TRANSACTIONS

I.—ON THE RELATION OF THE VISCOSITY OF MIXTURES OF SOLUTIONS OF CERTAIN SALTS TO THEIR STATE OF IONIZATION. — BY JAMES BARNES, B. A., *Dalhousie College, Halifax, N. S.*

The present paper is the result of a piece of work undertaken at the suggestion of Prof. MacGregor, for the summer vacation of 1899, the object being to find out in the case of mixtures of aqueous solutions of certain electrolytes with a common ion, whether or not it is possible, by the aid of the dissociation conception, to predict the viscosities of the mixtures, when sufficient data as to the viscosities and conductivities of the constituent solutions are available.

The salts selected were sodium chloride, potassium chloride, barium chloride, sodium sulphate, potassium sulphate, and copper sulphate, the viscosities of simple solutions of these salts having been determined by [1] Reyher and [2] Wagner, and that of mixtures of them by [3] Kanitz, and extensive series of observations on the conductivity by Kohlrausch and by former students of Dalhousie College, being available. As will be seen below I found [4] Kohlrausch's values of the conductivity sufficient for my purpose.

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[1] Ztschr. f. phys. Chemie, 2, 744, 1888.
[2] *Ibid.*, 5, 31, 1890.
[3] *Ibid.*, 22, 336, 1897.
[4] Kohlrausch u. Holborn : Leitvermögen der Elektrolyte, 1898, pp. 159, 160, tab. 2.

[1]Professor MacGregor has pointed out that, both on theoretical grounds and because of the way in which the ionization coefficients and such physical properties as specific gravity, viscosity, etc., in general, vary with the concentration in simple solutions, it is to be expected that the value of any such property, for a simple solution which is so dilute that the dissociated and undissociated molecules may be regarded as without mutual action, will be expressed by the formula :

$$P = P_w + k(1-a)\, n + l\, a\, n, \dots\dots\dots\dots (1)$$

where P is the numerical value of the property for the solution, P_w that of the same property for water under the same physical conditions, n the concentration expressed in gramme-equivalents per unit volume, a the ionization coefficient of the electrolyte in the solution, and k and l constants, called ionization constants.

He has further shown that the value of a property for a mixture of two electrolytes will be given in terms of the values of the ionization constants as determined for the simple solutions, by the expression :

$$P = P_w + \frac{1}{p}\Big[\Big(k_1(1-a_1)\,n_1 + l_1\,a_1\,n_1\Big)\frac{v_1}{v_1 + v_2}$$
$$+ \Big(k_2(1-a_2)\,n_2 + l_2\,a_2 n_2\Big)\frac{v_2}{v_1 + v_2}\Big]\dots(2)$$

where the n's are the concentrations of the constituent solutions (the electrolytes being indicated by 1 and 2), the a's the ionization coefficients of the respective electrolytes in the mixture, the v's the volumes of the constituent solutions, and p the ratio of the volume of the mixture to the sum of the volumes of the constituent solutions.

The application of the first expression to simple solutions is, as [2] Prof. MacGregor has shown, of little theoretical interest; but that of the second to mixtures, because of its being based on the dissociation theory and involving no arbitrary constants, is of very considerable interest. It is the applicability of this expression (2) that the present paper is intended to test with mixtures of solutions of the above-mentioned salts.

[1] Trans. N. S. Inst. Sci., 9, 219, 1896-97.
[2] Trans. N. S. Inst. Sci., 10, 61 (foot note), 1898-99.

The observations of Reyher, Wagner and Kanitz were made on somewhat stronger solutions than those for which the above expressions might be expected to hold, but they were considered as probably sufficiently dilute to warrant the expectation of an approximate applicability of the expressions.

Simple Solutions.

For the determination of the ionization constants in expressions (1) and (2), one must know the ionization coefficients for the four solutions examined in the case of each salt by Reyher and Wagner. Unfortunately all the observations on the viscosity of these salts were made at 25° C., while all the available conductivity data, from which the ionization coefficients are obtained, were at 18°C., and thus it was necessary either to reduce the viscosity values from 25° to 18° or the conductivity values from 18° to 25°. This latter reduction was carried out, as data for the former were not available. This involved much work; because for the determination of the ionization coefficients at 25°, it was necessary to obtain both the specific molecular conductivity at 25° and the specific molecular conductivity at infinite dilution for 25°.

Determination of the Specific Molecular Conductivity at Infinite Dilution for 25°C.

The value of the specific molecular conductivity at infinite dilution for 25° for each salt was obtained from [1] Kohlrausch's value at 18° by aid of [2] Déguisne's data. These data were employed in obtaining the specific molecular conductivity at 25° from the values at 18°, for the three weakest solutions given in [3] Kohlrausch's and Déguisne's tables; and the ratio

$\dfrac{\mu_{25} - \mu_{18}}{\mu_{18}}$ was then determined, where μ_{25} and μ_{18} are the specific molecular conductivity at 25° and 18° respectively.

Table I gives the values thus obtained. The concentrations are expressed in gramme-equivalents per litre, and the specific molecular conductivities in terms of this unit and of 10^{-4} times [4] Kohlrausch's new unit of conductivity (ohm^{-1} cm.$^{-1}$).

[1] Kohl. u. Holb., *loc. cit.*, p. 200, tab. 8.

[2] *Ibid.*, p. 195, tab. 7.

[3] *Ibid.*, pp. 159, 160, tab. 2.

[4] *Ibid.*, p. 1.

TABLE I.

Concentration.	Sp. Mol. Cond. at 18° C. (μ_{18})	Sp. Mol. Cond. at 25° C. (μ_{25})	$\dfrac{\mu_{25} - \mu_{18}}{\mu_{18}}$
Na. Cl.			
.0005	1085	1262	.163
.0002	1092	1270	.163
.0001	1097	1276	.163
K Cl			
.0005	1283	1484	.156
.0002	1291	1494	.157
.0001	1295	1499	.157
$\frac{1}{2}$ Ba Cl$_2$.			
.0005	1183	1375	.162
.0002	1198	1394	.163
.0001	1205	1402	.163
$\frac{1}{2}$ K$_2$ SO$_4$.			
.0005	1308	1516	.159
.0002	1327	1540	.160
.0001	1335	1549	.160
$\frac{1}{2}$ Na$_2$ SO$_4$.			
.0005	1083	1266	.169
.0002	1096	1281	.169
.0001	1105	1292	.169

As the ratio $\frac{\mu_{25}-\mu_{18}}{\mu_{18}}$ was thus found to be constant for the two most dilute solutions of every salt, and as these solutions are very dilute, this ratio may be assumed to approximately hold for infinite dilution. Observations on the conductivity of weaker solutions at different temperatures were not at hand; and the writer used the value of this ratio for the solution of concentration .0001 for the calculation of the specific molecular conductivity at infinite dilution for 25° C.

The following Table II gives the values of the specific molecular conductivity at infinite dilution for 25° C. as thus obtained from the values at 18° C. In the case of copper sulphate this method could not be employed for want of data. A somewhat doubtful value obtained by [1]Bredig was therefore used. The conductivities are expressed as in Table I.

TABLE II.

Electrolyte.	Specific Molecular Conductivity at Infinite Dilution.	
	18° C.	25° C.
Na Cl.	1103	1283
K Cl.	1312	1519
$\frac{1}{2}$ Ba Cl$_2$.	1232	1433
$\frac{1}{2}$ K$_2$ SO$_4$.	1350	1566
$\frac{1}{2}$ Na$_2$ SO$_4$.	1141	1334
$\frac{1}{2}$ Cu SO$_4$	....	1423

Determination of the Ionization Coefficients at 25° C. for Simple Solutions.

The ionization coefficient for a simple solution is taken to be the ratio of the specific molecular conductivity to the specific

[1] Ztschr. f. phys. Chem., 13, 220, 1894,

molecular conductivity at infinite dilution. Before this ratio could be found for 25° C. it was necessary to determine the values of the specific conductivity at 25° from [1] Kohlrausch's values at 18° by means of [2] Déguisne's and [3] Kohlrausch and Grotrian's temperature coefficients. The concentrations of solutions of the salts for which Kohlrausch gives conductivity values, did not in all cases correspond to the concentrations of solutions for which Reyher and Wagner determined the viscosity. In such cases (concentrations 0.25 and 0.125), the values of the specific conductivities at 25° were obtained by interpolation.

Table III gives both the values of the specific conductivity at 25°C. determined as above from the values at 18°, and the calculated ionization coefficients at 25°. Only those coefficients are given which are necessary in the calculation of the viscosities. Under copper sulphate are given a few conductivity values of higher concentration, these being necessary for the determination of the ionization coefficients in the mixtures by the method used. The concentrations are expressed as in Table I, and conductivities in terms of 10^{-4} times Kohlrausch's new unit.

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[1] Kohl. u. Holb., *loc. cit.*, p. 159, table 2.

[2] *Loc. cit.*

[3] Kohl. u. Holb., p. 145, tab. 1.

TABLE III.

Concentration.	Specific Conductivity at 18° C.	Specific Conductivity at 25° C.	Ionization Coefficients at 25° C.
Na Cl.			
1.0	744.0	862	.672
0.5	404.5	469	.732
0.3	255.6	296	......
0.25	.. ...	252	.786
0.2	176.4	205	......
0.125	......	131	.817
0.1	92.5	107	......
K Cl.			
1.0	982.0	1128	.743
0.5	511.5	588	.774
0 3	315.9	363	.... .
0.25	......	308	.811
0.2	215.4	248	......
0.125	......	159	.838
0.1	111.9	129	......
$\frac{1}{2}$ Ba Cl$_2$.			
1.0	703	811	.566
0.5	388	448	.624
0.3	249	287	......
0.25	......	245	.684
0.2	173.4	200	......
0.125	......	130	.726
0.1	92.2	106	... .

TABLE III.—*(Continued.)*

Concentration.	Specific Conductivity at 18° C.	Specific Conductivity at 25° C.	Ionization Coefficients at 25° C.
		$\frac{1}{2} K_2 SO_4$	
1.0	718.0	827	.528
0.5	393.5	453	.578
0.3	253.2	292	......
0.25	......	251	.640
0.2	177.8	205	......
0.125	......	135	.690
0.1	95.9	111	......
		$\frac{1}{2} Na_2 SO_4$.	
1.0	508 0	591	.443
0.5	298.5	347	.520
0.3	199.8	230	.....
0.25	.... .	201	.604
0.2	142.8	166	......
0.125	......	110	.662
0.1	78.4	91.4	......
		$\frac{1}{2} Cu SO_4$.	
2.631	458	534	......
2.194	421	489	......
1.0	258	297	.209
0.5	154	177	.249
0.3	106.5	122	......
0.25	......	107	.302
0.2	78.4	89.9	......
0.125	......	61.7	.347
0.1	45.0	51.6	......

Determination of the Ionization Constants.

Table IV gives the values of the ionization constants (k and l) determined by the method of least squares from the data given in Tables III and V, the observed values of the viscosity of the four solutions of each salt being used. The relative magnitude and the sign of the ionization constants would seem to show that the undissociated molecules exert the greater influence in increasing the viscosity, while the free ions have in some cases a diminishing effect.

TABLE IV.

Electrolyte.	$k.$	$l.$
Na Cl.	$+0.11213$	$+0.089765$
K Cl.	$+0.30645$	-0.12289
$\frac{1}{2}$ Ba Cl$_2$.	$+0.20327$	$+0.061009$
$\frac{1}{2}$ K$_2$ SO$_4$.	$+0.21347$	$+0.0088236$
$\frac{1}{2}$ Na$_2$ SO$_4$.	$+0.30418$	$+0.13348$
$\frac{1}{2}$ Cu SO$_4$.	$+0.46500$	-0.058144

Results of Calculations on Simple Solutions.

Table V gives a comparison of the calculated and observed values of the viscosity of simple solutions, the calculated values being determined by expression (1) with the ionization coefficients and ionization constants, as given in the above tables. In this table all the viscosity results are relative to water at 25°C., and the concentrations are expressed as in Table I.

TABLE V.
VISCOSITY AT 25° C.

Concentration.	Observed Value.	Calculated Value.	Difference.
	Na Cl. (Reyher.)		
1.0	1.0973	1.0971	$-0.0_3 2$
0.5	1.0471	1.0479	$+0.0_3 8$
0.25	1.0239	1.0236	$-0.0_3 3$
0.125	1.0126	1.0117	$-0.0_3 9$

TABLE V.—*(Continued)*.

Concentration.	Observed Value.	Calculated Value.	Difference.
K Cl. (Wagner.)			
1.0	.9872	.9874	$+ 0.0_3 2$
0.5	.9874	.9871	$- 0.0_3 3$
0.25	.9903	.9896	$- 0.0_3 7$
0.125	.9928	.9933	$+ 0.0_3 5$
$\frac{1}{2}$ Ba Cl$_2$. (Wagner.)			
1.0	1.1228	1.1228	$\pm 0.0_3 0$
0.5	1.0572	1.0572	$\pm 0.0_3 0$
0.25	1.0263	1.0265	$+ 0.0_3 2$
0.125	1.0128	1.0125	$- 0.0_3 3$
$\frac{1}{2}$ K$_2$SO$_4$. (Wagner.)			
1.0	1.1051	1.1054	$+ 0.0_3 3$
0.5	1.0486	1.0476	$- 0.0_2 1$
0.25	1.0206	1.0206	$\pm 0.0_3 0$
0.125	1.0078	1.0090	$+ 0\ 0_2 12$
$\frac{1}{2}$ Na$_2$SO$_4$. (Wagner.)			
1.0	1.2291	1.2286	$- 0\ 0_3 5$
0.5	1.1058	1.1078	$+ 0.0_2 2$
0.25	1.0522	1.0502	$- 0.0_2 2$
0.125	1.0235	1.0239	$+ 0.0_3 4$
$\frac{1}{2}$ Cu SO$_4$. (Wagner.)			
1.0	1.3580	1.3556	$- 0.0_2 24$
0.5	1.1603	1.1675	$+ 0.0_2 72$
0.25	1.0802	1.0767	$- 0.0_2 35$
0.125	1.0384	1.0354	$- 0.0_2 30$

As both Reyher and Wagner regard their results as affected by a possible error of about $\pm$ 3 in the third decimal place, it is seen that the agreement between the calculated and observed values for all the salts except copper sulphate is very satisfactory, the differences being well within the limit of experimental error. In the case of copper sulphate, the agreement is not so satisfactory. But it was noticed on plotting the observed values against the concentration that the points do not lie on a smooth curve, and that the point corresponding to the concentration 0.5 is at quite a distance from this curve, which leads one to think that this observed value cannot be correct. The poor agreement in this case might also be partly due to the doubtful value of the specific molecular conductivity at infinite dilution used. Thus it seems that for all the salts examined, copper sulphate perhaps excepted, expression (1) gives the viscosity of a solution within the limit of experimental error throughout a concentration range of 1.0 to 0.125.

Mixtures of Solutions.

As there is no change of volume on mixing the constituent solutions of the above electrolytes of the concentrations given below[1], and as the solutions mixed were of equal volume and also equimolecular, the expression (2) for the value of a property in the case of a mixture of two electrolytes with a common ion, reduces to :

$$P = P_w + \frac{n}{2}\left[k_1\,(1 - a_1) + l_1\,a_1 + k_2\,(1 - a_2) + l_2\,a_2 \right] \cdot (3)$$

where n is the concentration of the solutions and the k's and l's have the values obtained above for simple solutions of the respective electrolytes. For the application of this equation to the calculation of the viscosity of a mixture, all the quantities required are known except the a's, the ionization coefficients in the mixture.

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[1] See Trans. N. S. Inst. Sci., 9, 125, 1895-96; also 9, 297 and 310, 1897-98.

Determination of Ionization Coefficients in the Mixture.

The method proposed by [1] Prof. MacGregor for finding the ionization coefficients in a mixture of two electrolytes having an ion in common, is by solving graphically the following equations :

$$\frac{a_1}{V_1} = \frac{a_2}{V_2}, \qquad \cdots \qquad (4)$$

$$N_1 V_1 + N_2 V_2 = 1, \qquad \cdots \qquad (5)$$

$$\frac{a_1}{V_1} = f_1(V_1), \qquad \cdots \qquad (6)$$

$$\frac{a_2}{V_2} = f_2(V_2), \qquad \cdots \qquad (7)$$

where the electrolytes are denoted by 1 and 2, the concentrations (in gramme-equivalents per litre) of the mixture with respect to them by N_1 and N_2 respectively, their ionization coefficients by a_1 and a_2, and their regional dilutions (in litres per gramme equivalent) by V_1 and V_2, the regional dilutions being the dilutions of the electrolytes in the regions which they are supposed to occupy in the mixture, or the dilutions of the constituent isohydric solutions.

His graphical mode of solving these equations involves the drawing of dilution-ionic-concentration curves, which, as they have great curvature for moderately dilute solutions, cannot be drawn with great accuracy unless a large number of observations of the conductivity are available. As mentioned above, extensive series of observations of the conductivity in the case of the salts under consideration were available ; but they were all made at 18° C. and required therefore to be reduced to 25° C. before they could be used. In order to reduce this labour as much as possible I devised another mode of solution which requires only a comparatively small number of observations. It is based on the fact that the specific-conductivity-concentration

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Trans. N. S. Inst. Sci., 9, 101, 1895-96 ; also 10, 68, 1898-99.

curve of an electrolyte exhibits only slight curvature and can therefore be drawn with fair accuracy from a small number of observations.

The above equations may be expressed in terms of specific conductivity and concentration as follows. Since

$$\frac{a_1}{V_1} = \frac{\mu_1}{V_1 \mu_{\infty 1}} = \frac{k_1}{\mu_{\infty 1}}, \quad \cdot \quad \cdot \quad (8)$$

and

$$\frac{a_2}{V_2} = \frac{k_2}{\mu_{\infty 2}}, \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

where k_1 and k_2 are the specific conductivities of the electrolytes in the regions which they respectively occupy in the mixture, and the μ_{∞}'s the specific molecular conductivities at infinite dilution for each electrolyte, equation (4) becomes :

$$\frac{k_1}{\mu_{\infty 1}} = \frac{k_2}{\mu_{\infty 2}},$$

or,

$$k_1 = \frac{\mu_{\infty 1}}{\mu_{\infty 2}} k_2. \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

From equation (5) we obtain :

$$\frac{N_1}{C_1} + \frac{N_2}{C_2} = 1, \quad \cdot \quad \cdot \quad \cdot \quad (11)$$

where C_1 and C_2 are the regional concentrations. Equations (6) and (7) are based on the fact that at a definite temperature the conductivity is a function of the concentration alone. They therefore take the following forms :

$$k_1 = f_1 (C_1), \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

and

$$k_2 = f_2 (C_2). \quad \cdot \quad \cdot \quad \cdot \quad (13)$$

There are thus four equations (10—13) for the determination of the four unknown quantities : k_1, k_2, C_1, and C_2.

These equations can be solved graphically. Equation (12) is employed by drawing a curve having as abscissæ the values of the specific conductivities and corresponding values of the concentrations as ordinates. Before equation (13) is used the values

of the conductivities are multiplied by the constant $\frac{\mu_{\infty 1}}{\mu_{\infty 2}}$. Then these new values are plotted against the corresponding concentrations, on the same coordinate paper, to the same scale as employed for equation (12). From these two curves one finds by inspection two points, one on each curve, having a common abscissa, according to equation (10), and ordinates (C_1 and C_2) such that by substituting their values in equation (11) it will be satisfied. These points can be found after two or three trials. Thus one has determined k_1, C_1, and C_2; k_2 being found by multiplying k_1 by the constant $\frac{\mu_{\infty 2}}{\mu_{\infty 1}}$. The a's are now obtained from equations (8) and (9); for the reciprocals of the C's give the V's.

Results of the Calculations on Mixtures.

The following Table VI contains the requisite data for the calculation, by formula (3), of the viscosity of mixtures of solutions of the salts under consideration; and it shows the agreement of the values thus calculated with the observed values The ionization coefficients of the salts in the mixture are determined as above and the concentrations are expressed as in the former tables.

TABLE VI.

VISCOSITY AT 25°. (KANITZ).

Concentration Constituent Solutions.		Ionization Coefficients in Mixture.		Observed Values.	Calculated Values.	Difference.
K Cl.	Na Cl.	K Cl.	Na Cl.			
1.0	1.0	.745	.667	1.0390	1.0419	$+0.0_229$
0.5	0.5	.775	.728	1.0180	1.0173	-0.0_37
0.25	0.25	.807	.783	1.0070	1.0069	-0.0_31
K Cl.	$\frac{1}{2}$ Ba Cl$_2$.	K Cl.	$\frac{1}{2}$ Ba Cl$_2$.			
1.0	1.0	.756	.552	1.0429	1.0533	$+0.0101$
0.5	0.5	.779	.613	1.0159	1.0220	$+0.0_261$
0.25	0.25	.811	.675	1.0049	1.0082	$+0.0_233$
K$_2$SO$_4$.	$\frac{1}{2}$Na$_2$SO$_4$.	$\frac{1}{2}$ K$_2$ SO$_4$.	$\frac{1}{2}$Na$_2$ SO$_4$.			
1.0	1.0	.535	.434	1.1660	1.1670	$+0.0_21$
0.5	0.5	.597	.517	1.0773	1.0768	-0.0_35
0.25	0.25	.641	.604	1.0334	1.0354	$+0.0_22$
K$_2$ SO$_4$.	$\frac{1}{2}$ Cu SO$_4$.	$\frac{1}{2}$ K$_2$ SO$_4$.	$\frac{1}{2}$ Cu SO$_4$.			
1.0	1.0	.559	.152	1.2240	1.2423	$+0.0183$
0.5	0.5	.612	.210	1.1060	1.1107	$+0.0_247$
0.25	0.25	.668	.256	1.0485	1.0510	$+0.0_225$

Kanitz regards his observed values as affected by a possible error of ± 3 in the third decimal place. Considering the many calculations necessary to obtain the calculated values,—first, in finding the specific molecular conductivity at infinite dilution for 25°C., and also ionization coefficients at 25° from data at 18° and then in the determination of the ionization coefficients of the salts in the mixture by the graphical method,—the agreement between the observed and the calculated values (calculated,

it should be noted, with the ionization constants obtained for the simple solutions), is very satisfactory, especially in the case of solutions of potassium chloride and sodium chloride and solutions of potassium sulphate and sodium sulphate, where the differences are all within the limit of experimental error. In the case of the stronger solutions of potassium chloride and barium chloride and of potassium sulphate and copper sulphate, the differences are not within the limit of error; but a close agreement, as was pointed out in the beginning, could not be expected. It will be noticed, however, that the differences in these cases diminish and approach the experimental error as concentration diminishes. Observations on the viscosity of weaker solutions of these salts were not available.

From these results, therefore, it may be concluded, that the viscosity of mixtures of dilute solutions of the salts under consideration can be predicted, by the aid of the dissociation theory, within the limit of experimental error, from data as to the viscosity and conductivity of the constituent solutions only.