The Viscosity of Concentrated Aqueous Solutions of Strong Electrolytes

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It has been pointed out that the viscosity η of aqueous solutions of strong electrolytes can be expressed by the following empirical equation given by Jones and Dole1),

$$\eta/\eta_0 = 1 + Ac^{1/2} + Bc \qquad (1)$$

where η_0 is the viscosity of pure water, A and B are parameters independent of concentration c (mol./l. solution). Moreover, it is indicated that contrary to the positive value of A, the B-parameter can possess either sign corresponding to each pair of individual ionic species, and that the magnitude of B is several times greater larger than that of A. It is noteworthy that the second term in Eq. 1 can be derived from the Debye-Hückel limiting law, and that the accord of theoretical derivation with the A-parameter obtained experimentally is very satisfactory. This excellent work focused in the ion-ion interaction was done by Falkenhagen and his coworkers2). On the other hand, the consideration of the parameter B has probably been treated more qualitatively compared with A. It is generally accepted that B may be determined additively from the specific value of the individual ion3) and its temperature coefficient can be used as a measure indicating the effect of ion-solvent interaction in flow3,4). However, we should bear in mind the fact that the above-mentioned consideration should be limited to a narrow range of extremely dilute solutions. Frank and Thompson5) have recently given fundamental reconsideration to some thermodynamic quantities and called our attention to the limit of the validity of the Debye-Hückel theory. According to their conclusion the Debye-Hückel formalism breaks down around the critical concentration c_0 owing to

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1) E. g., H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions", Reinhold Publ. Corp., New York (1950), p. 172.

2) H. Falkenhagen and E. L. Vernon, *Phys. Z.*, 33, 140 (1932); *Phil. Mag.*, (7) **14**, 537 (1932).

3) E. C. Bingham, *J. Phys. Chem.*, **45**, 885 (1941); M. Kaminsky, *Discuss. Faraday Soc.*, **24**, 171 (1957).

4) R. J. Podolsky, *J. Am. Chem. Soc.*, **80**, 4442 (1958).

5) H. S. Frank and P. T. Thompson, *J. Chem. Phys.*, **31**, 1086 (1959); "The Structure of Electrolytic Solutions", John Wiley & Sons, Inc., New York (1959), p. 113.

TABLE I. RELATIVE VISCOSITIES OF 1-1 ELECTROLYTE SOLUTIONS

Lithium chloride, 25°C		Lithium bromide, 27°C		Sodium chloride, 30°C by Suryanarayana and Venkatesan		Sodium bromide, 25°C	
c, mol./l.		c, mol./l.		c, mol./l.		c, mol./l.	
0.7141	1.119	0.597	1.065	1.00	1.107	0.496	1.028
1.189	1.188	1.055	1.104	1.50	1.152	0.973	1.058
1.666	1.265	1.505	1.147	2.00	1.212	1.458	1.095
2.123	1.343	1.968	1.199	2.50	1.284	1.946	1.146
2.608	1.433	2.441	1.250	3.00	1.356	2.429	1.197
3.078	1.517	2.897	1.320	3.50	1.434	2.918	1.256
3.540	1.634	3.376	1.380	4.00	1.522	3.403	1.345
4.016	1.735	3.802	1.441	4.50	1.614	3.888	1.437
4.485	1.879	4.265	1.516	5.00	1.709	4.373	1.528
4.964	2.020	4.728	1.654			4.861	1.651

Sodium iodide, 23°C		Potassium fluoride, 26°C		Potassium chloride, 25°C by Kume and Tanaka	
c, mol./l.		c, mol./l.		c, mol./l.	
0.499	1.022	0.525	1.067	0.4985	0.998
0.998	1.042	1.034	1.135	0.7321	0.996
1.487	1.055	1.564	1.218	0.9692	0.995
1.982	1.094	2.081	1.291	1.0000	0.997
2.470	1.127	2.582	1.382	1.433	0.997
2.963	1.212	3.107	1.474	1.883	1.002
3.457	1.247	3.619	1.588	2.318	1.010
3.951	1.371	4.149	1.701	2.742	1.020
4.450	1.447	4.661	1.816	3.528	1.053
4.937	1.596	5.220	1.944	3.550	1.054
		6.032	2.194	3.728	1.064
		6.445	2.320	3.932	1.078
				4.132	1.093
				4.174	1.097

Potassium bromide, 21°C		Potassium iodide, 21°C		Cesium chloride, 25°C	
c, mol./l.		c, mol./l.		c, mol./l	
0.4315	0.983	0.610	0.964	0.5975	0.980
0.8439	0.967	1.208	0.931	1.509	0.964
1.271	0.953	1.817	0.904	2.267	0.956
1.692	0.942	2.426	0.919	3.088	0.977
2.104	0.943	3.015	0.925	4.058	1.010
2.524	0.937	3.626	0.943		
2.942	0.947	4.831	1.022		
3.379	0.954	6.039	1.152		
3.802	0.966				
4.206	0.986				

the failure of the fine-grainedness* of the ion cloud. It is estimated that $c_0 \approx 10^{-3}$ mol./l. for 1-1 electrolytes at 25°C.

The aim of this paper is directed to the concentrated range reaching the saturation specified at a given temperature.

Experimental

The measurements of viscosity were made with conventional Ostwald viscometers in a water bath. According to the Hagen-Poiseuille law, the viscosity can be generally determined by

$$\eta = K\rho t \tag{2}$$

where ρ is the density of solution; t is the efflux time and K is a constant of the viscometer for a constant charge of liquid. Kinetic energy correction term $K'\rho/t$ (K'=constant) can be omitted in our present systems because the amount is negligible. The values of K of two viscometers used were 3.214×10^{-5} and 2.895×10^{-5}, respectively. These

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* It is noticeable that the various quantities defined in the ion cloud are to be essentially nonfluctuating. Let us consider one volume element in the cloud. Then, the frequency with which one ion happens to exist there should be sufficiently small. They introduce a new term of "fine-grainedness" to express the degree of averaging. Of course, in the limiting case of extremely dilute solution this requirement would be strictly justified.—The ion cloud would have the character of infinitely fine-grained matter.

values were determined by blank tests with pure water at different temperatures. The density ρ of each solution was measured with a picnometer.

Lithium chloride, lithium bromide, sodium bromide, sodium iodide, potassium fluoride, potassium bromide, potassium iodide and cesium chloride were used as electrolytes. These samples were all special-grade commercial products. They were dried in a thermostat long enough before they were made into solutions.

Results

Our experiments were carried out at room temperature by varying the concentration of solutions.

Suryanarayana and Venkatesan⁶⁾ have already reported the viscosities of sodium chloride solutions from 1 molal to saturation and from 30 to 55°C. Kume and Tanaka⁷⁾ have also presented a paper on some kinds of electrolytic solutions, in which the data of sodium chloride and potassium chloride are included. Consequently, for sodium chloride and potassium chloride we can utilize these data. In Table I our results are listed together with some of them. All the results are also shown in Fig. 1.

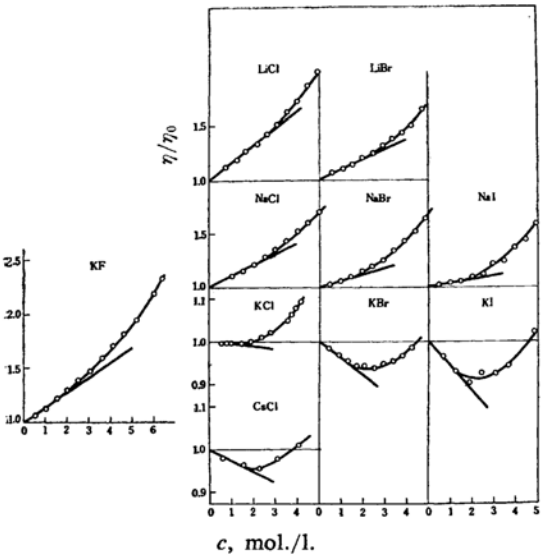

Fig. 1. Plots of relative viscosity against concentration.

Discussion

One might easily admit that the relative viscosity vs. concentration curves could be generally classified into two groups. In the first type the relative viscosity varies almost linearly with the concentration in the dilute range (the slope is all positive) and then deviates clearly from the linearity after passing a critical point of concentration. The second type is one that indicates so-called negative viscosity — the behavior as a whole is not greatly different from the former, but it can be distinguished on one point, namely that its slope in the dilute range is negative. We would claim that the concentration corresponding to deflection point might be closely related with a critical concentration that is characterized in our model concerning the structure of electrolytic solutions. As general tendencies, with increasing temperature the absolute value of the tangent becomes greater and the deflection point moves to a higher concentration. But the displacement of the latter is so small that it can be neglected in the present problem. Derived from the data by Suryanarayana and Venkatesan⁶⁾ the temperature coefficient of the displacement under consideration is estimated as the order of 0.02 mol./l. deg^{-1}. These behaviors are shown in Fig. 2.

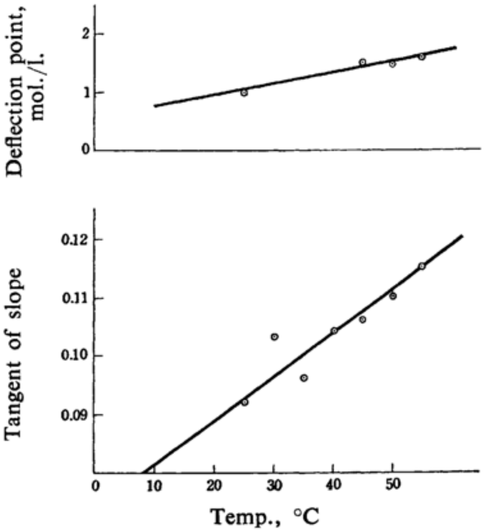

Fig. 2. Temperature coefficient of deflection point and tangent of slope against concentration (NaCl solution). After Suryanarayana and Venkatesan.

Let us continue the consideration in more detail. It is convenient to take series, e.g. anion series—in one series a cation is substituted corresponding to a fixed anion. In Fig. 3 the dependence of the ionic radius upon the tangent is plotted. One may notice the general feature that the tangent becomes smaller with increasing ionic radius (at a virtual value** its sign changes from positive

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6) C. V. Suryanarayana and V. K. Venkatesan, *Trans. Faraday Soc.*, **54**, 1709 (1958).

7) T. Kume and M. Tanaka, *J. Chem. Soc. Japan*, *Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 534 (1960).

** It is interesting to note that a critical value may probably satisfy a condition, in which a sum of both radii of the ions involved in one series is equal to 3.1~3.3Å. In the Cl series K$^+$ is incidentally fitted in this relationship.

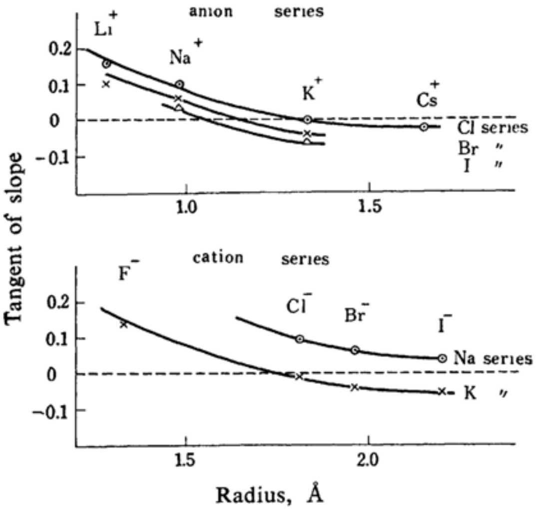

Fig. 3. Tangent of slope vs. ionic radius.

to negative) and the deflection point moves to a lower concentration***. Concerning the dilute range in which the viscosity varies linearly with the concentration, we would conform to Broersmas' treatment[8]. According to his assumption of local viscosity, the viscosity η can be set,

$$\eta \approx \eta_{0-0} + 2\sum \frac{n_i v_i}{N v_0}(\eta_{i-j} - \eta_{0-0}) \qquad (3)$$

where $\eta_{i-j}(=\eta_{j-i})$ is a local viscosity in a region containing neighboring water molecules in the ith and jth hydration layers, consequently η_{0-0} is a local viscosity in a region containing both free waters; v_i, n_i and v_0, n_0 are the volume and the number per unit volume of water molecules existing in these respective states. N, the total number of water molecules per unit volume can be written:

$$N = n_0 + n(n_{1(+)} + n_{1(-)} + n_{2(+)} + n_{2(-)})$$

where $n_{1(+)}$, $n_{1(-)}$ and $n_{2(+)}$, $n_{2(-)}$ are the hydration numbers of primary and secondary layers surrounding a cation and an anion respectively. Equation 3 is considered to be based upon the following fundamental concepts. Local friction force is proportional to the total cross-sectional area of the molecules which are proportional to their volumes and the velosity gradient (a const) and the resultant of these effects contribute to the bulk viscosity. Factor 2 enters because the layers considered are identical so that element i and j can meet either way. The higher terms containing more than the square of concentration, $(n_i/N)^2$, are neglected. In other words the bulk viscosity is assumed to be givin by averaging the effect of local viscosity with the weights of relative volume and concentration of the water molecule in different state.

From the standpoint of our model Eq. 3 can be written,

$$\begin{aligned}\eta \approx \eta_{0-0} &+ 2\frac{n_{1(+)} n v_{1(+)}}{N v_0}(\eta_{1(+)-2(+)} - \eta_{0-0}) \\ &+ 2\frac{n_{2(+)} n v_{2(+)}}{N v_0}(\eta_{2(+)-0} - \eta_{0-0}) \\ &+ 2\frac{n_{1(-)} n v_{1(-)}}{N v_0}(\eta_{1(-)-2(-)} - \eta_{0-0}) \\ &+ 2\frac{n_{2(-)} n v_{2(-)}}{N v_0}(\eta_{2(-)-0} - \eta_{0-0}) \qquad (4)\end{aligned}$$

If we assume that $\eta_{1(+)-2(+)} \approx \eta_{1(-)-2(-)}$, $\eta_{2(+)-0} \approx \eta_{2(-)-0}$, the equation can be transformed to,

$$\begin{aligned}\frac{\eta}{\eta_0} \approx 1 + 2\frac{n}{N}\Big[&(n_{1(+)} + n_{1(-)})\frac{v_1}{v_0}\Big(\frac{\eta_{1-2}}{\eta_{0-0}} - 1\Big) \\ &+ (n_{2(+)} + n_{2(-)})\frac{v_2}{v_0}\Big(\frac{\eta_{2-0}}{\eta_{0-0}} - 1\Big)\Big] \qquad (5)\end{aligned}$$

Since $n = cN/1000$, where N is the Avogadro number, we find that the relative viscosity varies linearly with the concentration. The factor of the linear term can clearly possess either sign. Since an inequality $\eta_{1-2} > \eta_{0-0}$ is admitted as being always valid, the correlation between η_{2-0} and η_{0-0} is likely to have a casting vote in the determination of the sign. When $\eta_{2-0} > \eta_{0-0}$, the sign shows positive. When $\eta_{2-0} < \eta_{0-0}$, the sign shows positive or negative corresponding to the inequality:

$$\begin{aligned}&(\eta_{1-2} - \eta_{0-0})/(\eta_{0-0} - \eta_{2-0}) \\ &\quad \gtreqless (v_2/v_1)(n_{2(+)} + n_{2(-)})/(n_{1(+)} + n_{1(-)})\end{aligned}$$

It turns out, therefore, that the condition of negative viscosity is given by

$$\eta_{2-0} < \eta_{0-0}, \ (\eta_{1-2} - \eta_{0-0})/(\eta_{0-0} - \eta_{2-0}) < 5 \qquad (6)$$

in rough approximation[9].

It should be understood that the abovementioned consideration does not contradict Eq. 1. As the concentration reaches nearly 0.1 mol./l., the linear term becomes predominant compared with the Debye-Hückel-Falkenhagen term. Of course, we could not express the relationship exactly only with a linear term. Kaminsky[10] has recently clarified the fact that we have to supply a quadratic term in order to obtain a more precise formula even in the range up to 0.5 mol./l. However, since the factor of linear term is larger than two other

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*** This facts can be deduced from our data in spite of slight differences of temperature.

[8] S. Broersma, *J. Chem. Phys.*, 24, 659 (1956).

[9] T. Satoh and K. Hayashi, *J. Phys. Soc. Japan*, **15**, 1658 (1960).

[10] M. Kaminsky, *Z. Phys. Chem.*, **5**, 154 (1955); **8**, 173 (1956).

terms by one degree of order of magnitude, it is apparent that it plays a leading role in the concentrated range over 0.1 mol./l.

Suryanarayana and Venkatesan[6] have proposed that if one plotted a function $\ln(\eta/\eta_0)/C_*$ against reduced concentration C_*, where C_* is the ratio of the mole fraction to that at saturation, one could probably represent the entire behavior except in dilute solutions. We suppose that the breakdown in their formalism may be essentially due to our critical phenomenon.

Summary

The coefficients of the viscosity of concentrated aqueous solutions of 1–1 type electrolytes were measured at room temperature. Judging from the relationship between relative viscosity and concentration the electrolytes would be classified into two groups. One is normal and the other shows negative viscosity. It is the linear term that makes the most predominent contribution in the dilute range. We analyzed its factor by the use of Broersma's concept of local viscosity. From the expression obtained, a condition of negative viscosity was derived as 6 in approximation. According to our interpretation, negative viscosity does not result from individual characters of ions of each electrolyte in question, but from delicate correlations between the local viscosities of neighboring hydration layers.

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