

TEMPERATURE DEPENDENCE OF VISCOSITY B -COEFFICIENTS OF AQUEOUS SOLUTIONS OF CHLORIDES OF Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Cr^{3+}

Muhammad AFZAL, Muhammad J. IQBAL and Habib AHMAD

*Department of Chemistry,
Quaid-I-Azam University, Islamabad, Pakistan*

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The viscosity B -coefficients of the aqueous chlorides of Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Cr^{3+} have been calculated from the parameters of an empirical equation of the form $\eta = a_0 \exp(b_0 c_M + d_0 c_M^2)$ and were found to be comparable with literature values. The variation of B -values with temperature between 20 – 50 °C has been described in terms of structure making/breaking behaviour of the cations.

The Jones–Dole equation¹ and several other equations^{2–7} etc. are used to determine the viscosity B -coefficients which are explainable in terms of ion–solvent interactions. These equations are normally applicable to viscosity data obtained at lower concentrations. However, Out and Los⁸, and Phang and Stokes⁹ have applied the Jones–Dole equation in the form

$$\eta/\eta_0 = 1 + A c_M^{1/2} + \sum_{i=1}^5 B_i c_{M_i} \quad (1)$$

to the viscosity data on aqueous electrolyte solutions within a concentration range of 1 – 5 mol dm⁻³. Mahiuddin and Ismail¹⁰ have described the concentration dependence of viscosity by an empirical equation of the form

$$\eta = a_0 \exp(b_0 c_M + d_0 c_M^2), \quad (2)$$

where a_0 , b_0 and d_0 are parameters for a particular system at a particular temperature, and c_M is the concentration in (mol dm⁻³). Afzal et al.¹¹ have recently reported the suitability of Eq. (2) for application to the viscosity data of concentrated aqueous solutions (0.1 – 5 mol dm⁻³) of NaCl, KCl, MgCl₂, CaCl₂, BaCl₂, SrCl₂, CoCl₂, NiCl₂,

CuCl_2 and CrCl_3 , and also computed the least-square values of a_0 , b_0 and d_0 from plots of $\ln \eta$ vs $(b_0 c_M + d_0 c_M^2)$ yielding straight lines.

In the present paper, the viscosity data and the parameters a_0 , b_0 and d_0 reported by Afzal et al.¹¹ are used to calculate the B -coefficients using Eqs (1) and (2) for the above mentioned electrolyte solutions at different temperature between 20 to 50 °C. The product of a_0 and b_0 terms is considered to be equivalent to the viscosity B -coefficient as has been shown by Mahiuddin and Ismail¹². The dependence of B -values on temperature (dB/dT) has been described in terms of structure making/breaking behavior of the cations. The experimental details, the viscosity data and the values of a_0 and b_0 are given elsewhere¹¹.

RESULTS AND DISCUSSION

The calculated values of the viscosity B -coefficients together with their literature values compiled by Marcus¹ are given in Table I. However the data were corrected for salts by the addition of a small negative term (e.g. -0.014) representing the chloride ion as reported¹³. At lower concentration the values computed from both the equations were comparable. However, at higher concentration, the values calculated using Eq. (1) were found to be larger than their literature values. This deviation may be due to the fact that Jones–Dole equation¹ is applicable for less concentrated solutions only and deviate particularly at higher concentration¹⁴. However the values calculated by applying Eq. (2) were reasonably comparable even at higher concentrations.

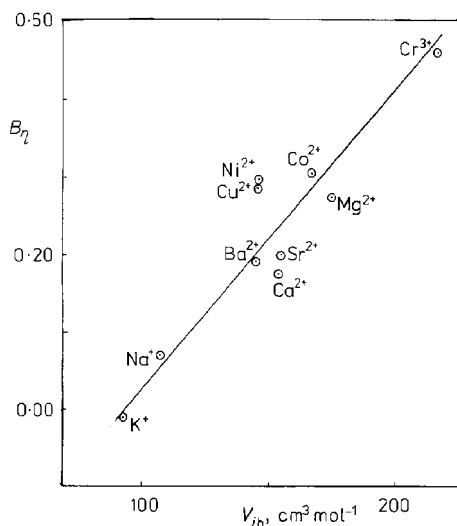


FIG. 1

Plot of the viscosity B -coefficients (B_η) vs hydrated volumes of the ions at 25 °C

TABLE I

Ionic radii, r , hydrated volumes, v_{ih} , parameters a_0 and b_0 and the viscosity B -coefficients calculated using Eq. (2) for various electrolytes in water solution for temperature of 25 °C

Electrolyte	r^a , Å	v_{ih}^a cm ³ mol ⁻¹	Parameters of Eq. (2)		B -Coefficient	
			a_0	b_0	calc.	lit.
NaCl	0.95	109.0	0.883	0.078	0.069	0.074
KCl	1.33	094.4	0.883	-0.011	-0.010	-0.009
MgCl ₂	0.65	176.9	0.919	0.294	0.270	0.371
CaCl ₂	0.94	156.7	0.916	0.188	0.172	0.284
BaCl ₂	1.35	146.7	0.888	0.213	0.189	0.215
SrCl ₂	1.13	156.7	0.894	0.222	0.198	0.258
CoCl ₂	0.72	169.6	0.895	0.340	0.304	0.362
NiCl ₂	0.70	147.8	0.898	0.329	0.296	0.361
CuCl ₂	0.70	147.8	0.897	0.319	0.285	0.354
CrCl ₃	0.62	219.5	0.911	0.503	0.458	-

^a Ref. ¹³.

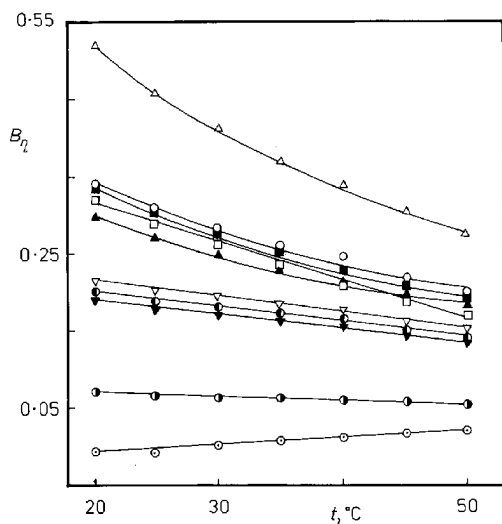


FIG. 2
Plot of viscosity B -coefficients (B_{η}) of aqueous electrolytic solutions at different temperatures. Δ CrCl₃, \circ CoCl₂, \blacksquare NiCl₂, \square CuCl₂, \blacktriangle MgCl₂, ∇ SrCl₂, \circ BaCl₂, \blacktriangledown CaCl₂, \circ NaCl, \circ KCl

Table I shows that B -values are positive for all the salt solutions. However, for KCl solution, B -values up to 30 °C are found to be negative. Table I and Fig. 1 indicate that ions with higher surface charge density have higher B -values as well as higher hydrated volumes. This is in agreement with Einstein theory of viscosity^{2,15} that

$$B = 2.5 \varphi / c_M, \quad (3)$$

where φ is the volume of the ions per cm³ of solution and c_M is the molar concentration of electrolyte. For polar solvent like water, the values of B -coefficients for different ions may be proportional to the hydrated volume of the ions (φ) and not simply to the r^3 (r is ionic radius) as has been suggested by Gopal and Rastogi¹⁶. Thus the B -values are proportional to the hydrated volumes of the ions. Ions of higher hydrated volume having higher values of B and vice versa as shown in Fig. 1.

The temperature dependence of the viscosity B -coefficients for the electrolyte solutions is shown in Fig. 2 and given in Table II. The B -values are found to decrease with rise in temperature for all the systems except for KCl which shows an increasing trend in the B -values. The negative values of dB/dT obtained for all cations (except for K⁺) indicate that Na⁺, Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Co²⁺, Ni²⁺, Cu²⁺ and Cr³⁺ ions are structure promoters; the ability of the ions to organize the water molecules decreases with increasing temperature as result of increasing thermal motion. The multiple charged ions would strongly attract the surrounding water molecules and thus the distance among the

TABLE II
Viscosity B -coefficient in the concentration range of 0.1 – 0.5 mol dm⁻³ in aqueous solutions at different temperatures (°C)

Electrolyte	20	25	30	35	40	45	50
NaCl	0.075	0.069	0.067	0.062	0.059	0.056	0.053
KCl	-0.002	-0.010	0.000	0.006	0.011	0.015	0.016
MgCl ₂	0.297	0.270	0.246	0.227	0.214	0.196	0.181
CaCl ₂	0.190	0.172	0.169	0.159	0.149	0.140	0.131
BaCl ₂	0.196	0.189	0.182	0.172	0.164	0.154	0.145
SrCl ₂	0.211	0.198	0.188	0.175	0.162	0.152	0.145
CoCl ₂	0.340	0.304	0.277	0.253	0.244	0.210	0.180
NiCl ₂	0.332	0.296	0.270	0.245	0.220	0.201	0.183
CuCl ₂	0.320	0.285	0.257	0.228	0.206	0.183	0.165
CrCl ₃	0.523	0.458	0.412	0.369	0.334	0.303	0.274

water molecules in the first solvation layer would be shorter than pure water¹⁷, the structure around these ions may therefore be enhanced. Also, these ions owing to higher surface charge density (compared with K^+) can polarize water molecules in the region beyond the first solvation layer and so they act as structure promoters.

On the other hand, the value of dB/dT is found to be positive for KCl as shown in Fig. 2. The positive value of dB/dT shows that K^+ is a net structure breaking ion; less structure is present in the KCl solution than in pure water. Ion K^+ is a univalent ion of radius 1.33 Å at 25 °C and would have a low surface charge density. The interaction between ion and water is therefore not very strong so that water structure around K^+ ion is less stable than that of pure water. The intrinsic viscosity of the solution decreases slower than that of pure water and hence dB/dT is positive. It is evident from the Table II that the change in intrinsic viscosity of KCl solution and that of pure water is the same at this temperature.

Referring to Fig. 2 it may be noted that the dB/dT values for divalent cations are smaller for larger ones (Ca^{2+} , Ba^{2+} , Sr^{2+}) as compared to those for smaller size (e.g. Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}). The trivalent Cr^{3+} is much smaller (ionic radius 0.62 Å) and the dB/dT values are found to be the largest for all the cations studied in this work.

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