·0*N*, it was first necessary to determine these, in order to deduce the modulus. The figures taken for the densities of the solid anhydrous manganese salts were : for the chloride, $d = 2{\cdot}977$ (Baxter and Hines, *J. Amer. Chem. Soc.*, 1906, **28**, 1574), whence its molecular volume in the solid state = 42·3 c.c.; for the sulphate, $d = 2{\cdot}954$ (Bassermann, " Dichtigkeitsmessungen," Heidelberg, 1873), whence its molecular volume= 51·3 c.c. The density of anhydrous manganese nitrate is not known, on account of the difficulty of obtaining it pure. An approximate calculation of the molecular volume was, however, made from the known density of the hexahydrate, assuming the water of crystallisation to have the density of ice. The value obtained was 39 c.c. Owing to this uncertainty, the refractive indices of the solid are not given.

The volumetric apparatus was standardised before use. The solutions were made up in the first place by weighing, and checked by analysis. Crystalline, hydrated A.R. salts were used.

The refractive indices were measured for the hydrogen C and F lines, a Zeiss–Pulfrich refractometer being used. Water at 20° was circulated through the apparatus, which was standardised with pure water.

It was shown by Bender (*Wied. Ann.*, 1890, **39**, 89) that the refractive indices of salt solutions can be calculated by means of an equation identical with that already given for densities. The standard of reference is potassium chloride solution, and moduli are deduced for ions other than $K^{\cdot}$ and Cl'. Here also, the refractivity moduli have been deduced and, as a necessary preliminary, the refractive indices of potassium chloride solutions determined. In the case of the manganese salt solutions, the refractivity modulus, the molecular refractivity $[R_L]$ of the anhydrous solid salt, and the molecular dispersion of the anhydrous solid salt were calculated for the concentrations 0·5*N*, 0·3*N*, and 0·2*N*. The specific refractivity of the anhydrous solid salt is obtained by means of the mixture formula. Below the above strengths, an experimental error of 1′ introduces such variations into the derived magnitudes as to render them ambiguous; for instance, with 0·1*N*-manganese chloride, it would cause an error of about 25% in the modulus, and a much greater error in the molecular dispersion. With the concentrations for which calculations have been made, the variations in the latter, though not great, are not believed to have any theoretical significance. The results have therefore been averaged. For the more dilute solutions, the refractive index only is given.

In the tables, the concentrations are given in equivs. per litre, $m_{\frac{1}{2}Mn}$ is the density modulus for manganese, and E.-S. is the electrostriction (in c.c.)

Results.

Densities of Dilute Ammonium Chloride Solutions.

Conc.	$d_{15^\circ}^{15^\circ}$.	Conc.	$d_{15^\circ}^{15^\circ}$.
0·5	1·00828	0·05	1·00095
0·3	1·00521	0·02	1·00033
0·2	1·00346	0·01	1·00019
0·1	1·00169	0·005	1·00009

	Manganese Chloride Soltns.			*Manganese Sulphate Soltns.*		
Conc.	$d_{15^\circ}^{15^\circ}$.	$m_{\frac{1}{2}Mn} \times 10^4$.	E.-S.	$d_{15^\circ}^{15^\circ}$.	$m_{\frac{1}{2}Mn} \times 10^4$.	E.-S.
0·5	1·02599	354	20·4	1·03654	365	46·5
0·3	1·01587	355	22·3	1·02217	365	48·1
0·2	1·01033	343·5	19·75	1·01493	374	49·6
0·1	1·00507	338	17·85	1·00733	364·5	46·9
0·05	1·00240	290	12·45	1·00366	342	46·7
0·02	1·00094	300·5	10·8	1·00142	345	42·3
0·01	1·00047	280	10·45	1·00071	320	42·0

Manganese Nitrate Solutions.

Conc.	$d_{15^\circ}^{15^\circ}$.	$m_{\frac{1}{2}Mn} \times 10^4$.	E.-S.
0·573718	1·03685	350	−11·5
0·344231	1·02226	346	−10·5
0·229395	1·01493	352	− 9·9
0·114744	1·00742	348	−10·0
0·057372	1·00367	325	−12·0
0·022940	1·00160	445	+ 7·0
0·011474	1·00085	425	+ 8·0

A few determinations of the densities of dilute manganese chloride, sulphate, and nitrate solutions have been made by Wagner (*Z. physikal. Chem.*, 1890, **5**, 31) and the agreement is satisfactory. Long (*Wied. Ann.*, 1880, **11**, 37) has determined the densities of more concentrated solutions, but his results appear to be untrustworthy.

Refractive Indices of Solutions at 20°.

Conc.	Potassium chloride. n_C.	n_F.	Manganese chloride. n_C.	n_F.	Manganese sulphate. n_C.	n_F.
0·5	1·33636	1·34239	1·33803	1·34415	1·33770	1·34378
0·3	1·33437	1·34044	1·33535	1·34148	1·33535	1·34141
0·2	1·33327	1·33918	1·33402	1·34014	1·33377	1·33992
0·1	1·33228	1·33822	1·33254	1·33858	1·33253	1·33866
0·05	1·33196	1·33785	1·33196	1·33793	1·33171	1·33770
0·02	1·33163	1·33756	1·33163	1·33757	1·33131	1·33731
0·01	1·33147	1·33742	1·33147	1·33742	1·33123	1·33723
0·005	1·33131	1·33727	—	—	—	—
Pure water	1·33113	1·33713	—	—	—	—

Manganese Chloride.

Equiv. norm. Conc.	Modulus ($\frac{1}{2}$Mn) × 10^3, C line.	F line.	$[R_L]_C$ for anhydrous salt.	$[R_L]_F$	$[R_L]_F - [R_L]_C$.
0·5	3·3	3·5	20·3	20·5	0·217
0·3	3·3	3·5	20·0	20·4	0·377
0·2	3·8	4·8	21·2	21·7	0·537
Means	3·5	3·9	20·5	20·9	0·377

From the mean values of the molecular refractivities, the refractive indices of solid anhydrous manganese chloride were calculated to be: $n_C = 1·96$, $n_F = 2·00$.

Manganese Sulphate.

Conc.	$[R_L]_C$ for anhydrous salt.	$[R_L]_F$	$[R_L]_F - [R_L]_C$.
0·5	16·4	16·6	0·151
0·3	16·4	16·7	0·406
0·2	15·3	16·1	0·783
Means	16·0	16·5	0·447

Hence, refractive indices of solid anhydrous manganese sulphate: $n_C = 1·54$, $n_F = 1·56$.

Manganese Nitrate.

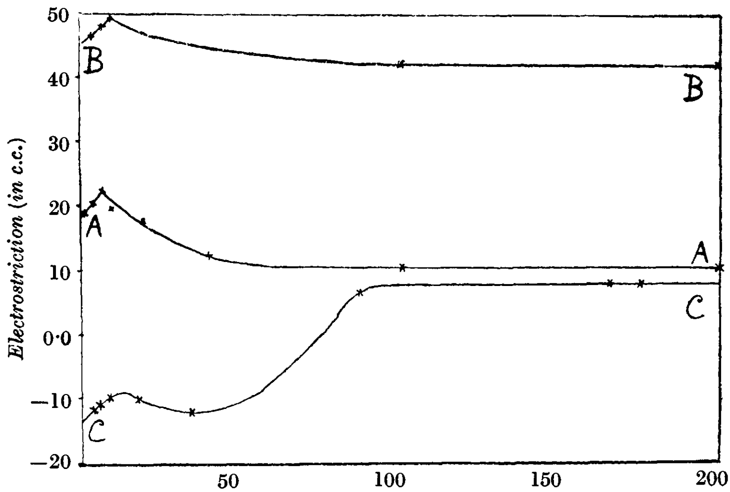
Conc.	$[R_L]_C$ for anhydrous salt.	$[R_L]_F$	$[R_L]_F - [R_L]_C$.
0·573718	24·8	25·5	0·657
0·344231	24·4	25·4	0·91
0·229395	24·5	25·8	1·54
Means	24·6	25·6	1·036

Jones and Getman (*Amer. Chem. J.*, 1904, **31**, 303) have determined the refractive indices, presumably for the sodium line, of manganese chloride, sulphate, and nitrate solutions; the figures they obtain for dilute solutions, however, are less than the refractive index of pure water, a state of affairs only possible with a concentrated solution of a substance of very low refractive index. Otherwise, their figures are concordant amongst themselves. It is suggested that their instrument was affected by a constant error.

The following table contains the electrostrictions, calculated on the assumption that the expression $M(n^2 - 1)/d(n^2 + 2)$ represents the true molecular volume of the salt.

$MnCl_2$.		$MnSO_4$.		$Mn(NO_3)_2$.	
Conc.	E.-S.	Conc.	E.-S.	Conc.	E.-S.
0·5	− 1·4	0·5	+11·2	0·573718	−25·9
0·3	+ 0·5	0·3	+12·8	0·344231	−24·9
0·2	− 2·1	0·2	+14·3	0·229395	−24·3
0·1	− 4·0	0·1	+11·6	0·114744	−24·4
0·05	− 9·4	0·05	+11·4	0·057372	−26·4
0·02	−11·0	0·02	+ 7·0	0·022940	− 7·4
0·01	−11·4	0·01	+ 6·7	0·011474	− 6·4

FIG. 1.



Dilution (*litres per mol.*).

A. Manganous chloride solutions.
B. ,, sulphate ,,
C. ,, nitrate ,,

Conclusion.

In the first place, it is obvious from the tables that the density modulus is fairly constant, except at very high dilutions, and therefore the density can be calculated down to $0{\cdot}1N$ by using the mean modulus of 355. In calculating the modulus from sulphate and nitrate solutions, it was necessary to employ the accepted moduli for $\frac{1}{2}SO_4$ and NO_3 (200 and 150, respectively).

The forms of the electrostriction curves are remarkable. Exactly the same forms of curves are given by Wagner's figures (*loc. cit.*). Presumably the maxima indicate, as suggested by Baxter and Wallace (*loc. cit.*), the existence of two opposing processes, one preponderating on each side of the maximum. The forms of the curves are of course independent of the values assigned to the densities and molecular volumes of the anhydrous solid salts.

It would appear from the last table that the effect of calculating with the "true molecular volume" is to indicate, in the cases of manganese chloride and manganese nitrate solutions, a negative electrostriction, *i.e.*, an expansion of the solvent.

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