A New Viscosity Relationship in a Wide Concentration Range of Aqueous Solutions of Potassium Chloride

By C. V. SURYANARAYANA and V. K. VENKATESAN*

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Viscosity of strong electrolytes in dilute solutions conformed to an equation given on experimental basis by Jones and Dole[1] and Joy and Wolfenden[2]. This equation fails at higher concentrations. So far no equation satisfactorily explained the quantitative relationship between viscosity and concentration in the entire range from infinite dilution up to saturation. In a recent[3] systematic study by us, of electrical conductance of highly concentrated solutions of strong electrolytes up to saturation, we have derived a new concept of concentration and a modified viscosity term. In brief, the following is the basis of the new formulations.

A new concept of concentration.—Let

$$P = f(X) \qquad (1)$$

represent the physical property of a solution at a given temperature for a given solvent as a function of 'X', the mole fraction concentration of the solute. When we compare the physical property 'P' of solutions of different solutes in the same solvent, it is clear that in equation (1) 'X' can not have all possible values from zero to unity. For each electrolyte 'X' can vary from the common zero limit in all cases to the saturation limit at which the mole-fraction of the solute is not unity. Further the mole-fraction concentration at saturation is different for different electrolytes in the same solvent. If 'X' values vary in an identical range, the 'P' values of different salt solutions will be comparable at the same temperature. In other words, in the extreme limit of saturation, for different salt solutions the 'X' values must be such that they tend to an identical limit at which the 'P' values in their limit will be comparable even though they will not be identical. Therefore there is need for a new concept

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* Present Address: Central Electrochemical Research Institute, Karaikudi, India.

[1] G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).

[2] W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc.* (London), **A134**, 413 (1931).

[3] C. V. Suryanarayana and V. K. Venkatesan, *Nature*, **178**, 1461 (1956).

of concentration (X^1) such that, at a given temperature, its value varies between the same limits for different electrolyte solutions. We may write

$$P = f(X^1) \qquad (2)$$

such that 'X^1' is the ratio of the mole-fraction of the solute at any given molal concentration to that at saturation at the same temperature. Such a ratio should tend to unity at saturation for all solutions at all temperatures irrespective of the nature of the solute and the solvent. This ratio of mole-fractions, was called by us the "concentration potential" (C_p). Now it is clear that a given physical property of a solution plotted against its "concentration potential" will be a curve worthy of comparison with similar ones for different electrolytes in a given solvent. The concentration potential newly conceived herein is a truly thermodynamic concept of concentration dependent only on the initial and final states of stability of a solution and independent of any arbitrary scale of concentration or the nature of both the solvent and the solute.

A new concept of viscosity.—So far in literature the relative viscosity of a solution has been relative to the solvent and our modification consists in making it relative to that at saturation at the same temperature. This modified viscosity term (η_p), as with the concentration potential, will tend to a maximum of unity at saturation for all electrolyte solutions.

Some previous workers[4~20] collected viscosity data for potassium chloride solutions in different ranges of concentrations at a few temperatures. We have measured viscosity of potassium chloride solutions from 1.00 molal to saturation, at temperatures of 30 to 55°C.

Experimental

All solutions were made by weighing water and the required amount of solute to make a certain wanted molal concentration. A 100 cc. pyrex beaker was weighed and the process repeated after adding about 50 cc. of water. Exactly the required amount of a salt was weighed into the beaker. After gentle stirring of the solution the whole of it was transferred and kept in a well-stoppered 250 cc. pyrex bottle. This solution was used for finding the viscosity and density. All solutions except at saturation were thus made so that the concentration was independent of volume. The potassium chloride used was of guaranteed quality. Viscosity measurements were made using an Ostwald viscometer kept in a Gallenkamp b-12210 thermostat provided with a glass tank and giving an accuracy ±0.05°C. At saturation, viscosity determination required great care and repeated verification. A pyrex beaker containing the saturated solution in equilibrium with the undissolved salt was kept stirred continuously by a mechanical stirrer. After attainment of equilibrium an aliquot amount of the saturated solution was sucked through a tube plugged with cotton wool and attached to a pipet. The pipet itself was kept at the same temperature of the thermostat to avoid crystallization of the saturated solution. Soon after withdrawing into the pipet the glass-tube stuffed with cotton wool was quickly disconnected and the solution was transferred into the viscometer. After sufficient repetitions the whole technique could be mastered.

Density determination.—Density was determined in each case using the density bottle whose volume was ascertained by knowing the weight of water filling it at a known temperature and making use of exact density of water at the same temperature from tables given in Lange[21]. The density of the saturated solution was determined by weighing the volume of solution transferred by a calibrated pipet.

Solubility data of each salt at different temperatures were obtained from Seidell's "Solubilities of Organic and Inorganic Compounds"[22]. Results obtained are given in Table I.

Discussion

Figs. 1 and 2 show plots of $\log \eta_p$ vs. C_p at each temperature. At temperatures of 35, 40, 45, 50 and 55°C the plots are straight lines. Only at 30°C the plot though not a straight line, is made up of

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TABLE I

Temp. °C	Molality	C_p	Relative viscosity water=1	η_p	Temp. °C	Molality	C_p	Relative viscosity water=1	η_p
30	1.00	0.2156	1.010	0.8814	45	1.000	0.1950	1.024	0.8307
	1.50	0.3206	1.021	0.8910		1.500	0.2900	1.046	0.8484
	2.00	0.4236	1.028	0.8973		2.000	0.3832	1.058	0.8582
	2.50	0.5249	1.035	0.9033		2.500	0.4747	1.086	0.8810
	3.00	0.6244	1.046	0.9128		3.000	0.5650	1.104	0.8954
	3.50	0.7226	1.064	0.9285		3.500	0.6536	1.125	0.9124
	4.00	0.8189	1.079	0.9417		4.000	0.7406	1.148	0.9311
	4.50	0.9128	1.093	0.9539		4.500	0.8624	1.170	0.9491
	4.963	1.0000	1.145	1.0000		5.540	1.0000	1.233	1.0000
35	1.00	0.2079	1.014	0.9419	50	1.00	0.1895	1.034	0.8136
	1.50	0.3091	1.020	0.8800		1.50	0.2819	1.059	0.8333
	2.00	0.4088	1.022	0.8816		2.00	0.3727	1.076	0.8468
	2.50	0.5064	1.049	0.9048		2.50	0.4617	1.104	0.8686
	3.00	0.6027	1.060	0.9145		3.00	0.5494	1.122	0.8828
	3.50	0.6971	1.077	0.9315		3.50	0.6357	1.147	0.9024
	4.00	0.7900	1.103	0.9515		4.00	0.7202	1.173	0.9230
	4.50	0.8812	1.119	0.9651		4.50	0.8035	1.195	0.9404
	5.164	1.0000	1.159	1.0000		5.714	1.0000	1.271	1.0000
40	1.00	0.2005	1.018	0.8486	55	1.00	0.1841	1.039	0.7943
	1.50	0.2985	1.039	0.8662		1.50	0.2738	1.059	0.8098
	2.00	0.3945	1.044	0.8706		2.00	0.3617	1.081	0.8266
	2.50	0.4889	1.074	0.8958		2.50	0.4483	1.114	0.8517
	3.00	0.5817	1.089	0.9082		3.00	0.5335	1.135	0.8680
	3.50	0.6730	1.105	0.9212		3.50	0.6172	1.161	0.8880
	4.00	0.7628	1.130	0.9423		4.00	0.6993	1.188	0.9086
	4.50	0.8507	1.148	0.9572		4.50	0.7803	1.214	0.9283
	5.365	1.0000	1.199	1.0000		5.902	1.0000	1.308	1.0000

TABLE II

Temp. °C	Cons. A			Const. B
	Expt.	Extra-polated	% deviation	
30	0.8736	0.8710 (Ist line)	−0.3	0.03390
		0.8426 (IInd line)	—	0.05881
35	0.8630	0.8670	+0.4	0.07138
40	0.8339	0.8189	−1.8	0.07922
45	0.8112	0.8128	+0.2	0.09072
50	0.7868	0.7769	−1.27	0.10380
55	0.7647	0.7516	−1.7	0.11880

two non-collinear straight lines intersecting at a point corresponding to 2.336 molal. Therefore, in general the variation of η_p with concentration potential may be represented by the exponential equation

$$\eta_p = A\,e^{BC_p} \tag{3}$$

the constants A and B being dependent upon temperature. At 30°C and below potassium chloride solutions are known to exhibit negative viscosity. Even then, the above exponential equation is applicable at 30°C, the non-colliner straight lines signifying only variations in constants A and B of the above equation.

It is clear from equation (3) that at infinite dilution C_p is zero and η_p equals to A. In other words A is the ratio of the viscosity of water to that of the solution when saturated with potassium chloride at a given temperature. This value of A

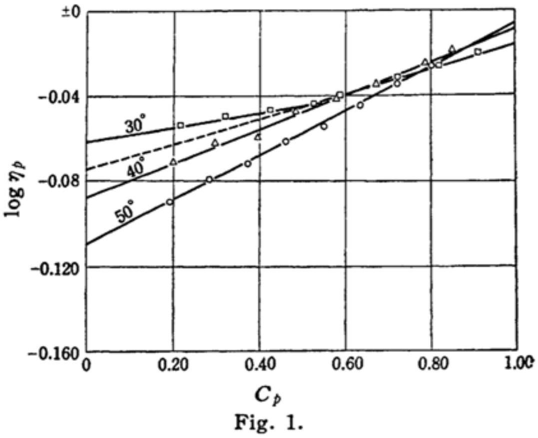

Fig. 1.

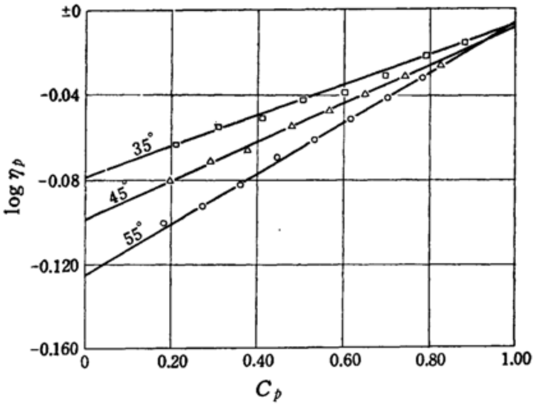

Fig. 2.

could be easily found from the experimental determination of the viscosity of the solution at saturation. Also by plotting at each temperature $\log \eta_p$ against C_p, by extrapolating $C_p = 0$ and by a small mathematical transformation of the value of the intercept we can obtain the value of 'A'. Thus in Table II in addition to the constant B at different temperatures the extrapolated and the experimentally determined values of 'A' are compared side by side. The percentage deviation between the extrapolated and the calculated values ranges from 0.2 to 1.80. Considering the difficulties involved in precision measurements of viscosity of saturated solutions and errors involved in extrapolation of values quite small in magnitude, the agreement is quite within limits. The constant 'B' may be probably related to the properties of the solute and requires further elucidation in furture.

Summary

A systematic investigation of viscosity from 1.00 m. to saturation of aqueous solutions of potassium chloride at temperatures of 30, 35, 40, 45, 50 and 55°C has been made. New concepts of concentration and viscosity have been defined. At a given molal concentration the ratio of the mole-fraction at that concentration to that at saturation at the same temperature has been called concentration potential C_p. The newly defined viscosity term η_p is the ratio of the viscosity at a given concentration to that at saturation at the same temperature. Using these two quantities the variation of viscosity with concentration could be expressed for potassium chloride solutions by a simple exponential equation:

$$\eta_p = A\, e^{BC_p}$$

where A and B are constants.

Physico-Chemical Laboratory
Annamalai University
Annamalainagar
South India