A VISCOSITY FORMULA FOR BINARY MIXTURES, THE ASSOCIATION DEGREES OF CONSTITUENTS BEING TAKEN INTO CONSIDERATION. X. THE VISCOSITY OF AQUEOUS SOLUTIONS OF ELECTROLYTES.

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Much attention has been paid to the study of the viscosity of strong electrolyte solutions since Jones and Dole(1) proposed in 1929 an empirical equation:

$$\eta^* = 1 + A\sqrt{c} + Bc\,,$$

where η^* is the specific viscosity of a salt solution, c the concentration in mols per litre, and A and B constants. Falkenhagen, Dole, and Vernon(2)

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(1) Jones and Dole, *J. Am. Chem. Soc.*, **51** (1929), 2950.
(2) Papers summarized in *Phil. Mag.*, **14** (1932), 537.

made a brilliant success in evaluating the coefficient A from the ion-atmosphere theory in terms of the well-known physical constants, i.e.

$$A = \frac{12.78\times 10^{-10}\sqrt{\frac{N}{1000}}\sqrt{\frac{P_1 z_1}{z_1+z_2}}}{\sqrt{4\pi DkT}}\cdot$$

$$\frac{\varepsilon}{\eta_0}\left\{\frac{z_1^3}{L_1}+\frac{z_2^3}{L_2}-\frac{\frac{4z_1^3 z_2^3}{L_1 L_2}\left(\frac{L_1}{z_1^2}-\frac{L_2}{z_2^2}\right)^2}{\left[\sqrt{\frac{L_1}{z_1}+\frac{L_2}{z_2}}+\sqrt{(z_1+z_2)\left(\frac{L_1}{z_1^2}+\frac{L_2}{z_2^2}\right)}\right]^2}\right\}$$

where ε is the unit charge of electricity in e.s.u. ($\varepsilon=4.77\times10^{-10}$), N Avogadro's number ($N=6.06\times10^{23}$), P_1 the number of, say, positive ions formed in dissociation, L_1, L_2, and z_1, z_2, the ionic molar conductance and numerical values of the valencies of positive and negative ions respectively, D and η_0 the dielectric constant and the viscosity of the solvent, k Boltzmann's constant ($k=1.37\times10^{-16}$ ergs/degree), and T the absolute temperature.

Wolfenden and his coworkers(3) pointed out that the approximate additivity for individual ions might exist in the coefficient B.

The Falkenhagen-Dole-Vernon theory tells us that the interionic forces acting on the viscosity of electrolyte solutions may become negligibly small as compared with the rapid increase of the viscosity in suitably high concentration, and the Jones-Dole equation which serves at present only for the estimation of the coefficient A in accord with the former theory has no great rôle in an unknown field of more concentrated solutions.

Experimental works on the viscosity of concentrated solutions of various electrolytes have been done in earlier times and have thrown more interesting problems than that of dilute solutions. Hübner(4), Sprung(5), Wagner(6) and others observed the curious phenomenon showing the viscosities less than that of water which they termed "negative viscosity". In fact, some salts of Cs, Rb, K and NH_4 produce negative viscosities. All electrolytes except these show viscosities greater than that of water. The name of "positive viscosity" is often used as an antonym to negative viscosity.

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(3) Cox and Wolfenden, *Proc. Roy. Soc. London*, **145** A (1934), 475; Laurence and Wolfenden, *J. Chem. Soc.*, **1934**, 1144.

(4) Hübner, *Pogg. Ann.*, **157** (1873), 130.

(5) Sprung, *ibid.*, **159** (1876), 1.

(6) Wagner, *Z. physik. Chem.*, **5** (1891), 31.

It is generally observed, however, in the case of the negative viscosity that the viscosity lowers with the increase of concentration more and more in a certain range of concentration, but this tendency suddenly ceases at a suitable concentration, thus showing a minimum value, and at still higher concentration the viscosity increases acceleratedly with the increasing concentration even showing the positive viscosity. The temperature also influences the negative viscosity remarkably in such a manner that it gradually turns out to the positive viscosity as the temperature rises.

In certain cases the inter-ionic forces veil the negative viscosity at extremely low concentration as readily understood from the sign of the sum of the second and third terms in the Jones-Dole equation.

Among many proposed explanations for this anormalous phenomenon of negative viscosity the suggestions made by Jones and Veazay(7) and by Getman(8) are worth mentioning first. These authorities stated that it was due to the cations to lower the viscosity of the solvent while the anions and the undissociated molecules always increased it, and moreover Jones and Veazay pointed out that the salts of K, Rb, and Cs having the highest atomic volumes known showed the marked negative viscosity. Tammann and Rabe(9) who discovered the parallelism between the curve viscosity versus concentration and the curve viscosity versus pressure for aqueous solutions of salts emphasized that the negative viscosity was due to this effect of salts to increase the internal pressure of the solvent. Rabinovich(10) made an extensive study on the cause of the negative viscosity in consideration of many factors acting upon the viscosity of solutions, especially those lowering the internal friction of the solvent, and came to the conclusion that the depolymerization of solvent molecules alone was adequate to explain the negative viscosity and that what was stated by the above-mentioned investigators was self-explaining from this consideration.

Judging from Rabinovich's idea which seems to represent all the explanations hitherto made on this subject, it may be acknowledged that the negative viscosity depends solely on the action of ions—especially of cations, but not on the action of undissociated molecules.

Recently one of the present writers(11) has put forward the assumption that an associated molecule of a liquid is a grouping of single mole-

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(7) Jones and Veazay, *Am. Chem. J.*, **37** (1907), 405.
(8) Getman, *J. Am. Chem. Soc.*, **30** (1908), 721.
(9) Tammann and Rabe, *Z. anorg. allgem. Chem.*, **168** (1927), 73.
(10) Rabinovich, *J. Am. Chem. Soc.*, **44** (1922), 954.
(11) Ishikawa, this Bulletin, **4** (1929), 5, 25, 149, 288; **5** (1930), 47, 117; **8** (1933), 280, 293; **9** (1934), 155.

cules which have the self-same dimension with singly existing molecules and the difference between them is no other than the abrupt greatness of the cohesion force of the former in comparison with that of the latter, and has deduced the following viscosity formula for a binary mixture which is fairly calculable from the constants of the constituents provided that no chemical reactions take place on mixing them:

$$\eta = \frac{\eta_1 k_1 a_1(1-z_m)+\eta_2 k_2 a_2 z_m}{k_1 a_1(1-z_m)+k_2 a_2 z_m} \quad \dots\dots\dots\dots\dots\dots \quad (1)$$

where η, a, k, with suffixes 1 and 2 signify the viscosities, the association degrees and his so called "field constants" of component 1 and 2 respectively; z_m a formal molar fraction of component 2. The above formula indicates that the share of each component viscosity consists of two factors of equal importance, the molecular attraction force presumably proportionate to the association degree and the number of molecules, i.e. it is expressed, in fraction, by $\frac{k_1 a_1(1-z_m)}{k_1 a_1(1-z_m)+k_2 a_2 z_m}$ for component 1 or $\frac{k_2 a_2 z_m}{k_1 a_1(1-z_m)+k_2 a_2 z_m}$ for component 2. The validity of this equation has been already justified with numerous examples of organic non-electrolytes, and has proved to be valid and always superior to other noted empirical equations containing several arbitrary constants. It has also been shown that his equation is fairly applicable to the special case where one of the component is a solid substance such as naphthalene or diphenyl. Ishikawa has made a further success in expressing the viscosity of a binary mixture which forms a molecular compound in solution, i.e.

$$\eta = \frac{\eta_1 k_1 a_1(1-z_m)+\eta_2 k_2 a_2 z_m}{k_1 a_1(1-z_m)+k_2 a_2 z_m} + C(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \dots\dots\dots \quad (2)$$

where ν_1 and ν_2 are respectively the molecular numbers of component 1 and 2 in the molecular compound, and C is a constant which varies with the temperature or more closely

$$C = C_0(\eta_1^{\nu_1}\eta_2^{\nu_2})^{\frac{m}{\nu_1+\nu_2}}$$

in which C_0 and m are constants independent of the temperature and concentration.

He has also found that m in the above relation takes the value 2 if the molecular compound firmly exists without dissociation, but takes a lower value if the molecular compound suffers ionic or molecular dissociation. Equation (2) has merits that it furnishes us with a reliable means for determining the composition of the molecular compound formed as well as it expresses quantitatively the viscosity of a binary mixture of any kind.

For one more example, the mixture of pyridine (1) and acetic acid (2) will be here adopted from the recent measurements done by Swearingen and Heck⁽¹²⁾ over a wide range of temperature. The fusion curve of this mixture studied quite recently by Swearingen and Ross⁽¹³⁾ indicated two maxima: one corresponded to a compound $C_5H_5N{\cdot}CH_3COOH$ and the other, a hidden maximum, corresponded probably to $C_5H_5N{\cdot}4CH_3COOH$ or $C_5H_5N{\cdot}5CH_3COOH$ according to their opinion. The curve viscosity versus concentration, however, showed no peculiarity at the former composition, but a marked maximum at the latter.

Now for the estimation of the products ka of the respective liquids we have fortunately the viscosity data at 30°C. of a physical mixture of pyridine and ethyl acetate observed by Puschin and Pinter⁽¹⁴⁾, from which we have evaluated that of pyridine to be 0.76 as referred to that of benzene. Take this value and 0.82 for acetic acid as previously obtained, or put $\frac{k_2a_2}{k_1a_1}=\frac{0.82}{0.76}=1.08$, which is presumably invariant for the temperature studied, in equation (2). Then the difference between the observed viscosity values (η) and thus calculated (η_0) (η_0^* as appears in other tables means its specific value) can be obtained. Fig. 1 illustrates the values $\eta-\eta_0$ divided by $(1-z_m)z_m$ as ordinate and z_m as abscissa. The horizontal line up to $z_m=0.45$ indicates the existence of $C_5H_5N{\cdot}CH_3COOH$ which can not be found directly from the curve viscosity versus concentration, and a curve which begins at $z_m=0.5$ and increases rapidly upwards at higher concentration is the strong indication of $C_5H_5N{\cdot}5CH_3COOH$ as clearly seen from Fig. 2 in which the values $\eta-\eta_0$ divided by $(1-z_m)z_m^5$ is taken as ordinate. The temperature variation of C of these compounds are completely expressed by the following equations respectively:

$$\log C_{1:1}=1.145+\frac{1.44}{1+1}\log(\eta_1\eta_2)$$

and

$$\log C_{1:5}=3.537+\frac{2.00}{1+5}\log(\eta_1\eta_2^5)\,.$$

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(12) Swearingen and Heck, *J. Phys. Chem.*, **38** (1934), 395.
(13) Swearingen and Ross, *J. Phys. Chem.*, **38** (1934), 1085.
(14) Puschin and Pinter, *Z. physik. Chem.*, **151** (1930), 135.

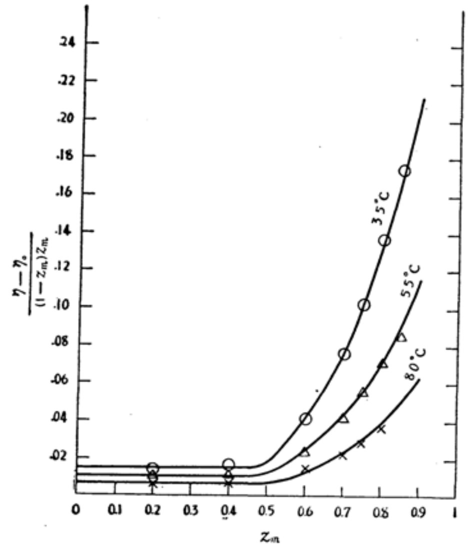

Fig. 1.

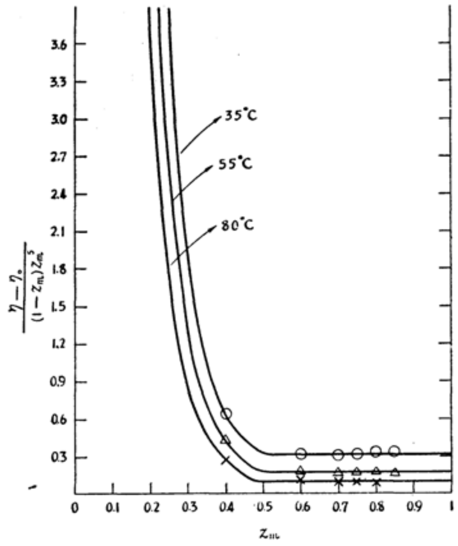

Fig. 2.

The extreme coincidence between the observed and calculated values is shown in Table 1.

Table 1.

t°C.	Molecular compound $C_5H_5N \cdot CH_3COOH$		Molecular compound $C_5H_5N \cdot 5CH_3COOH$	
	$C_{obs.}$ (mean)	$C_{calc.}$	$C_{obs.}$ (mean)	$C_{calc.}$
35	0.0156	0.0155	0.327	0.324
45	0.0129	0.0122	0.235	0.230
55	0.0107	0.0102	0.175	0.177
65	0.0077	0.0087	0.138	0.140
75	0.0074	0.0074	0.108	0.110
80	0.0068	0.0068	0.097	0.096

The present paper is contributed to the study of the viscosity of electrolyte solutions from the same standpoint of view, the Falkenhagen effect being taken into account.

Before entering into further study, the writers have, in this place, to introduce their conception upon the negative viscosity: The chief factor of the negative viscosity depends on no other than the viscosity of the solute or, more correctly to say, the solutional viscosity of the salt, though other investigators considered it to be the depolymerizing action of cations against solvent molecules. As regards the solutional viscosity there have been few descriptions in the literature. Rabinovich supposed it to be of high value enough to compare with the viscosity of a solid, but Kendall(15) estimated it to be of the same order as that of ordinary organic solvents by using his cube-root formula. Ishikawa also calculated the solutional viscosities of naphthalene and diphenyl to be nearly equivalent as estimated by Kendall, i.e. 0.0265 and 0.0541 at 25°C. respectively. Quite recently Castiglioni(16) observed that camphor and menthol in oleic acid had the solutional viscosities less than the solvent, giving the additional proof for the validity of the Ishikawa formula, although unfortunately we find his mistake in recalculating molar fractions of the solute from its weight percentages: i.e. the solutional viscosity of menthol at 20°C. has the value 0.02596 against the value of the solvent 0.03235 at the same temperature.

It may be probable to consider such a case that the solutional viscosity of a salt differs not so much from the viscosity of water, and if the former is less than the latter, the negative viscosity results according to our theory. The question why the negative viscosity disappears when the concentration sufficiently increases may be easily answered by postulating the solvation or hydration effect as in the pyridine-acetic acid mixture above cited.

In general, the following three cases for the solutional viscosity less than the viscosity of water may be assumed: Firstly, no hydration takes place and negative viscosity is observed throughout the concentration; secondly, a slight hydration takes place so that negative viscosity appears distinctly at low concentration but becomes less distinct or disappears in high concentration; and thirdly, a marked hydration takes place in such a degree that no negative viscosity is perceptible even in low concentration. That when solutional viscosity is greater than the viscosity of water the positive viscosity results is self-evident from the above consideration.

In the following treatment, aqueous solutions of alkali chlorides and nitrates will be taken as adequate examples of the different cases mentioned above.

For simplicity, we rewrite equation (2) in the following form:

$$\eta^{**}=1+\frac{(H-1)Kz_m}{1-z_m+Kz_m}+C^*(1-z_m)^{\nu_1}z_m^{\nu_2} \quad \cdots\cdots\cdots\cdots \quad (3)$$

where H is the specific solutional viscosity of the solute, the viscosity of water being taken as unity, K a positive characteristic constant of the solute relative to that of water, and C^* a constant independent of the

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(15) See Hatschek's "The Viscosity of Liquids", London (1928).

(16) Castiglioni, *Gazz. chim. ital.*, **63** (1933), 395; **64** (1934), 465.

concentration but dependent on the temperature. η^{**} denotes the difference between the observed specific viscosity and the viscosity caused by the inter-ionic forces according to the Falkenhagen-Dole-Vernon theory, though this correction may not be strictly rigorous in high concentration, yet the error thereby may be inappreciable.

Differenciate equation (3) and take the limit when z_m tends to 0, we have

$$\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right) = (H-1)K + C^{*}\nu_2 \lim_{z_m \to 0} z_m^{\nu_2-1} \quad \ldots\ldots\ldots\ldots \quad (4)$$

As readily seen from equations (3) and (4), since $\lim_{z_m \to 0}\left(\frac{d\eta^{**}}{dz_m}\right)$ is not always negative even when H is smaller than unity unless $C^{*}=0$ or $\nu_2 > 1$, the positive viscosity is not always an indication of H greater than unity, when hydration takes place.

As it has been proved in the previous studies that the value of K is invariant in the small range of temperature, the following two equations at 18° and 25°C. are obtained:

$$\eta_{18}^{**} = 1 + \frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} + C_{18}^{*}(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \ldots\ldots\ldots\ldots \quad (5)_1$$

$$\eta_{25}^{**} = 1 + \frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} + C_{25}^{*}(1-z_m)^{\nu_1} z_m^{\nu_2} \quad \ldots\ldots\ldots\ldots \quad (5)_2$$

where suffixes 18 and 25 denote the respective values at 18° and 25°C.

Putting $\frac{H_{25}-1}{H_{18}-1} = q$ and $\frac{\eta_{25}^{**}-1}{\eta_{18}^{**}-1} = r$, we have

$$(\eta_{25}^{**}-1) - q(\eta_{18}^{**}-1) = (C_{25}^{*} - qC_{18}^{*})(1-z_m)^{\nu_1} z_m^{\nu_2}$$

or

$$r = q + (C_{25}^{*} - q\,C_{18}^{*})\frac{(1-z_m)^{\nu_1} z_m^{\nu_2}}{\eta_{18}^{**}-1} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

In the simplest case where no hydration takes place, equation (6) reduces to

$$r = q = \text{a constant,} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

since C_{18}^{*} and C_{25}^{*} vanish.

Also from equations $(5)_1$ and $(5)_2$ the following equations readily come, if no hydration occurs,

$$\eta_{18}^{**} = 1 + \frac{(H_{18}-1)Kz_m}{1-z_m+Kz_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)_1$$

$$\eta_{25}^{**} = 1 + \frac{(H_{25}-1)Kz_m}{1-z_m+Kz_m} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (8)_2$$

For these special cases, a method of determining the values of H and K has been given in Part V, yet again another will be shown below. Transform, say, equation $(8)_1$, then we obtain

$$\frac{z_m}{\eta_{18}^{**}-1} = \frac{1}{(H_{18}-1)K} + \frac{(K-1)}{(H_{18}-1)K} z_m \quad \cdots\cdots\cdots\cdots\cdots \quad (9)$$

A linear relation exists between $\frac{z_m}{\eta_{18}^{**}-1}$ and z_m, which enables us to find H and K by the use of ordinary graphical method.

Among the salts studied, the three salts CsCl, RbCl, and $CsNO_3$ are found to be good examples of this simple case. They have no hydrates in the studied concentration range and all show the solutional viscosities less than the viscosity of water. The coincidence between the observed and calculated viscosity values are satisfactory as seen from Tables 2, 3, and 4.

Table 2. CsCl.(17)

z_m	18°C.		25°C.		r	
	$\eta^*_{\text{obs.}}$	η^*_0	$\eta^*_{\text{obs.}}$	η^*_0		
0.00448	0.986	0.986	0.992	0.9925	0.64	mean 0.60
0.00893	0.973	0.973	0.985	0.985	0.61	
0.01771	0.952	0.953	0·975	0.974	0.57	
0.03478	0.927	0.927	—	—	—	

$$\left.\begin{aligned} A_{18} &= 0.00472 \ H_{18} = 0.8296 \\ A_{25} &= 0.00489 \ H_{25} = 0.8997 \end{aligned}\right\} K = 24.28$$

Table 3. RbCl.(17)

z_m	18°C.		25°C.		r	
	$\eta^*_{\text{obs.}}$	η^*_0	$\eta^*_{\text{obs.}}$	η^*_0		
0.00448	0.990	0.990	0.995	0.995	0.58	mean 0.56
0.00893	0.980	0.980	0.990	0.990	0.56	
0.01771	0.965	0.965	0.983	0.982	0.55	
0.03478	0.943	0.941	—	—	—	

$$\left.\begin{aligned} A_{18} &= 0.00472 \ H_{18} = 0.8577 \\ A_{25} &= 0.00488 \ H_{25} = 0.9194 \end{aligned}\right\} K = 21.37$$

Table 4. $CsNO_3$, (Merton).(18)

z_m	18°C.		25°C.		r	
	$\eta^*_{\text{obs.}}$	η^*_0	$\eta^*_{\text{obs.}}$	η^*_0		
0.000419	0.9986	0.9979	0.9988	0.9986	(0.92)	
0.000929	0.9960	0.9949	0.9970	0.9964	(0.81)	
0.001976	0.9899	0.9889	0.9926	0.9918	0.77	mean 0.77
0.002885	0.9844	0.9838	0.9882	0.9881	0,79	
0.004665	0.9752	0.9746	0.9811	0.9811	0.79	
0.006059	0.9681	0.9680	0.9761	0.9761	0.77	
0.008853	0.9561	0.9561	0.9671	0.9671	0.77	
0.01132	0.9470	0.9469	0.9604	0.9601	0.77	
0.01516	0.9347	0.9345	0.9518	0.9508	0.76	

$$\left.\begin{aligned} A_{18} &= 0.00486 \ H_{18} = 0.7939 \\ A_{25} &= 0.00504 \ H_{25} = 0.8415 \end{aligned}\right\} K = 33.37$$

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(17) Quoted from Internat. Crit. Tab. V.
(18) Merton, *J. Chem. Soc.*, **97** (1910), 2454.

In the cases of $RbNO_3$, KCl, and KI, it is observed generally that r takes a constant value at low concentration, but that it soon rapidly increases or decreases when the concentration reaches a point at which the amount of hydrating molecules begins discontinuously to be appreciable.

Provided that equation (9) is fortunately applicable to these solutions at the concentration range containing no hydrates, it is not difficult to require the composition of hydrates as well as H and K, because the viscosity increase owing to the hydrates can be easily calculated by the use of equation (5), though some ambiguity may exist in the determination of ν_1 unless accurate measurements of viscosities of the wide range of concentration can be had. The calculation thus made are tabulated in Tables from 5 to 7.

Table 5. $RbNO_3$, (Smith, Wolfenden and Hartley).(19)

z_m	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$		
0.00169	0.9925	0.9920	0.0005	—	—	0.9942	0.9945	-0.0003	—	—	(0.81)	
0.00265	0.9877	0.9873	0.0004	—	—	0.9910	0.9912	-0.0002	—	—	0.75	mean **0.74**
0.00342	0.9839	0.9838	0.0001	—	—	0.9885	0.9887	-0.0002	—	—	0.75	
0.00468	0.9785	0.9785	0.0000	—	—	0.9849	0.9849	0.0000	—	—	0.73	
0.00911	0.9628	0.9623	0.0005	—	—	0.9738	0.9733	0.0005	—	—	0.73	
0.00914	0.9623	0.9623	0.0000	—	—	0.9733	0.9733	0.0000	—	—	0.74	
0.01416	0.9483	0.9482	0.0001	—	—	0.9631	0.9631	0.0000	—	—	0.74	
0.01817	0.9410	0.9390	0.0020	(3.4×10^2)	0.9413	0.9588	0.9566	0.0022	(3.7×10^2)	0.9591	0.72	
0.02039	0.9374	0.9347	0.0027	(3.3×10^2)	0.9379	0.9563	0.9534	0.0029	(3.4×10^2)	0.9570	0.72	
0.02737	0.9313	0.9234	0.0079	4.0×10^2	0.9312	0.9542	0.9454	0.0088	4.4×10^2	0.9539	0.69	
0.03495	0.9306	0.9141	0.0165	4.0×10^2	0.9301	0.9572	0.9387	0.0185	4.5×10^2	0.9564	0.65	
0.04187	0.9339	0.9073	0.0266	3.8×10^2	0.9348	0.9639	0.9339	0.0300	4.2×10^2	0.9642	0.59	
				mean **3.9×10^2**					mean **4.3×10^2**			

$$A_{18} = 0.00485 \qquad H_{18} = 0.8387$$
$$A_{25} = 0.00498 \qquad H_{25} = 0.8814$$
$$\left.\begin{matrix} H_{18} \\ H_{25} \end{matrix}\right\} K = 37.19$$

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(19) Smith, Wolfenden and Hartley, *J. Chem. Soc.*, **1931**, 403.

Table 6. KCl.(17)

z_m	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^3}$	$\eta_{calc.}^*$		
0.00180	0.998	0.998	0.000	—	—	0.999	1.000	-0.001	—	—	(0.79)	
0.00448	0.995	0.994	0.001	—	—	0.998	0.999	-0.001	—	—	(0.76)	
0.00893	0.990	0.989	0.001	—	—	0.997	0.997	0.000	—	—	0.48	mean **0.44**
0.01335	0.985	0.986	-0.001	—	—	0.996	0.996	0.000	—	—	0.43	
0.01771	0.982	0.983	-0.001	—	—	0.995	0.995	0.000	—	—	0.43	
0.02632	0.980	0.978	0.002	(1.0×10^2)	0.981	0.997	0.994	0.003	(1.7×10^2)	0.998	0.35	
0.03478	0.982	0.975	0.007	(2.1×10^2)	0.982	1.002	0.993	0.009	2.2×10^2	1.002	0.20	
0.04315	0.987	0.973	0.014	1.8×10^2	0.986	1.010	0.992	0.018	2.3×10^2	1.009	-0.12	
0.05130	0.994	0.972	0.022	1.7×10^2	0.993	1.021	0.992	0.029	2.3×10^2	1.020	-0.91	
0.06725	1.017	0.970	0.047	1.7×10^2	1.018	1.050	0.992	0.058	2.0×10^2	1.054	5.13	
				mean **1.7×10^2**					mean **2.2×10^2**			

$$\left.\begin{array}{ll} A_{18} = 0.00484 & H_{18} = 0.9471 \\ A_{25} = 0.00500 & H_{25} = 0.9765 \end{array}\right\} \quad K = 40.39$$

Table 7. KI.(17)

z_m	18°C.					25°C.					r	
	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^2}$	$\eta_{calc.}^*$	$\eta_{obs.}^*$	η_0^*	$\eta^*-\eta_0^*$	$\frac{\eta^*-\eta_0^*}{(1-z_m)z_m^2}$	$\eta_{calc.}^*$		
0.00180	0.9908	0.9907	0.0001	—	—	0.993	0.992	0.001	—	—	(0.79)	
0.00448	0.9768	0.9768	0.0000	—	—	0.981	0.981	0.000	—	—	0.84	mean **0.84**
0.00893	0.9561	0.9561	0.0000	—	—	0.964	0.964	0.000	—	—	0.84	
0.01771	0.9228	0.9227	0.0001	—	—	0.936	0.936	0.000	—	—	0.84	
0.03478	0.898	0.877	0.021	17.8	0.898	0.915	0.898	0.017	(14.5)	0.919	0.85	
0.05130	0.892	0.848	0.044	17.8	0.892	0.916	0.873	0.043	17.1	0.917	0.79	
0.08266	0.916	0.802	0.114	18.2	0.912	0.951	0.844	0.107	17.0	0.953	0.63	
0.1120	0.978	0.790	0.188	16.8	0.987	1.030	0.826	0.204	18.3	1.021	-0.51	
0.1191	1.003	0.787	0.216	17.3	1.007	—	—	—	—	—	—	
				mean **17.6**					mean **17.5**			

$$\left.\begin{array}{ll} A_{18} = 0.00481 & H_{18} = 0.6929 \\ A_{25} = 0.00497 & H_{25} = 0.7420 \end{array}\right\} \quad K = 20.20$$

It is worth mentioning that there appears to exist in solution as yet unknown hydrates such as $3RbNO_3 \cdot H_2O$, $3KCl \cdot H_2O$, and $2KI \cdot H_2O$, these salts, however, having long been considered to form no hydrates. The reason of the missing of these hydrates depends probably on the neglect because of their small water contents when expressed in weight percentage.

It happens, of course, that in the cases where hydration takes place at zero concentration as are the cases NaCl, LiCl, and $LiNO_3$, no methods of calculating H and K are employable and consequently ν_1 and ν_2 are not determined directly. The determination of ν_1 and ν_2 in such cases, however, may be done by the help of equation (6) as follows.

At first, calculate the values of r i.e. $\frac{\eta_{25}^{**}-1}{\eta_{18}^{**}-1}$. Remembering that q and $(C_{25}^{*}-qC_{18}^{*})$ are constants, r is linear against the values $\frac{(1-z_m)^{\nu_1} z_m^{\nu_2}}{\eta_{18}^{**}-1}$ provided that the suitable values of ν_1 and ν_2 are taken, and therefore the graphical method is applicable in the determination of the values of ν_1 and ν_2 as well as of q, these values having, of course, to be checked by the relation:

$$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^{\nu_1} z_m^{\nu_2}} = \text{a constant.}$$

Table 8. NaCl.(17)

z_m	$\eta^{*}_{18,\text{(obs.)}}$	$\eta^{*}_{25,\text{(obs.)}}$	r	$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^2 z_m}$	$\eta^{*}_{25(\text{calc.})}$ fr. $\eta^{*}_{18(\text{obs.})}$
0.00180	1.0085	1.009	1.059	(0.50)	1.009
0.00448	1.0205	1.022	1.080	(0.58)	1.023
0.00893	1.0405	1.046	1.148	(0.90)	1.045
0.01771	1.0840	1.094	1.127	(0.89)	1.091
0.03478	1.192	1.205	1.071	(0.80)	1.203
0.05130	1.329	1.341	1.038	0.74	1.341
0.06725	1.498	1.509	1.021	0.73	1.509
0.08266	1.700	1.706	1.007	0.75	1.706
				mean **0.74** q = **0.932**	

$A_{18} = 0.00585$ $A_{25} = 0.00601$

Table 9. $LiNO_3$.(17)

z_m	$\eta^{*}_{18,\text{(obs.)}}$	$\eta^{*}_{25,\text{(obs.)}}$	r	$\frac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^3 z_m}$	$\eta^{*}_{25(\text{calc.})}$ fr. $\eta^{*}_{18(\text{obs.})}$
0.00090	1.0060	1.0060	1.000	—	(1.0064)
0.00180	1.0109	1.0116	1.080	0.44	1.0116
0.00448	1.0259	1.0277	1.075	0.43	1.0277
0.00893	1.0503	1.0534	1.068	0.40	1.0535
0.01771	1.0996	1.1063	1.070	0.42	1.1060
0.03478	1·2110	1.2230	1.058	0.39	1.2226
0.05130	1.341	1.358	1.048	0.41	1.358
0.06725	1.492	1.514	1.046	0.45	1.511
0.08266	1.670	1,694	1.035	0.43	1.692
0.09761	1.874	1.898	1.027	0.41	1.897
				mean **0.42** q = **0.991**	

$A_{18} = 0.00685$ $A_{25} = 0.00696$

The results thus calculated from the viscosity values of the solution of NaCl, and LiNO$_3$ are shown in Tables 8 and 9 with the reference of Fig. 3 for LiNO$_3$. These salts appear to have a hydrate throughout the concentration studied, although the accurate composition of their hydrate may not be hoped for on account of the difficulty of deciding ν_1, yet it may be sure that one and only one molecule of these salts combines with water molecules more than one i.e. hydrates NaCl·mH$_2$O and LiNO$_3$·nH$_2$O, the plausible values of m and n being 2 and 3 respectively. Lowitz(20) obtained NaCl·2H$_2$O as a monoclinic crystal, and Mellor(20) mentioned two hydrates LiNO$_3$·3H$_2$O and 2LiNO$_3$·H$_2$O, the transition point lying at 29.6°C.

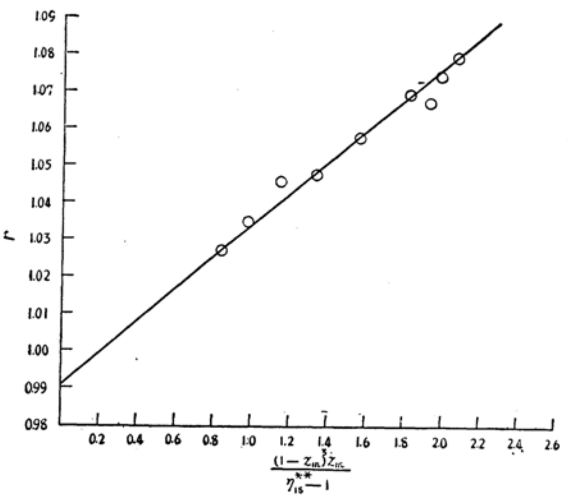

Fig. 3.

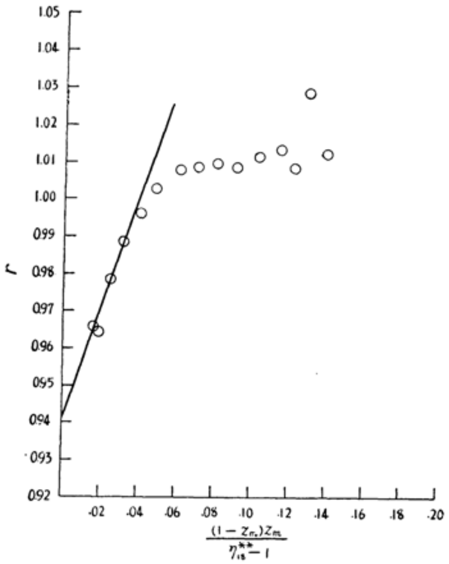

Fig. 4.

With regard to LiCl somewhat different manner is observed as compared with NaCl and LiNO$_3$. The curve r versus $\frac{(1-z_m)z_m}{\eta_{18}^{**}-1}$ in Fig. 4 apparently shows two or more sets of lines, one being distinctly an inclined straight line and others being curved, points, however, lying somewhat complicatedly. The former indicates the existence of a hydrate LiCl·H$_2$O, and the value of q (0.941) obtained from the intersection of this line and the vertical axis may be considered as more reliable than the values obtained from other lines, in which H and K take negative values. Taking this

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(20) See Mellor's "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", II, London (1922), 554, 815, 542.

q, we proceed to the further calculation as shown in Table 10. In this case two hydrates more are postulated: $LiCl \cdot 2H_2O$ and $2LiCl \cdot 4H_2O$ besides $LiCl \cdot H_2O$. Bogorodsky⁽²⁰⁾ obtained three hydrates $LiCl \cdot 3H_2O$, $LiCl \cdot 2H_2O$, and $LiCl \cdot H_2O$, the transition temperature of $LiCl \cdot 3H_2O$ to $LiCl \cdot 2H_2O$ being −15°C., while that of $LiCl \cdot 2H_2O$ to $LiCl \cdot H_2O$ being 12.5°C. From this reference it may be concluded that in the aqueous solution of LiCl exist two hydrates $LiCl \cdot H_2O$ and $LiCl \cdot 2H_2O$ with this double molecules, but not $LiCl \cdot 3H_2O$ at the temperature range between 18° and 25°C.

Table 10. LiCl, (Green).⁽²¹⁾

z_m	η_{18}^*(obs.)	η_{25}^*(obs.)	γ	$\dfrac{(\eta_{25}^{**}-1)-q(\eta_{18}^{**}-1)}{(1-z_m)^{\nu_1} z_m^{\nu_2}}$		η_{25}^*(calc.) fr. η_{18}^*(obs.)
0.0018	1.0136	1.0137	1.009	(0.44)	mean **0.63** ($\nu_1 = 2$, $\nu_2 = 1$)	1.0140
0.0036	1.0271	1.0273	1.008	(0.45)		1.0280
0.0090	1.0692	1.0700	1.013	0.51		1.0711
0.0180	1.144	1.148	1.029	0.69		1.147
0.0271	1.225	1.227	1.009	0.60		1.228
0.0362	1.312	1.316	1.014	0.65		1.315
0.0543	1.511	1.517	1.012	0.72		1.513
0.0727	1.747	1.754	1.009	12.8	mean **12.7** ($\nu_1 = 4$, $\nu_2 = 2$)	1.754
0.0912	2.035	2.046	1.010	12.3		2.048
0.1098	2.401	2.413	1.009	12.2		2.417
0.1284	2.878	2.893	1.008	12.9		2.891
0.1473	3.530	3.539	1.011	13.4		3.531
0.1663	4.430	4.417	0.9961	13.8 (1.33)	mean **1.43** ($\nu_1 = 1$, $\nu_2 = 1$)	4.403 (4.431)
0.1854	5.707	5.653	0.9886	1.44		5.652
0.2046	7.550	7.409	0.9786	1.46		7.404
0.2240	10.102	9.777	0.9642	(1.16)		9.824
0.2289	11.523	11.159	0.9656	1.38		11.168
					$q = $ **0.941**	

$A_{18} = 0.00662$ $A_{25} = 0.00665$

As already stated, no method of finding the values of H and K are available in case a solution shows positive viscosity, but even in such a case it is possible only to know whether H is greater than unity or not. Since H is known to become greater as the temperature rises, we may have the following simple relation:

$$\left.\begin{array}{lll} & \text{If } q > 1, & H_{18},\ H_{25} > 1, \\ \text{and} & \text{If } 1 > q > 0, & H_{18},\ H_{25} < 1. \end{array}\right\} \cdots\cdots\cdots\cdots \quad (10)$$

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(21) Green, *J. Chem. Soc.*, **93** (1908), 2023.

By the use of the criterion it may be obvious that the solutional viscosities of NaCl and LiCl also must be smaller than the viscosity of water. As for $LiNO_3$, q being nearly unity, such decision may not be hoped for, yet H is undoubtedly nearly unity.

From the several examples given above the following conclusion may be reached: The negative viscosity is entirely due to the smaller solutional viscosity of the solute than the viscosity of water, but not to the ionic behaviours suggested by other investigators. The viscosity formula formerly proposed and developed by Ishikawa for a binary mixture of liquids proves to have a general applicability in a new field of aqueous solutions of electrolytes, and at the same time, to play an important rôle in finding their hydrates in solution.

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