

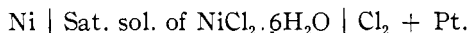
approximately equal, as was found to be true in all other cases for which this calculation has been made.

4. Precision Discussion.

The term $2EF$ in formula (3) amounts to 79,040 calories, the second term to only 4600 cal., from which it is evident that even a large error in the vapor pressures would have only a relatively small effect on the final result. Assuming an error of 0.1 mm. in p_{sol} , p_2 and 0.1 mm. in p , which seems an outside limit, the resultant effect is 600 calories, or about 0.8 per cent. error in ΔF . Assuming a possible error of 0.02 volt in E the combined error in ΔF would be 990 cal., or 1.3 per cent.

5. Summary.

The free energy ΔF of NiCl_2 was determined by measuring the potential of the cell.



A formula for ΔF was deduced, involving this potential, the vapor pressure of the saturated solution, of the system $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - \text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O} - \text{NiCl}_2$. The pressure of the last system was obtained both by direct and by indirect measurement. The free energy and total energy of NiCl_2 were found to be approximately equal.

ELECTROCHEMICAL LABORATORY,
MASS. INST. OF TECH., BOSTON.

A STUDY OF THE SOLUTIONS OF SOME SALTS EXHIBITING NEGATIVE VISCOSITY.

FREDERICK H. GETMAN.

Received March 10, 1908.

In 1873 Hübner¹ determined the viscosities of a series of solutions of alkaline halides of equal densities and observed that some of the salts diminished the viscosity of water.

Subsequently Sprung² made an extensive study of the viscosities of saline solutions between the temperatures 0° and 60° C.

He divided the salts examined into two groups as follows:

(1) KCl , KBr , KI , KNO_3 , KClO_3 , NH_4Cl , NH_4Br , NH_4NO_3 .

(2) K_2SO_4 , NaCl , NaBr , NaI , NaNO_3 , NaClO_3 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, BaCl_2 , SrCl_2 , CaCl_2 , LiCl , MgSO_4 .

He pointed out that at low temperatures the salts of the first group lower the viscosity of water and at higher temperatures they increase it. The salts of the second group always increase the viscosity of the solvent, the viscosity of the solution becoming less as the temperature is raised.

¹ *Pogg. Ann.*, 157, 130.

² *Ibid.*, 159, 1.

The experimental work of Sprung was later confirmed by the investigations of Slotte¹ and Wagner,² the latter having studied the viscosities of the solutions of forty different salts at several concentrations.

Arrhenius,³ Kanitz⁴ and Mützel⁵ have measured the viscosities of saline solutions which show the phenomenon of negative viscosity and still more recently Ranken and Taylor⁶ have made some extremely accurate determinations of the viscosities of solutions of potassium chloride and ammonium iodide at different temperatures.

One of the first to offer an explanation of negative viscosity was Euler,⁷ who made use of the theory of electrostriction proposed by Nernst and Drude.⁸ In terms of this theory the ions are enveloped in a strong electric field, owing to their charges, and the intervening liquid is subjected to great stress, so that the tendency of the ions to increase the viscosity in inverse proportion to their speeds of migration is offset by the electrostriction.

Wagner⁹ has pointed out that Euler's theory is untenable, since the viscosity of the solvent may be diminished by solutes which are non-electrolytes.

As a possible explanation of the phenomenon, Wagner suggests that the amount of solvent in a given space is diminished by the solute and that this leads to a lowering of the viscosity.

If the solute have a high viscosity, then the viscosity of the solution will be greater than that of the solvent.

Ranken and Taylor¹⁰ have pointed out that at 8° urea diminishes the viscosity of water, but as the temperature is raised the viscosity of the solution becomes greater than that of the solvent.

Recently the author¹¹ determined the viscosities of several solutions of potassium salts having lower viscosities than that of the solvent. The determinations were extended from dilute to concentrated solutions and it was found that in every case the viscosity-concentration curves passed through a minimum.

The suggestion was put forward that the abnormal behavior of the potassium salts resulted from the combined action of the ions and the undis-

¹ *Wied. Ann.*, 20, 257.

² *Z. physik. Chem.*, 5, 31.

³ *Ibid.*, 1, 285.

⁴ *Ibid.*, 22, 336.

⁵ *Wied. Ann.*, 43, 15.

⁶ *Trans. Roy. Soc., Edinburgh*, 45, 397.

⁷ *Z. physik. Chem.*, 25, 536.

⁸ *Ibid.*, 15, 79.

⁹ *Ibid.*, 46, 867.

¹⁰ *Loc. cit.*

¹¹ *J. chim. phys.*, 5, 344.

sociated molecule. The potassium ion appearing to lower the viscosity of the solvent, while the different anions and the undissociated molecules tended to increase it.

Shortly after this paper was written Jones and Veazey¹ suggested a possible explanation of negative viscosity.

In the course of their investigations the anomalous behavior of potassium thiocyanate directed their attention to this phenomenon and they found that the solutes which diminish the viscosity of water are those whose cations have large atomic volumes. If the ions of the solute are large, relative to the molecules of the solvent, then the effect of the dissolved salt will be to reduce the viscosity of the solvent.

In view of what has been done in this field it has seemed of sufficient importance to extend my work and include other saline, aqueous solutions exhibiting negative viscosity.

The salts chosen for more careful study were ammonium chloride, ammonium bromide, ammonium iodide, ammonium nitrate, and rubidium iodide.

Apparatus and Method.

The method of measuring the viscosities was the well-known transpiration method of Poiseuille-Ostwald. The viscometers were placed in a bath of water maintained at constant temperature and the times of transpiration were measured with a stop-watch which had been carefully compared with an accurate chronometer.

The densities were determined with a pycnometer of the Sprengel-Ostwald type.

The viscometers were frequently cleaned with chromic acid and special precautions were taken to protect them from dust.

The constants of the tubes were frequently checked by measuring the times of transpiration of pure distilled water and solving for k in the formula

$$k = \frac{\eta}{dt},$$

where η is the absolute viscosity of water at a definite temperature, d the density of water at the same temperature, and t the time of transpiration as measured by the stop-watch.

The values of η and d were obtained from the tables of Landolt and Börnstein.

The concentration of the solutions was determined either by direct weighing or by analysis.

The salts used were obtained from Kahlbaum and were sufficiently pure to warrant using them without recrystallization.

¹ *Am. Chem. J.*, 37, 405.

Results.

In the tabulation of results the symbols have the following significance:

m = concentration of solution in gram-molecules per liter.

d = density of solution referred to water at 4° C.

η = viscosity in C. G. S. units (dynes per square centimeter).

TABLE I.
NH₄Cl—25°.

m .	d .	η .
0.4437	1.0071	0.00889
0.8874	1.0138	0.00885
1.3311	1.0204	0.00882
1.7748	1.0268	0.00880
2.2185	1.0331	0.00878
2.6622	1.0394	0.00887
3.1059	1.0458	0.00897
3.5496	1.0516	0.00904
4.437	1.0630	0.00925

TABLE II.¹
NH₄Cl.

m .	η_{10° .	η_{30° .	η_{50° .
0.68	0.0128	0.0080	0.0057
1.62	0.0123	0.0081	0.0058
2.93	0.0120	0.0082	0.0061
4.34	0.0120	0.0085	0.0064

TABLE III.
NH₄Br—25°.

m .	d .	η .
0.216	1.0121	0.008867
0.432	1.0247	0.008796
0.647	1.0352	0.008756
0.863	1.0468	0.008680
1.079	1.0583	0.008644
1.323	1.0715	0.008575
1.588	1.0858	0.008480
2.646	1.1414	0.008254
3.486	1.1758	0.008356
4.357	1.2273	0.008470
4.920	1.2605	0.008560

TABLE IV.²
NH₄Br.

m .	η_{10° .	η_{30° .	η_{50° .
1.63	0.0116	0.0077	0.0056
2.58	0.0112	0.0077	0.0057
3.76	0.0111	0.0079	0.0061

¹ Sprung, *Pogg. Ann.*, **159**, 1.

² Sprung, *Loc. cit.*

TABLE V.
NH₄I--25°.

<i>m.</i>	<i>d.</i>	η .
0.500	1.0447	0.008577
0.751	1.0675	0.008440
1.001	1.0913	0.008237
1.501	1.1377	0.008086
2.002	1.1839	0.007827
2.502	1.2304	0.007779
3.002	1.2765	0.007842
4.003	1.3692	0.007997
5.004	1.4591	0.008321

TABLE VI.
NH₄I—30°.

<i>m.</i>	<i>d.</i>	η .
0.125	1.0071	0.00792
0.25	1.0181	0.00786
0.5	1.0401	0.00774
1.0	1.0944	0.00753
4.0	1.3513	0.00729
6.0	1.5285	0.00823

TABLE VII.¹
NH₄I—45°.

<i>m.</i>	<i>d.</i>	η .
0.125	1.0026	0.005950
0.25	1.0145	0.005925
0.5	1.0380	0.005855
1.0	1.0853	0.005780

TABLE VIII.
NH₄I.

<i>t.</i>	<i>m.</i>	<i>d.</i>	η .
10	1.001	1.0944	0.01146
15		1.0937	0.01031
20		1.0929	0.009277
10	2.002	1.1889	0.01044
15		1.1874	0.009568
20		1.1859	0.008752
10	3.002	1.2826	0.009947
15		1.2806	0.009297
20		1.2786	0.008648
10	4.003	1.3763	0.00001
15		1.3738	0.00931
20		1.3717	0.008692
10	5.004	1.4661	1.01051
15		1.4641	0.009761
20		1.4611	0.009017

¹ Ranken and Taylor, *Loc. cit.*

TABLE IX.
NH₄NO₃—25°.

<i>m.</i>	<i>d.</i>	<i>η.</i>
0.256	1.0059	0.008853
0.512	1.0137	0.008797
0.767	1.0215	0.008724
1.023	1.0300	0.008655
1.279	1.0373	0.008602
1.454	1.0432	0.008579
2.012	1.0602	0.008504
2.245	1.0676	0.008500
2.587	1.0777	0.008565
2.909	1.0873	0.008627
3.636	1.1078	0.008850
4.664	1.1396	0.009308

TABLE X.¹
NH₄NO₃.

<i>m.</i>	<i>η</i> _{10°} .	<i>η</i> _{30°} .	<i>η</i> _{50°} .
0.745	0.0124	0.0079	0.00567
1.521	0.0119	0.0079	0.0057
3.367	0.0120	0.0085	0.0062
4.646	0.0128	0.0091	0.0070
6.22	0.0145	0.0113	0.0088

TABLE XI.
RbI—25°.

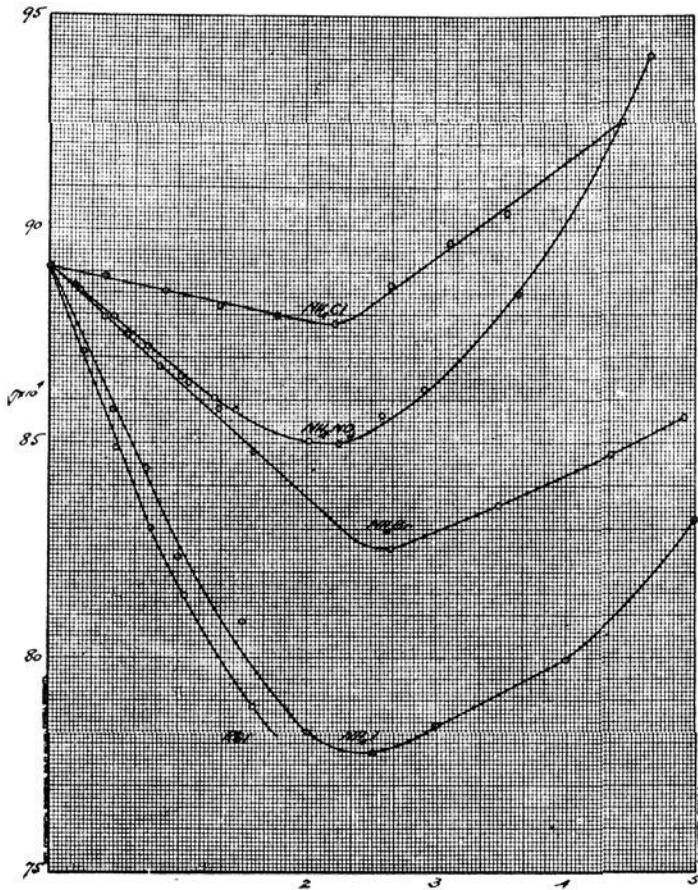
<i>m.</i>	<i>d.</i>	<i>η.</i>
0.264	1.0371	0.008714
0.528	1.0592	0.008489
0.792	1.1225	0.008303
1.056	1.1738	0.008147
1.583	1.2475	0.007887
1.758	1.2662	0.007918
2.639	1.4149	0.007796
2.931	1.4612	0.007870

In Fig. 1 the tabulated values of viscosity $\times 10^4$ are plotted as ordinates against the corresponding concentrations as abscissae. For convenience in comparison, Fig. 2 gives similar data for the corresponding potassium salts and for sodium chloride and sodium bromide. The curves in Fig. 1 are for 25° while those in Fig. 2 are for 18°.

The viscosity-concentration curves preserve the same order for the three bases, sodium, potassium and ammonium and apparently rubidium. In all cases the chlorides have the greatest and the iodides the least viscosity.

The ammonium salts depress the viscosity of water to a greater extent than the corresponding potassium salts, while rubidium iodide produces the maximum effect of all.

¹ Sprung, *Loc. cit.*



m.

Fig. 1.

In terms of the theory put forward by the author the minima in the viscosity-concentration curves are explained as due to equilibrium between the tendency of the cations to diminish the viscosity of the solvent and the tendency of the anions and the undissociated molecules to increase it.

At the minimum we find the solutions to be approximately 70 per cent. ionized.

Viscosity and Temperature.

Early in the study of the viscosity of pure liquids and solutions it was discovered that a slight variation in temperature produced a decided change in the viscosity, generally the viscosity being diminished by rise of temperature.

The attempts which have been made to express viscosity as a function of the temperature have been but partially successful.

Slotte¹ found that the viscosities of a series of chromate solutions at temperatures between 10° and 40° could be quite accurately determined by means of the formula

$$\eta = \frac{\gamma}{\alpha + t} - \beta, \quad (1)$$

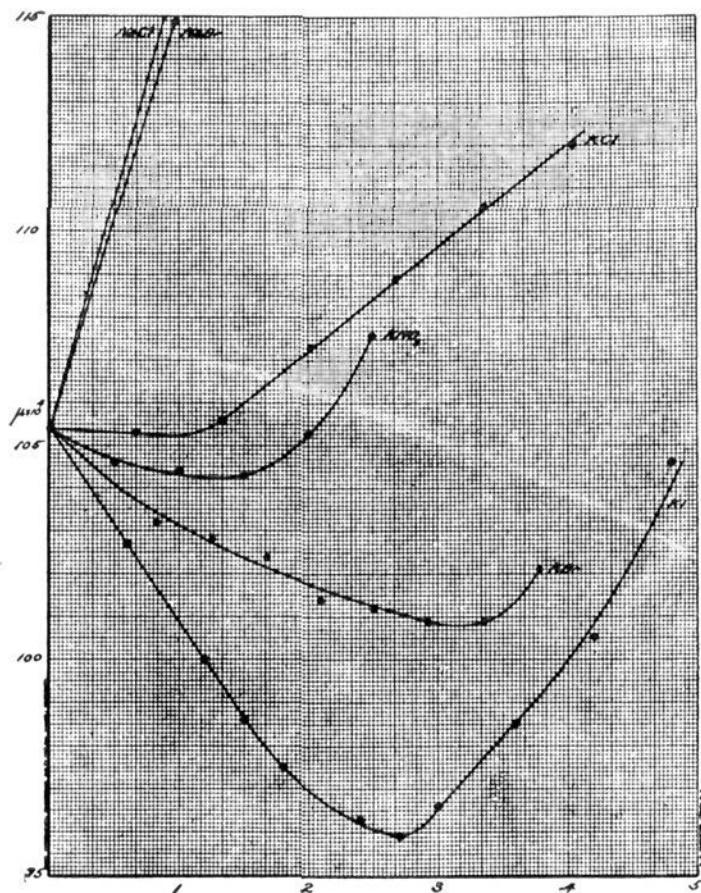
¹ *Wied. Ann.*, 14, 21.

where α , β , and γ are constants and t is the temperature.

Subsequently the same investigator¹ proposed the formula

$$\eta = \frac{c}{(\alpha + t)^n}, \quad (2)$$

α and c being constants and the exponent n varying in value from 1.6 to 1.9.



m.

Fig. 2.

From purely theoretical reasoning Graetz² suggested the formula

$$\eta = A \frac{t_c - t}{t - t_f},$$

in which A is a constant, t_c and t_f the critical and melting temperatures, respectively, and t the temperature at which the viscosity of the liquid is sought. This formula has been found to give good results for pure liquids within a limited range of temperature.

De Heen³ has proposed the formula

$$\eta = \left[\frac{e^{\frac{t}{n}} + A \eta_0 \frac{t}{t_f} - 1}{A e^n} \right],$$

¹ *Beibl.*, 16, 182.

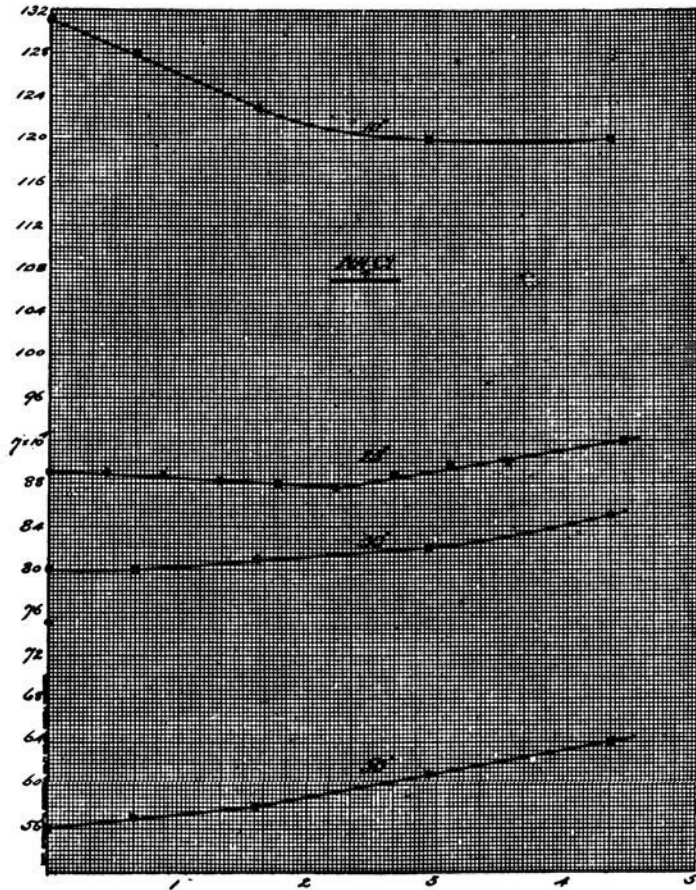
² *Wied. Ann.*, 24, 25.

³ *Bull. Ac. Belg.* (3), 11, 29.

where η_0 is the viscosity at 0° and A and n are constants.

Of the several formulae enumerated those of Slotte and Graetz appear to be most widely applicable.

The effect of change in temperature on the viscosities of the solutions studied is shown in Figs. 3 to 6, in which are given a series of viscosity-concentration isothermals.



m.

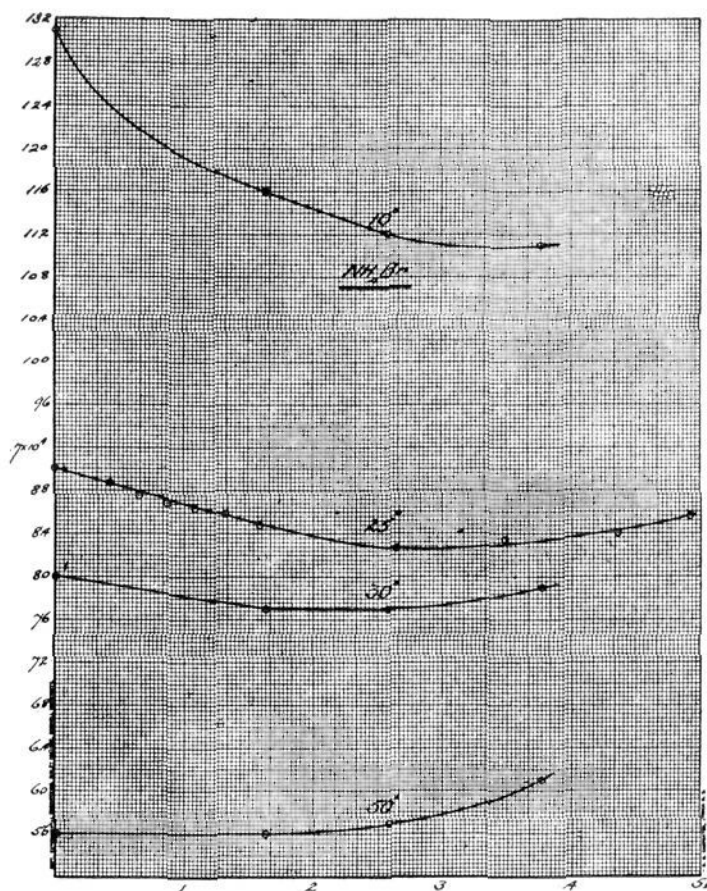
Fig. 3.

The solutions of ammonium chloride, ammonium bromide and ammonium nitrate become less and less negatively viscous as the temperature is raised, until at 50° , the temperature of the highest isothermals, they are all positive.

Ammonium iodide exhibits the same tendency but because of its marked negative viscosity it is evident that a higher temperature must be reached before the viscosity changes sign. The minimum in the viscosity-concentration isothermals shifts toward the more dilute region as the temperature is raised.

Since the isothermals are not parallel, it is evident that the rate of change of viscosity is not uniform at different temperatures.

The viscosities of thermal solutions of the salts studied in this and a



m .
Fig. 4.

previous investigation¹ can be calculated with a fair degree of accuracy by formula (1) of Slotte.¹

Tables XII to XXII give the observed and calculated values of η for different temperatures together with their differences, Δ . In every case the greatest difference occurs in the values for 10° , the calculated value being, with but two exceptions, too large. It is evident that the formula ceases to be applicable below 15° .

Neglecting the values for 10° and eliminating several values which are known to be slightly in error, the average departure from the observed value is 8 units in the fifth place of decimals.

The results for three salts, ammonium chloride, ammonium iodide and potassium chloride, are shown graphically in Fig. 7, the observed values being designated by a cross and the calculated by a small circle.

TABLE XII.

NaCl.

$\alpha = 27.$	$\beta = 0.0007.$		$\gamma = 0.5523.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
17.6	0.01163	0.01168	-0.00005
18	0.0116	0.01157	+0.00003
20	0.01109	0.01105	+0.00004
25	0.00978	0.00992	-0.00014

¹ *Loc. cit.*

TABLE XIII.

NaBr.

$\alpha = 27.$	$\beta = 0.0011.$		$\gamma = 0.5523.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01358	0.01383	-0.00025
25	0.00948	0.00952	-0.00004
30	0.00853	0.00859	-0.00006
50	0.00610	0.00607	-0.00003

TABLE XIV.

NaNO₃.

$\alpha = 27.$	$\beta = 0.00103$		$\gamma = 0.5523.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.0138	0.0139	-0.00010
17.6	0.01118	0.01135	-0.00017
20	0.01107	0.01066	+0.00041
25	0.00949	0.00959	-0.00010
30	0.00866	0.00866	0.00000
50	0.00617	0.00614	+0.00003

TABLE XV.

KCl.

$\alpha = 30.$	$\beta = 0.00101.$		$\gamma = 0.05520.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01270	0.01279	-0.00009
18	0.01055	0.01049	+0.00006
20	0.01004	0.01004	0.00000
25	0.00902	0.00902	0.00000
30	0.00814	0.00819	-0.00005
50	0.00580	0.00589	-0.00009

TABLE XVI.

KBr.

$\alpha = 30.$	$\beta = 0.00124.$		$\gamma = 0.5520.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01222	0.01256	-0.00033
18	0.01030	0.01026	+0.00004
30	0.00796	0.00796	0.00000
50	0.00574	0.00566	+0.00008

TABLE XVII.

KI.

$\alpha = 30.$	$\beta = 0.0015.$		$\gamma = 0.5520.$
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01180	0.01230	-0.00050
18	0.01007	0.01000	+0.00007
30	0.00760	0.00770	-0.00010
50	0.00553	0.00540	+0.00013

TABLE XVIII.

 KNO_3 .

$\alpha = 30.$	$\beta = 0.0010.$	$\gamma = 0.5520.$	
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01242	0.01280	+0.00038
18	0.01044	0.01050	-0.00006
20	0.00995	0.01004	-0.00009
30	0.00820	0.00820	0.00000
40	0.00690	0.00689	+0.00001
50	0.00585	0.00590	-0.00005

TABLE XIX.

 NH_4Cl .

$\alpha = 30.$	$\beta = 0.0011.$	$\gamma = 0.5520.$	
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01275	0.01270	+0.00005
17.6	0.01040	0.01049	-0.00009
25	0.00808	0.00893	-0.00085
30	0.00808	0.00810	-0.00002
50	0.00578	0.00580	-0.00002

TABLE XX.

 NH_4Br .

$\alpha = 30.$	$\beta = 0.0015.$	$\gamma = 0.5520.$	
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01220	0.01230	-0.00010
25	0.00866	0.00953	-0.00087
30	0.00780	0.00770	+0.00010
50	0.00570	0.00540	+0.00030

TABLE XXI.

 NH_4I .

$\alpha = 30.$	$\beta = 0.0018.$	$\gamma = 0.5520.$	
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01146	0.01200	-0.00054
15	0.01031	0.01047	-0.00016
20	0.00928	0.00924	+0.00004
25	0.00824	0.00823	+0.00001
30	0.00753	0.00740	+0.00013
50	0.00578	0.00556	+0.00022

TABLE XXII.

 NH_4NO_3 .

$\alpha = 30.$	$\beta = 0.0013.$	$\gamma = 0.5520.$	
$t.$	$\eta(\text{Observed}).$	$\eta(\text{Calculated}).$	$\Delta.$
10	0.01223	0.01250	-0.00027
25	0.00866	0.00873	-0.00007
30	0.00790	0.00790	0.00000
50	0.00568	0.00560	+0.00008

Viscosity and Conductivity.

As early as 1856, G. Wiedemann¹ called attention to the fact that viscosity and conductivity are related. From a study of solutions of copper sulphate he was led to formulate the relation

$$\frac{k\eta}{m} = \text{constant},$$

where η is the viscosity and k is the conductivity of the solution whose concentration is m .

Gotrian² measured the viscosity and conductivity of solutions at different temperatures, but failed to establish any clear relation between them.

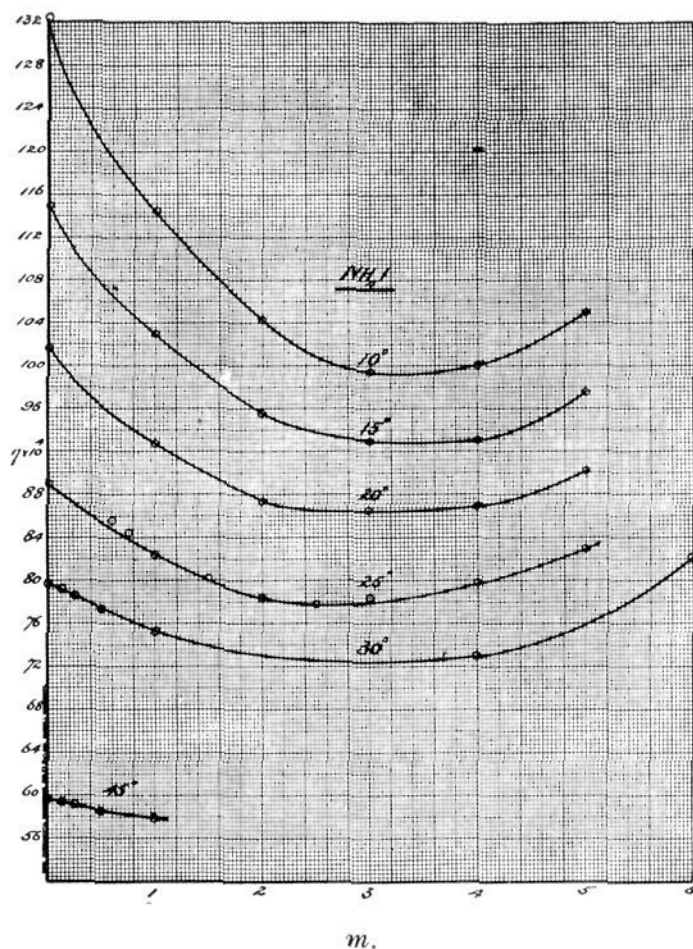


Fig. 5.

Later, Grossman³ recalculated Gotrian's results and found that the product of the viscosity by the conductivity was a constant, independent of the temperature.

Several empirical relations have been pointed out by various workers,

¹ *Pogg. Ann.*, **99**, 229.

² *Ibid.*, **157**, 130.

³ *Wied. Ann.*, **18**, 119.

among whom may be mentioned Arrhenius,¹ Euler,² Strindberg,³ and Holland.⁴

In 1896 Moore,⁵ in an investigation of the viscosities of some salt solutions, attempted to find some relation between viscosity and conductivity, but without much success. He makes the significant remark

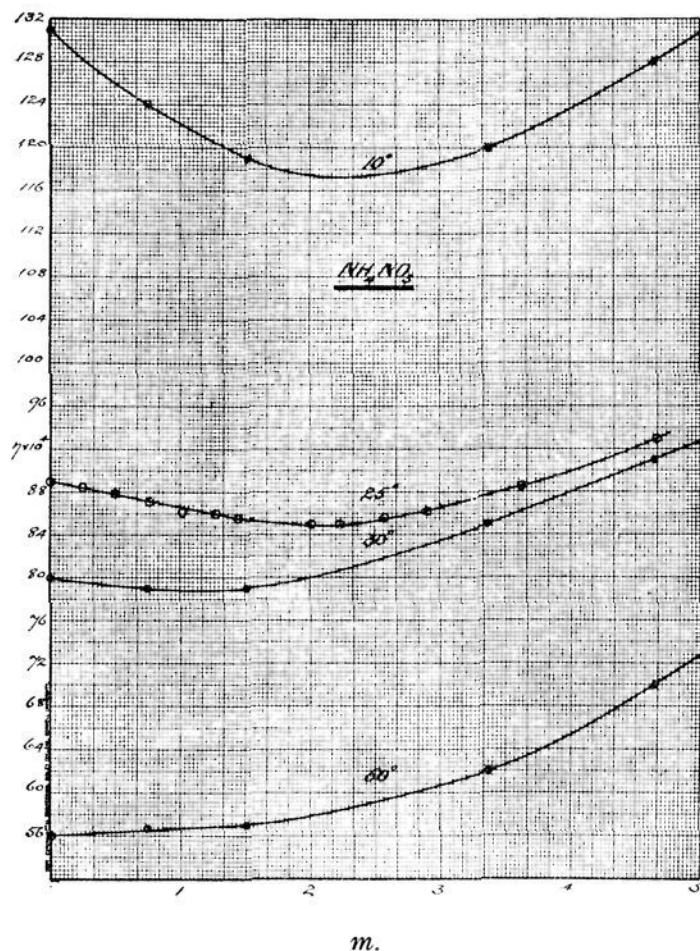


Fig. 6.

that "more extended observations must be made upon the relation of viscosity and conductivity, perhaps even some new method of comparison arrived at, before the two subjects are placed in their right relation."

The recent work of Bousfield and Lowry⁶ has led to the formula

$$\frac{k_t}{k_o} = \frac{\rho_v}{\rho_o} (1 + bt)^n e^{-at}$$

connecting conductivity and temperature, the parenthesis being Slotte's expression for the change in viscosity with temperature.

¹ *Z. physik. Chem.*, 9, 487.

² *Ibid.*, 35, 536.

³ *Ibid.*, 14, 221.

⁴ *Wied. Ann.*, 50, 261.

⁵ *Phys. Rev.*, 3, 321.

⁶ *Proc. Roy. Soc.*, 74, 280.

It seemed of interest to compare the viscosities of the normal solutions with their conductivities as given by Kohlrausch,¹ making use of Wiedemann's relation.

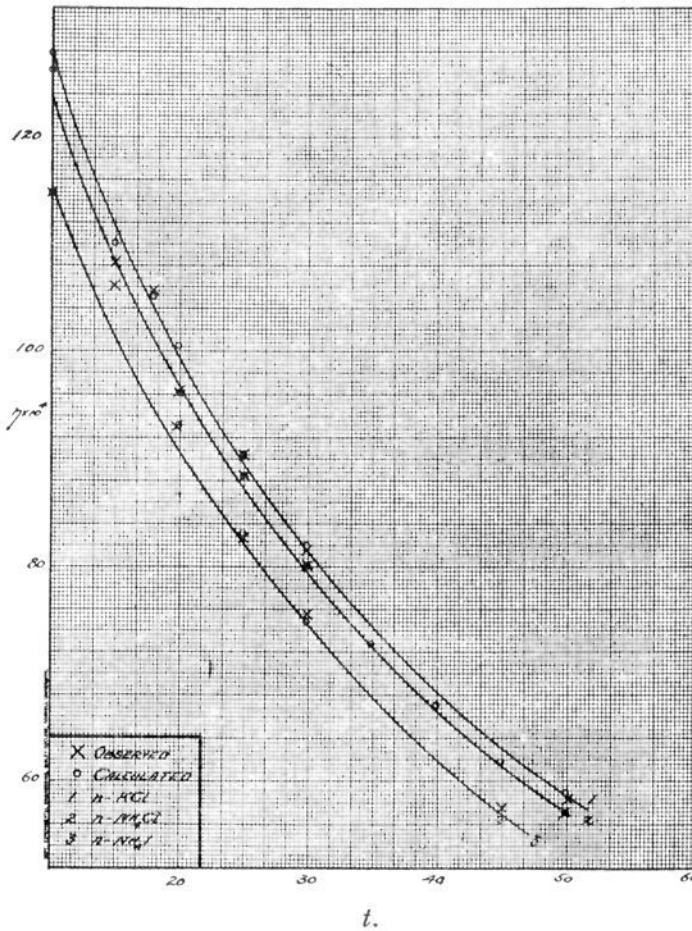


Fig. 7.

The results are given in Table XXIII, λ denoting the equivalent conductivity.

TABLE XXIII.

Temp. = 18°.

	η .	λ	$\eta\lambda$.
NaCl.....	0.0116	74.4	0.863
NaBr.....	0.0115	70.5	0.811
NaNO ₃	0.0114	66.0	0.752
KCl.....	0.0105	98.2	1.031
KBr.....	0.0103	103.7	1.069
KI.....	0.0101	103.4	1.041
KNO ₃	0.0104	80.4	0.839
NH ₄ Cl.....	0.0103	97.0	0.999
NH ₄ Br.....	0.0101	102.9	1.039
NH ₄ I.....	0.00977	104.0	1.016
NH ₄ NO ₃	0.0101	88.9	0.901

¹ Das Leitvermögen der Elektrolyte.

The values of $\eta\lambda$ for the halogen salts of potassium and ammonium are nearly constant, the average value being 1.032.

It is evident, however, that some other factor besides those given is required to establish the relation between viscosity and conductivity.

Discussion of Results.

A survey of the results obtained with the potassium, ammonium and rubidium salts examined seems to confirm the theory suggested by the author, that the phenomenon of negative viscosity is due to a tendency of the cations to lower the viscosity of the solvent while the anions and the undissociated molecule tend to increase it. Jones and Veazey¹ have called attention to the fact that those salts whose cations have the greatest atomic volumes exhibit negative viscosity when dissolved, provided the atomic volumes of the anions are not so small as to counteract the effect of the cations.

In terms of their theory we should expect, for a series of salts having the same anion, that the lowering of the viscosity would vary directly with the atomic volume of the cation. These authors have shown this to be approximately true for the normal solutions of the chlorides of potassium, rubidium and caesium. From Figs. 1 and 2 we find that rubidium iodide lowers the viscosity to a greater extent than potassium iodide while the lowering produced by ammonium iodide is slightly less than that produced by rubidium iodide. Owing to scarcity of material it was impossible to extend the measurements on rubidium iodide to more concentrated solutions.

Differences in the degree of dissociation at different temperatures cannot be employed to explain the greater negative viscosity observed in each case for the lower temperatures.

It is probable that the lower temperatures favor the formation of molecular complexes which, owing to greater volume and smaller surface, tend to diminish the viscosity.

Dunstan² has furnished experimental evidence for the formation of these complexes, which are stable only at relatively low temperatures.

By means of this supposition it is possible to explain the case of negative viscosity presented by urea at 8° and other instances of negative viscosity observed with solutions of non-electrolytes.

The empirical formula of Slotte for calculating viscosities at various temperatures is found to apply to the solutions studied between 15° and 20°.

Assuming with Wiedemann that the migration velocity varies inversely with the viscosity for a fixed potential gradient, the product of

¹ Jones and Veazey, *Loc. cit.*

² *J. Chem. Soc.*, **85**, 817; *Z. physik. Chem.*, **49**, 590.

the viscosity and conductivity should give a constant. It has been found that this relation is only approximately true for the solutions investigated.

COLUMBIA UNIVERSITY, March, 1908.

THE ACTION OF VARIOUS ANHYDROUS CHLORIDES ON TELLURIUM AND ON TELLURIUM DIOXIDE.

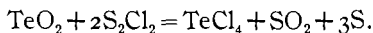
BY VICTOR LENHER.

Received February 25, 1908.

In an earlier paper¹ the action of sulphur monochloride on elementary tellurium has been shown to result in the production of tellurium tetrachloride and sulphur, when the sulphur monochloride is in excess, while Krafft and Steiner,² in studying this reaction, observed that when an excess of tellurium is heated with sulphur monochloride, tellurium dichloride results.

Further study on the action of tellurium and the dioxide with active reagents has shown that with many of the anhydrous chlorides, especially with those which are liquid at the ordinary temperature, tellurium tetrachloride is produced. In certain cases the tetrachloride immediately separates from the solution in pure form while with a number of reagents of this character actual union takes place and a crystalline condensation product separates.

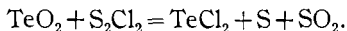
Tellurium Dioxide and Sulphur Monochloride.—Tellurium dioxide, when treated with an excess of sulphur monochloride, is transformed into the tetrachloride, sulphur dioxide being formed at the same time, according to the equation:



Analysis, TeCl_4 : Calculated, Cl, 52.79; Te, 47.21.

Found, Cl, 52.07; Te, 46.65.

When, on the other hand, an excess of tellurium dioxide is heated with sulphur monochloride, the reducing action of this reagent steps in and the result is that the dichloride of tellurium is formed, thus:



The formation of tellurium tetrachloride by the action of excess of sulphur monochloride on tellurium dioxide takes place readily; the reaction can be materially hastened by warming, and under these conditions, preparation of a large amount of the tetrachloride can be accomplished in a very short time. Extraction of the salt with carbon bisulphide is advisable in order to remove an excess of sulphur.

Behavior of the Oxychlorides of Sulphur toward Tellurium and Tellurium

¹ THIS JOURNAL, 24, 188.

² Ber., 34, 560.