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ON THE VISCOSITY OF CERTAIN SALT SOLUTIONS.

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THE subject of Viscosity was first taken up by Poiseuille,¹ who used a method depending upon the transpiration of the liquid through capillary tubes. Coulomb, in studying the same subject, observed the damping of a magnetic needle or bar when vibrating in the liquid investigated. This method was also extensively used by O. E. Meyer,² Grotian,³ and others. Still a third method has been developed by Helmholtz, who placed the solution to be studied in a hollow sphere, and observed the behavior of the sphere when oscillated.

These methods have led to very different results. König⁴ modified the method of Coulomb and used in the place of the swinging rod, a sphere, the equation of motion of which Kirchhoff had solved, and for which the theory can be completely developed. For calculation König made use of the expression by Kirchhoff as extended and completed by Boltzman, and reached the conclusion that the values obtained for viscosity by Coulomb's method were in complete agreement with the results obtained by allowing the liquid to flow through a capillary tube. Though the agreement

¹ *Memoirs des Savants Étrangers*, T. IX. *Pogg. Ann.*, Vol. LVIII., p. 434.

² *Pogg. Ann.*, Vol. CXIII., pp. 55, 193, 383. ³ *Pogg. Ann.*, Vol. CLVII., p. 130.

⁴ *Wied. Ann.*, Vol. XXXII., p. 193.

of results by the different methods is of great interest and importance, yet observers have generally preferred the original method due to Poiseuille, and that because of its simplicity. The method requires also a considerably smaller amount of the solution, and admits of a much easier and more accurate temperature regulation.

Among the earlier investigations on the subject of viscosity may be mentioned those of Graham,¹ whose results suggest the presence of hydrates in solution. He states further that "slow transpiration and low volatility go together." Later investigations by Rellstab² dealt with several organic liquids, while numerous experiments were made by Hübner³ on the salts of the chloride family. Sprung⁴ investigated a great many cases of varying concentration and temperature, the latter ranging from 0° to 60° C.

Hagenbach⁵ developed the mathematical formula for transpiration. His expression for viscosity (η) reduces, when correction for the velocity of flow is omitted, to the form known as Poiseuille's formula: $\eta = \frac{\pi}{8} \frac{r^4 h s t}{l v}$. Herein r denotes the radius of the capillary; h , the height of pressure column; s , specific gravity, and therefore the product of h and s the pressure; v represents the volume that transpires in time, t ; and l is used to designate the length of the capillary tube.

Pribam and Handl⁶ have made extensive observations on the viscosity of organic solution and stoichiometrical relations of the same. The careful work of Gartenmeister⁷ in this field should not be omitted. Grotian⁸ was the first to make extended comparisons of viscosity and conductivity of salt solutions. Slotte's⁹ investigations cover a number of chromates and he shows that the temperature variation in viscosity, η , can be expressed by a formula, $\eta = c(1 + bt)^n$, where c , b , and n are constants of the liquid.

¹ Royal Society Proceedings, XI., p. 381. 1860.

² Inaugural Dissertation, Bonn, 1868.

⁵ Pogg. Ann., Vol. CIX., p. 385.

³ Pogg. Ann. Vol. CL., p. 248.

⁶ Wien Ber., Vols. 78, 80.

⁴ Pogg. Ann., Vol. CLIX., p. 1.

⁷ Zeitschrift die Ph. Chem., Vol. VI., p. 524.

⁸ Pogg. Ann., Vol. CLVII, p. 130; Vol. CLX., p. 238. Wied. Ann., Vol. VIII., p. 530.

⁹ Wied. Ann., Vol. XIV., p. 13.

Since the announcement of the dissociation theory by Arrhenius, the subject of viscosity of solutions has had a much deeper interest, and experiments have been carried on, both trying to establish some stoichiometrical relation, and to establish a relation between viscosity and conductivity. With this idea in view, Arrhenius has made many investigations. In his first experiments¹ he shows that the viscosity is a function of x and y , or $H(x, y)$, where x and y express either percentage of substance in solution, or gram-equivalent per liter. We may say $\eta = H(x, y) = A^x B^y$, where A and B are constants of the solution. For a single salt in solution this reduces to $\eta = A^x$. Wagner² and Reyher³ validated this law for a great many solutions. In Gartenmeister's⁴ experiments the Arrhenius exponential formula is not so well satisfied. Reyher found a characteristic relation between the friction or viscosity of free acids and those of the sodium salts, according as a strong or weak acid was present. This variation he made to depend upon the unequal dissociation of the strong and weak acids. The dissociation theory has given great confidence to the belief in a relation of viscosity to conductivity. However, G. Wiedemann,⁵ previous to this theory, noticed that the friction which the ions undergo varies in the same way as inner friction; *i.e.* viscosity. The mobility of the ions must then be a function of their fluidity. Arrhenius showed that conductivity did not depend upon fluidity alone. This investigator made a strong point when he showed that the introduction of a non-conducting substance into an electrolyte affected both its conductivity and its viscosity in the same way.⁶ Other experimenters, by a direct comparison of conductivities and viscosities, have come to the conclusion that while the conductivities of a series of salts increased, the viscosities in general decreased. However, the increasing and decreasing series stand in no definite ratio to each other.

The following experiments have followed much in the same line.

¹ Zeitschrift die Ph. Chem., Vol. I., p. 285.

² Zeitschrift die Ph. Chem., Vol. V., p. 31.

³ Zeitschrift die Ph. Chem., Vol. II., p. 744.

⁴ Zeitschrift die Ph. Chem., Vol. VI., p. 524.

⁵ Pogg. Ann., Vol. XCIX., p. 177.

⁶ Zeitschrift die Ph. Chem., Vol. IX., p. 487.

The viscosities of a series of salts have been determined, and, in so far as was possible, the conductivities of the same compared with their viscosities.

The method employed was the one due to Poiseuille, the apparatus being similar to that used by Arrhenius. A glass vessel *A* (Fig. 1), of about 24 c.cm. capacity, is connected with two tubes, *a* and *b*, above and below respectively. Each tube has a diameter of about 4 mm. A stopcock closes *a* about 4 cm. from *A*. *b* was joined to a capillary tube *d*, some 40 cm. long. The lower end of the capillary dips into the solution to be studied, contained in a glass vessel, *B*, of about 200 c.cm. capacity. *B* is kept water-

Fig. 1.

tight by means of a rubber cork *e*, and is encased in a brass support *h*. Exactly 50 c.cm. of the solution was always brought into the vessel *B*, and the extremity *c* of the capillary brought into the plane of the upper edge of the brass casing *h*. This was done to secure a constant average height of pressure in all cases. But this was later proven to be an unnecessary precaution, as a change in the length of the capillary, amounting to 18 cm., only made a difference of 2.5 seconds in the transpiration of water at 18° C. The liquid is brought into the vessel *A* to some point *a'* by exhausting the air through a rubber tube *f*. The time of flow was taken between two marks on tubes *a* and *b*. As the mean height of the pressure column is constant, it is evident that the pressure

of the different liquids subjected to transpiration varies directly as their specific gravities. So that to obtain the transpiration at constant pressure, it was only necessary to multiply the observed time of flow by the specific gravity of the solution. The time of flow of water at 18° C. was taken as standard. The ratio of the corrected time of flow of a solution to that of water gives the relative viscosity in terms of water as unity. Should the absolute viscosity be desired, it is only necessary to multiply this result by the absolute value of water. Relative values only have been calculated, as the object was to make a comparison of solutions. The temperature was regulated by a water-bath, and two ther-

mometers enabled one to note the temperature to tenths of a degree. Hagenbach's correction for velocity of transpiration was sufficiently small to neglect in all cases.

The specific gravities of the solutions were determined by means of a calibrated Mohr's balance, which enabled one to take readings to the fourth decimal place. It was part of the original intention to make the solutions from weighed portions of the salts and of fixed molecular (*e.g.* double normal, normal, half normal, etc.) contents, but the discovery of a mistake in the weight of a crucible made it necessary to interpret in many cases the per cent of salt in solution from tables of percentages and specific gravities. Solutions of K_2CO_3 , KOH, NaOH, and K_2SO_4 were made from Kohlrausch's tables.¹ Solutions of Na_2CO_3 , $KHCO_3$, $NaHCO_3$, $KHSO_4$, Na_2HPO_4 , NaH_2PO_4 , $K_2C_2O_4$ and $NaHC_4H_4O_6$ were made from carefully weighed quantities of the salts. Solutions of K_3PO_4 , K_2HPO_4 , KH_2PO_4 were kindly loaned by Herr Forch. All other solutions were made from Landolt and Bernstein's Tabellen (*2te Auflage*). The specific gravities of solutions of Na_2CO_3 check well with Kohlrausch's tables, but not so well with those of Landolt and Bernstein. The specific gravities of Na_2HPO_4 differ also slightly from the latter tables and in solutions of $K_2C_2O_4$ the difference is quite large. However, specific gravities of $K_2C_2O_4$ interpolated from Landolt and Bernstein's Tabellen give a viscosity curve of doubtful character.

The time of flow was noted over considerable range of temperature from which the time transpiration at 18° was graphically interpolated. By repeated observation the error in time is reduced to about 0.3 seconds. In the following table of observations and results, m denotes the gram-molecular contents; s , the specific gravity; T , the time; and η , the calculated viscosities. In the rows containing neither T nor s , the values of m and η have been graphically interpolated.

¹ Kohlrausch: Leitfaden der practical Physik, 7^{te} Auflage.

TABLE I.

Na_2CO_3				NaHCO_3			
m	s	T	η	m	s	T	η
0.00	0.9987	197.0	1.000	0.00	0.9987	194.5	1.000
0.25	1.0250	220.6	1.120	0.25	1.0139	205.5	1.057
0.5	1.0517	251.0	1.274	0.5	1.0286	218.0	1.121
1.0	1.0980	328.5	1.667	1.0	1.0575	245.0	1.260
2.0	1.1880	616.2	3.128				
K_2CO_3				KHCO_3			
0.00	0.9987	197.0	1.000	0.00	0.9987	194.5	1.000
0.25	—	—	1.059	0.25	1.0146	200.5	1.031
0.273	1.0340	210.0	1.066	0.495	1.0298	206.5	1.062
0.4788	1.0577	223.0	1.132	0.5	—	—	1.065
0.5	—	—	1.138	1.0	1.0581	218.0	1.121
0.9456	1.1100	258.0	1.310	1.98	1.1149	250.0	1.285
1.0	—	—	1.341	2.0	—	—	1.290
1.974	1.2183	381.0	1.934				
2.0	—	—	1.950				

TABLE II.

NaHSO_4				NaOH			
m	s	T	η	m	s	T	η
0.00	0.9987	194.5	1.0000	0.00	0.9987	194.5	1.0000
0.25	1.0186	206.0	1.059	0.25	1.0099	206.0	1.059
0.5	1.0386	214.0	1.100	0.5	1.0212	215.5	1.108
1.0	1.0753	245.0	1.260	1.0	1.0425	240.0	1.234
2.0	1.1475	315.5	1.622	2.0	1.0843	299.0	1.537
4.0	1.2810	559.0	2.874	4.0	1.1551	552.0	2.837
				8.0	1.2786	1470.0	7.557
K_2SO_4				KOH			
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.0000
0.1195	1.0165	198.1	1.019	0.25	—	—	1.025
0.125	—	—	—	0.456	1.0212	203.0	1.044
0.243	1.0328	204.5	1.051	0.5	—	—	1.051
0.25	—	—	1.052	0.92	1.0433	213.5	1.098
0.49	1.0650	214.0	1.100	1.00	—	—	1.110
0.50	—	—	1.106	1.82	1.0864	235.5	1.211
KHSO_4				2.0	—	—	1.237
0.00	0.9987	194.5	1.0000	4.0	1.1793	307.0	1.578
0.5	1.0439	209.5	1.075	6.8	1.2900	452.0	2.324
1.0	1.0866	223.5	1.149				
2.0	1.1712	263.0	1.352				

TABLE III.

Na_2HPO_4				Na_3PO_4			
m	s	T	η	m	s	T	η
0.00	0.9987	194.5	1.000	0.00	0.9987	194.5	1.000
0.125	1.0190	211.3	1.086	0.125	—	—	1.098
0.25	1.0366	231.4	1.189	0.14	1.0222	214.9	1.105
0.5	1.0741	277.5	1.427	0.25	—	—	1.220
NaH_2PO_4				0.276	1.0440	242.3	1.246
0.00	0.9987	194.5	1.000	0.50	—	—	1.504
0.25	1.0184	209.3	1.076	0.54	1.0860	307.2	1.579
0.5005	1.0391	230.0	1.182	K_3PO_4			
1.001	1.0776	274.0	1.409	0.00	0.9987	194.5	1.000
2.002	1.1677	450.0	2.313	0.125	1.0227	208.5	1.070
KH_2PO_4				0.25	1.0471	219.0	1.126
0.00	0.9987	194.5	1.000	0.5	1.0933	252.5	1.298
0.25	1.0220	205.5	1.057	1.0	1.1805	342.2	1.759
0.5	1.0442	223.0	1.146	K_2HPO_4			
1.0	1.0885	254.0	1.306	0.00	0.9987	194.5	1.000
H_3PO_4				0.125	1.0167	202.0	1.039
0.00	0.9987	194.5	1.000	0.25	1.0343	213.0	1.095
0.25	1.0120	207.0	1.064	0.5	1.0700	234.0	1.206
0.5	1.0251	222.3	1.143	1.0	1.1383	300.0	1.542
1.0	1.0508	255.0	1.311	2.0	1.2633	449.0	2.309
2.0	1.1022	338.3	1.739				

TABLE IV.

$\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$					$\text{NaKC}_4\text{H}_4\text{O}_6$				
m	s	T	η		m	s	T	η	
0.00	0.9987	194.5	1.000		0.00	0.9987	194.5	1.000	
0.141	1.0185	209.0	1.075		0.20	1.0273	212.5	1.092	
0.25	—	—	1.148		0.25	—	—	1.112	
0.281	1.0368	226.0	1.162		0.40	1.0547	231.0	1.188	
0.5	—	—	1.335		0.50	—	—	1.252	
0.562	1.0730	269.0	1.383		0.789	1.1087	287.0	1.476	
1.0	—	—	1.823		1.0	—	—	1.679	
1.121	1.1427	395.0	2.031		1.656	1.2112	484.0	2.488	
$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$					$\text{K}_2\text{C}_4\text{H}_4\text{O}_6$				
0.00	0.9987	194.5	1.000		0.00	0.9987	194.5	1.000	
0.233	1.013	207.5	1.067		0.1815	1.0267	205.5	1.057	
0.25	—	—	—		0.25	—	—	1.080	
0.467	1.0269	221.5	1.139		0.363	1.0525	220.0	1.131	
0.5	—	—	1.160		0.5	—	—	1.195	
0.833	1.0542	256.0	1.316		0.7345	1.1036	255.0	1.342	
1.0	—	—	1.412		1.0	—	—	1.489	
1.478	—	330.0	1.696		1.48	1.2072	363.0	1.866	
1.666	1.1092	365.0	1.853		1.5	—	—	(1.883)	
$\text{C}_4\text{H}_6\text{O}_4$					$\text{K}_2\text{C}_2\text{O}_4$				
0.00	0.9987	194.5	1.000		0.00	0.9987	194.5	1.000	
0.242	1.0076	204.2	1.050		0.25	1.0283	204.0	1.049	
0.25	—	—	1.052		0.5	1.0571	214.5	1.103	
0.483	1.0166	215.0	1.105		1.0	1.1121	239.5	1.232	
0.5	—	—	(1.110)		1.5	1.1663	270.2	1.389	
$\text{H}_2\text{C}_2\text{O}_4$					$\text{NaHC}_2\text{H}_2\text{O}_6$				
0.00	0.9987	194.5	1.000		0.00	0.9987	194.5	1.000	
0.25	—	—	1.045		0.147	1.0121	205.5	1.056	
0.326	1.0146	206.0	1.059		0.25	—	—	1.094	
0.5	—	—	1.072		0.294	1.0256	217.0	1.116	
0.665	1.0300	217.5	1.118		0.441	1.0386	228.5	1.175	
0.848	1.0370	224.5	1.154		0.5	—	—	(1.198)	
1.0	—	—	(1.199)						

Curves.

The curves (Figs. 2, 3, 4, and 5) correspond to Tables I., II., III., and IV. of data respectively. The curve for H_2SO_4 (Fig. 3) is drawn from data by Grotian and is given in order to show

Fig. 2.

the effect of displacing an atom of hydrogen in sulphuric acid. Curves for K_2SO_4 and KH_2PO_4 are not shown, as they nearly coincide with 2KOH and H_3PO_4 respectively.

Discussion of Results.

The viscosity of sodium salts is invariably greater than that of the potassium salts, and both are greater than that of the corresponding acids. The effect of the hypothetical displacement of the first atom of hydrogen by a given base is generally not so marked as the second displacement by the same base. $\text{NaHC}_4\text{H}_4\text{O}_6$ is an exception. The effect of the second atom of Na and K in the phosphoric acid group (see Fig. 4) is very marked. Whether

the difference is due to the position of the hydrogen atom in the molecule is a question, perhaps, easier to raise than to answer

Fig. 3.

satisfactorily. Coincident with the entrance of the second atom of Na or K is the change from marked acid to basic character,

Fig. 4.

the ordinary phosphate Na_2HPO_4 and NaOH , which would make one accept the viscosity curve Na_3PO_4 with some hesitation. So that on the whole it would be rather difficult to draw conclusions

which also suggests that the first change in H_3PO_4 ($= \text{H} - \text{PO}_2 - \text{OH} - \text{OH}$) took place in the hydroxide radical, the second in the acid radical, and the third again in the hydroxide radical. The curve for KH_2PO_4 lies too near H_3PO_4 to be credited extensively. More confidence is to be placed in the results for H_3PO_4 than KH_2PO_4 , as Slotte's observations for H_3PO_4 fall practically upon the curve here given for that acid. Again the neutral phosphate Na_3PO_4 breaks up very easily in the presence of H_2O into

concerning changes in the radicals from the viscosities. So much difficulty does not present itself with the organic compounds. The addition of $(\text{CH}_2)_2$ to $\text{C}_2\text{H}_2\text{O}_4$ ($=\text{COOH}-\text{COOH}$) (see Fig. 5, curves), giving $\text{COOH}-\text{CH}_2-\text{CH}_2-\text{COOH}$, increases the vis-

Fig. 5.

cosity over three times as much as the substitution of potassium for hydrogen in $(\text{COOH})_2$. The farther substitution of two hydroxyl radicals for two atoms of H in $(\text{CH}_2)_2$ gives also a marked increase, and also greater than the effect of potassium substi-

tuted in $\text{H}_2\text{C}_2\text{O}_4$. Again, a comparison of curves for $\text{H}_2\text{C}_2\text{O}_4$ and $\text{K}_2\text{C}_2\text{O}_4$ with the curves for $\text{C}_4\text{H}_6\text{O}_4$ and $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ shows a marked difference in the effects of potassium on the two salts. In the first pair of solutions potassium entered the carboxyl, giving $\text{COOK}-\text{COOK}$, while in the second group the element potassium has worked upon the hydroxide, yielding $\text{COOH}-\text{CHOK}-\text{CHOK}-\text{COOH}$.

Arrhenius Exponential Formula.

When Arrhenius announced the exponential formula, $\eta = A^x$, he only tested it to 1.5 gram-molecule solutions. Wagner, who validated the law for so many solutions, did not go above the normal solution. So that it was thought well to see if such a formula would hold for more concentrated solutions. To test the validity of the law for very dilute solutions, where the law is most serviceable, it would be necessary to limit oneself to very narrow range of and small changes in temperature. It would be imperative to use a bulb A (Fig. 1) of smaller volume and a capillary d (Fig. 1) of very small bore. The latter invariably clogs and prevents accurate results. Even such precautions would, at the best, only give very small differences, and failure to observe these precautions could not account for the variations from the logarithmic law observed in these experiments. The logarithmic curve, which would represent the viscosities of the more dilute solutions of NaOH , *e.g.* would, if extended to 4 and 8 molecule solutions, give values 36 per cent and 75 per cent too small respectively. No other solutions show so great a divergence. Yet in the double normal solutions the agreement is rarely better than 3 per cent to 5 per cent.

Conductivities and Viscosities.

The values for A in the following table have been taken direct from the tables of observations on η , except in the phosphoric acid group, where A is reckoned from the equation $\eta = A^x$ and $x = m = \frac{1}{3}$. The conductivities K are those of the normal solutions except when otherwise noted. Only those salts are given

for which the conductivities could be learned. They are divided in four groups corresponding to Tables I., II., III., and IV. of Viscosities respectively.

TABLE V.

Substances.	A	$10^9 \cdot K$
$\frac{1}{2}$ Na ₂ CO ₃	1.274	42.7
$\frac{1}{2}$ NaHCO ₃	1.121	37.9
$\frac{1}{2}$ K ₂ CO ₃	1.138	66.2
$\frac{1}{2}$ KHCO ₃	1.065	61.3
NaOH	1.234	149.0
KOH	1.11	171.8
$\frac{1}{2}$ Na ₂ SO ₄	—	47.5
$\frac{1}{2}$ NaHSO ₄	1.10	—
$\frac{1}{2}$ K ₂ SO ₄	1.106	67.2
$\frac{1}{2}$ KHSO ₄	1.075	173.6
$\frac{1}{3}$ Na ₃ PO ₄	1.305	97.5
$\frac{1}{3}$ Na ₂ HPO ₄	1.260	79.6
$\frac{1}{3}$ NaH ₂ PO ₄	1.105	69.8
$\frac{1}{3}$ H ₃ PO ₄	1.08	20.0
$\frac{1}{2}$ C ₄ H ₆ O ₆	1.160	46.04
$\frac{1}{2}$ C ₄ H ₆ O ₄	1.110	16.03
$\frac{1}{2}$ C ₂ H ₂ O ₄	1.070	26.7
$\frac{1}{2}$ K ₂ C ₂ O ₄	1.100	68.8

$\left. \begin{array}{l} 97.5 \\ 79.6 \\ 69.8 \end{array} \right\} \frac{1}{32} \text{ normal solution.}$

$\left. \begin{array}{l} 46.04 \\ 16.03 \\ 26.7 \end{array} \right\} \frac{1}{16} \text{ normal.}$

That, while the viscosities in general decrease, the conductivities of a series of salts increase, as noted in the early part of this article, cannot be concluded at all from these salts. This action is noticeable, however, in passing from the sodium salt to the potassium in the first and second group, but when one passes either from sodium carbonate or from potassium carbonate to the acid salts, viscosities and conductivities increase and decrease together. The sulphates behave in the same manner. In the third or phosphate group, in passing from Na₃PO₄ to H₃PO₄, both viscosities and conductivities decrease. In the fourth or organic group, there is an irregularity in the conductivity column. This list, though small, is enough to show that there is little hope for a successful comparison of viscosity and conductivity, without an extended series of observations,

and that, too, with dilute solutions in which the increase in the viscosity of the solvent will be largely due to the ions, as it is the viscosity of the latter alone with which we have to deal in conductivity.

Conclusions.

1. The viscosity of solutions decreases quite rapidly with rise in temperature, but the character of this decrease is very different for different concentrations and for different salt solutions.¹

2. Stoichiometrical relations, though doubtless existing, are neither very definite nor convincing.

3. The Arrhenius exponential formula or law, though affording an excellent method for comparison of viscosities of dilute, even normal, solutions, does not hold good for the more concentrated solutions.

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

¹ Thorpe and Rodgers, Proc. Royal Soc., 55, p. 148, have pointed out that temperatures of equal slopes is an excellent method for comparison of viscosity. These experiments were in a measure completed when the article by Thorpe and Rodgers appeared, and the range of temperature not wide enough to make such a comparison.