

Electrical Conductance, Density, and Viscosity in Mixtures of Alkali-Metal Halides and Glycerol

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This paper presents the results of density, viscosity, and electrical conductivity measurements for glycerol solutions of some alkali-metal halides at 25°C. The apparent and partial molar volumes (V_ϕ and V_1) in mixtures of KCl, NaCl, KBr, KI, and glycerol were calculated from the density data. The Debye-Hückel limiting law was assumed to be valid at low concentrations, and values of the molar volumes at infinite dilution were obtained by extrapolation. The viscosity data were analyzed by means of the Jones-Dole equation. The Kaminsky method, based on reference electrolyte (on $B_{K^+} = B_{Cl^-}$), was used in glycerol. Viscosity B-coefficients are compared with those calculated applying existing theories based on the model of hard-charged spheres moving in a solvent continuum. Specific agreement between theory and experiment was not generally good. The electrical conductivities of solutions of salts (KCl, NaCl, KBr, NaBr, NaI, KI, and LiBr) in glycerol have been measured at three concentrations (approximately 0.01, 0.1, and 0.3 M) at 25°C. Values of the molar conductivity at infinite dilution were obtained by extrapolation using the conductance equation of Onsager. Using previously measured transference numbers for KCl and NaCl in glycerol, values of limiting Walden products for the individual alkali-metal and halide ions in glycerol have been derived and compared with those in aqueous and other alcohol solutions.

KEY WORDS: alkali-metal halides; density; electrical conductivity; electrolytes; glycerol; viscosity.

1. INTRODUCTION

The aim of these experiments is to determine whether electrolyte solutions in glycerol can be described and explained using the semiempirical models that have had success with aqueous solutions, despite the fact that at 25°C

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the viscosity of glycerol is nearly a thousand times greater than that of water. Glycerol is interesting among nonaqueous solvents because, like water, it is a hydrogen-bonded solvent with a high relative permittivity. It is thus natural to look for similarities in behavior between the two solvents.

Viscosities and partial molar volumes are known to provide useful insight into solution structure and interactions. A literature survey reveals that very few data are available regarding the density and viscosity of alkali-halide salts dissolved in glycerol [1–3]. This led us to study the viscometric as well as molar volume properties for glycerol solutions of a few alkali-halides salts (potassium chloride, potassium bromide, sodium chloride, and potassium iodide) at 25°C. We felt it is worthwhile to see if the conclusion from the analysis of molar volumes data is in agreement with that drawn from viscosity data, and also to compare the transport properties with those in water, as theories attempting to explain the behavior of electrolyte solutions can be better tested if data on aqueous as well as on nonaqueous systems are available.

The Redlich and Rosenfeld linear square-root relationship [4] derived from the Debye–Hückel theory was applied to calculate partial molar volumes at infinite dilution. The theory predicts a limiting law to be approached at low concentrations, and the common limiting slope does not depend on the nature of the electrolytes (except its valency type). The Jones–Dole expression [5], which accounts for the observed viscosity-concentration dependence of dilute electrolyte solutions, was used to determine the viscosity B-coefficients and from them to be able to define the properties of the electrolyte in solution.

Although the derivation of B remains an open question, this quantity was shown by Einstein [6] to be given by the equivalent quantity for suspensions of spherical macroscopic but very small particles. In a later paper, Clark [7] applied to viscosities the methods used by Zwanzig [8] for determining the contributions of dielectric relaxation to ionic conductivities.

Since previous experiments have provided values for the cation transference number of KCl in glycerol [9], it follows that ionic conductivities in the low concentration limit can be deduced for the alkali-metal and halide ions if the independent migration is assumed. There have been previous analyses of the concentration dependence of the molar conductivity of KCl, NaCl, and LiCl in glycerol at 25°C [10] where these workers have tested the Debye–Hückel–Onsager (D–H–O) equation in the limit of low concentration and found that this equation fits quite well up to $c \sim 0.01 \text{ mol} \cdot \text{dm}^{-3}$. We also extended the work to several other salts (KBr, NaBr, NaI, KI, and LiBr) in glycerol at 25°C, to compare the conductance-viscosity products of the single ions with values predicted by the Boyd–Zwanzig theory.

2. EXPERIMENTAL

2.1. Materials

Commercial glycerol, Aldrich gold label grade, quoted as 99.5+ % pure was further distilled under reduced pressure, the temperature at the top of the fractionating column being 140°C and the pressure, measured near the receiving flask, being about 0.034 kPa. The central fraction was used and found to have an electrical conductivity of $7.4 \times 10^{-9} \text{ S} \cdot \text{cm}^{-1}$ at 23.9°C; this value was not significantly altered by further distillation. The salts (NaCl, KCl, NaBr, KBr, NaI, KI, and LiBr) used to prepare solutions in glycerol were Aldrich anhydrous gold label, quoted as 99.999% pure. On account of the notoriously hygroscopic nature of glycerol and the salts, solution preparation was carried out in a high-purity argon-filled glovebox. A temperature control circuit was used to control the argon atmosphere temperature inside the box, which was 25°C, to within 0.1°C. All solutions were prepared by mass. The solution concentrations were initially calculated in terms of the mole fraction of solute x and converted to a molar basis c in moles per cubic meter of solution, using the density data. The density measurements were carried out in the argon thermostat, while those of viscosity in a glass-walled paraffin bath which was in turn placed in the thermostated argon atmosphere and whose temperature was kept constant within $\pm 0.05^\circ\text{C}$ throughout a viscosity run.

2.2. Apparatus and Procedures

2.2.1. Density and Viscosity Measurements

Measurements with kinematic viscometers are associated with accurate determination of the density, and 25 ml Technico density bottles (Type B5733) were used. The density bottle was first weighed empty and then weighed containing glycerol (or solution) to be studied. The difference gave the mass of the sample M_s . These weighings were performed inside the glovebox, with a Sartorius electronic balance to within 0.1 g, with a capacity of 170 g. The density bottle was reweighed empty and then weighed containing a liquid of known density (distilled water) in open air with an Oertling balance Model 520. The difference gave the mass of distilled water M_w . Since the density of water was known at 25°C ($d_w = 0.997\,075 \text{ g} \cdot \text{cm}^{-3}$), we calculated the density d of the sample solution using the formula:

$$d = d_w \frac{M_s}{M_w}.$$

Corrections for the buoyancy of air and argon affected the density value in its fifth place.

An ASTM 445 Technico Ubbelohde suspended bulb level viscometer, Type VHB-590-170F, size 3 C, was used for all viscosity measurements. Prior to each run the viscometer was flushed two or three times with a small amount taken from the solution to be studied. We felt that this method "of cleaning" would prevent frequent re-calibration of the viscometer due to temporal variations in the characteristics of the viscometer that may have arisen from attack of the viscometer capillaries by cleaning agents. The results were expressed in terms of the relative viscosity,

$$\eta_r = \frac{\eta}{\eta_0} = \frac{dt}{d_0 t_0}$$

where d , d_0 , η , η_0 , t , and t_0 are the densities, absolute viscosities, and flow times for the solution and the solvent, respectively. The experiments on viscosities involved making several measurements (d , d_0 , t , and t_0) to determine η/η_0 . The effect on the final result of the errors in each of the measurements were as follows. The flow time of the solvent t_0 in the viscometer was obtained as a mean of measurements in several different experiments. For the solutions, runs were repeated until three successive determinations of the flow time t were obtained within ± 0.5 s; this yielded an error in η of about 0.1%. Because all the flow times were greater than 300 s, a kinetic energy correction was not necessary. The temperature coefficient of viscosity is close to 0.8% per °C at 25°C. Thus, the uncertainty in η due to $\pm 0.05^\circ\text{C}$ uncertainty in the temperature of the thermostating system was 0.04%. From the density data, the precision achieved in d/d_0 was ± 0.0005 . Therefore, the percentage error in η (or η_0) due to the above uncertainties is 0.11%, and the uncertainty in η/η_0 is of the order of 0.15%.

2.2.2. Electrical Conductivity Measurements

The conductance cells were pyrex glass with platinum electrodes about 1 cm in diameter placed approximately 1 cm apart. The electrodes were platinized using a H_2PtCl_6 solution to which traces of lead acetate were added. The cells were filled under purified argon-atmosphere inside the glovebox, and sealed with rubber bungs and then placed in a newly built cryostat designed primarily for carrying out experiments on conductivity versus temperature. The cryostat has the form of two compartments: an inner chamber filled with high-purity helium which contained the sample cells and an outer chamber under high vacuum (10^{-8} kPa). The experimental details are described elsewhere [11]. The experiments were carried out at 25°C.

The impedance of the cells was measured using a Solatron frequency response analyzer (FRA), Type 1170, with its electrochemical interface (ECI), Type 1186. Readings carried out at various frequencies showed that in all cases the impedance of the cell filled with glycerol had a negligible imaginary component and was frequency independent in the range 100 Hz to 10 kHz. We took this as evidence that electrode polarization was not falsifying the readings. The values of conductivity σ divided by mole fraction x of solutions were calculated from the experimental ac conductance G , via the following equation,

$$\sigma/x = Gl/ax = k_c G/x,$$

where the ratio, $k_c = l/a$ is the cell constant of a conductance cell consisting of two electrodes of area a and distance l apart. The cell constants were measured using standard aqueous solutions of KCl in conjunction with the tables of Jones and Bradshaw [12]. The experiments on (σ/x) involved making several measurements, which were used to determine $\sigma/x = k_c G/x$. The effect of the uncertainties on this final result in each of the measurements was as follows. The average uncertainty in determining mole fractions due to weighing with the Sartorius balance was at most, 1%. Possible uncertainties in G were associated with the instrument, and the uncertainty of the FRA combined with the ECI was 1%, as stated by the manufacturer. This was checked with a Wayne Kerr bridge, which has an uncertainty of $0.1 \Omega^{-1}$ to $0.01 \mu\Omega^{-1}$. Errors in determining the cell constant k_c of the glass cells were mainly due to electrode phenomena. When the frequency changed by a factor of 10, a change of 1.5% in G of the calibration solution (aqueous KCl solution) caused an uncertainty of 1.5% in k_c . Therefore, the percentage errors in (σ/x) given by a kind of root-mean-squares process were 2%. The uncertainty due to the inhomogeneity of the temperature across the conductance cells was $\pm 0.01^\circ\text{C}$, and the uncertainty due to the thermocouple/NPL thermometer calibration (outside the cryostat in a thermostated oil bath) was $\pm 0.05^\circ\text{C}$ between 21 and 27°C , and 0.1°C between 27 and 50°C , thus giving a total uncertainty in the temperature of the order 0.12 to 0.14°C (between 0 and 50°C).

3. RESULTS AND DISCUSSION

3.1. Density Data

Figure 1 shows the graphs of experimental values of the partial and apparent molar volumes (V_1 and V_ϕ) of alkali halides salts in solution against $c^{1/2}$ for glycerol, calculated using a most convenient form:

$$V_1 \frac{d}{d_0} = \frac{M/M_0}{d/d_0} - \left(\frac{1}{x} - 1\right) \left(1 - \frac{d_0}{d}\right)$$

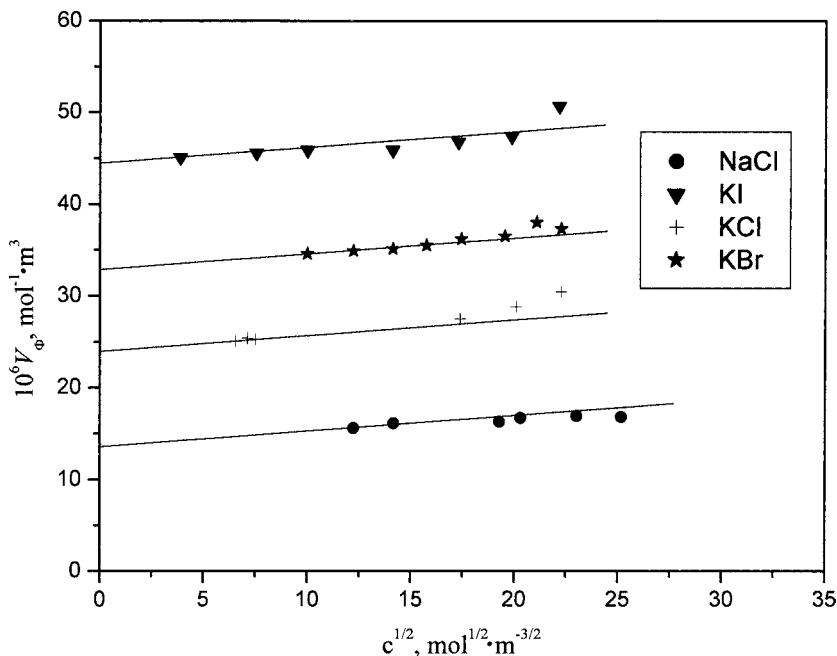


Fig. 1. Plots of experimental apparent molar volumes V_ϕ versus the square root of the concentration c for various salts in glycerol at 25°C. The full lines are the calculated theoretical Debye-Hückel limiting slopes.

where V_1 is the partial molar volume of the solute including attached solvent, M is the molar mass of the solute, M_0 is the molar mass of the solvent, and x is the mole fraction of the solute. The values of V_ϕ thus obtained are given in Table I, together with the values of the absolute density d of the solutions. The conversion of mole fraction x into concentration c of the solute, in moles of solute per unit volume of solution, was done using the following equation:

$$c = \frac{1}{V_1 + \left(\frac{1-x}{x}\right) \frac{M_0}{d_0}}$$

Figure 1 shows that the partial molar volume values are of insufficient accuracy at concentrations below 0.05 mol·dm⁻³; consequently, extrapolation to infinite dilution using Masson's equation [13] is unreliable. We assumed the Redlich and Rosenfeld theoretical equation was valid up to

Table I. Partial Molar Volumes V_ϕ and Absolute Densities d of Alkali-Halides in Glycerol as a Function of Concentration c at 25°C

c (mol·m ⁻³)	d (kg·m ⁻³)	V_ϕ (cm ³ ·mol ⁻¹)	c (mol·m ⁻³)	d (kg·m ⁻³)	V_ϕ (cm ³ ·mol ⁻¹)
NaCl					
149.6928	1.2638	15.6	412.2504	1.2733	16.7
200.5645	1.2656	16.1	529.4701	1.2776	16.9
371.4116	1.2719	16.3	632.8590	1.2815	16.8
KI					
14.9541	1.2596	45.1	298.2947	1.2899	46.8
56.7956	1.2642	45.6	394.3167	1.2999	47.4
99.7672	1.2688	45.9	489.9999	1.3079	50.7
198.7493	1.2795	45.9			
KCl					
42.8624	1.2598	25.1	302.0694	1.2700	27.5
50.5650	1.2601	25.4	403.5749	1.2734	28.8
56.1135	1.2604	25.3	494.7962	1.2759	30.45
KBr					
99.6181	1.2655	34.6	303.4020	1.2803	36.2
149.2165	1.2692	34.9	381.0602	1.2858	36.5
199.3800	1.2729	35.1	443.1977	1.2895	38.0
247.8270	1.2764	35.5	494.6095	1.2935	37.3

0.05 mol·dm⁻³ and extrapolated the V_ϕ 's to infinite dilution with the aid of the following expression:

$$V_1 = V_\phi^\infty + S_{th}c^{1/2} + Dc$$

$$S_{th} = N_A^2 e^3 \left(\frac{8\pi w^3}{(4\pi\epsilon_0\epsilon_r)^3 RT} \right)^{1/2} \left(\frac{\partial \ln \epsilon_r}{\partial p} - \frac{\beta}{3} \right) \quad (1)$$

where D is an empirical deviation constant, V_ϕ^∞ is the limiting apparent molar volume and is equal to the partial molar volume at infinite dilution V_ϕ^∞ , N_A is Avogadro's constant, e is the electronic charge, β is the compressibility of the solvent, R is the universal gas constant, T is the absolute temperature, p is the pressure, ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity of the solvent, and the factor w depends on the ionic valences: $w = 1$ for NaCl, KCl, KI, and KBr. We have calculated the theoretical limiting slope with: $\epsilon_r = 42$ and $T = 298.15$ K. The derivative $\partial \ln \epsilon_r / \partial p = 4.7 \times 10^{-10} \text{ m}^2 \cdot \text{N}^{-1}$ was calculated from the dielectric-pressure

dependence data of Miner and Dalton [14]. Values of the compressibility β are also given at 20°C ($21.1 \times 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$) and at 28.5°C ($21.7 \times 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$). At 25°C, a value of $21.4 \times 10^{-11} \text{ m}^2 \cdot \text{N}^{-1}$ was used in the determination of S_{th} . A common value of $0.17 \text{ cm}^3 \cdot \text{mol}^{-1}$ of the limiting slope was used in the determination of apparent molar volumes at infinite dilution V_{ϕ}^{∞} , i.e., $V_{\phi}^{\infty} = V_{\phi, \text{exp}} - 0.17c^{1/2}$. The set of full straight lines in Fig. 1 represents the theoretical limiting slopes of NaCl, KCl, KBr, and KI solutions in glycerol. Figure 2 shows the relative apparent molar volumes ($V_{\phi} - V_{\phi}^{\infty}$) as a function of $c^{1/2}$ at 25°C. This method of extrapolation does not introduce a serious error into the evaluation of V_{ϕ}^{∞} values, but if one extrapolates the high concentrations V_{ϕ} 's to infinite dilution using the linear portion above $c^{1/2} = 15 \text{ mol}^{1/2} \cdot \text{m}^{-3/2}$, errors up to $5 \text{ cm}^3 \cdot \text{mol}^{-1}$ will result.

The fit of the data to the Redlich and Rosenfeld equation shows that all the electrolytes studied were found to approach the limiting law behavior in dilute glycerol solutions below $0.4 \text{ mol} \cdot \text{dm}^{-3}$. Above this concentration

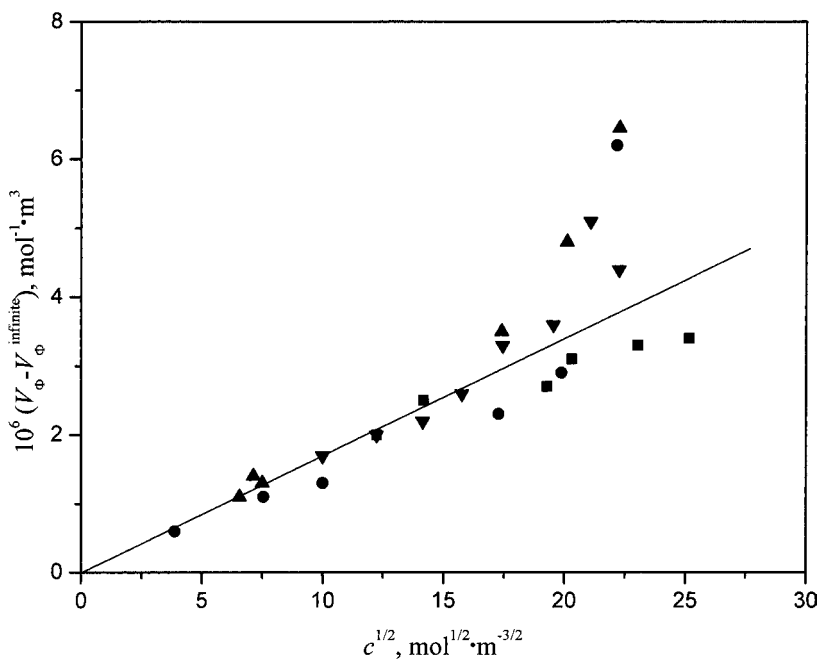


Fig. 2. Relative apparent molar volumes ($V_{\phi} - V_{\phi}^{\infty}$) versus the square root of the concentration c for various salts in glycerol at 25°C: (∇) KBr, (\bullet) KCl, (\blacksquare) NaCl, (\blacktriangle) KI. The full line is the calculated Debye-Hückel limiting slope ($V_{\phi} - V_{\phi}^{\infty} = 0.17 \sqrt{c}$), common to all the salts studied.

the data show rapid positive deviations from the D–H values for KCl, KI, and KBr, and a more slow negative deviation for NaCl. It is also of interest that the magnitude of the volume changes (V_{ϕ}^{∞}) in glycerol are quite close to those in ethylene glycol and in water.

3.2. Viscosity Data

The A and B-coefficients were evaluated from the Jones–Dole semi-empirical equation in the form,

$$(\eta_r - 1) c^{-1/2} = A + Bc^{1/2} \quad (2)$$

where the intercept A is determined by ion-atmosphere interaction and ionic mobilities and has been calculated from the ionic interaction theory by Falkenhagen and Vernon [15]. Their expression of the intercept A is

$$A = \frac{\kappa e F}{480\pi\eta_0 \sqrt{c}} \frac{A^{\infty}}{2\lambda_{-}^{\infty}\lambda_{+}^{\infty}} \left[1 - \frac{4(\sqrt{2}-1)}{\sqrt{2}+1} \left(\frac{\lambda_{+}^{\infty} - \lambda_{-}^{\infty}}{A^{\infty}} \right)^2 \right] \quad (3)$$

$$\kappa = \left(\frac{2e^2 c N_A}{\epsilon_0 \epsilon_r K_B T} \right)^{1/2}$$

where κ is the Debye–Hückel's (D–H) parameter, A^{∞} is the molar conductance of the electrolyte at infinite dilution, λ_{+}^{∞} and λ_{-}^{∞} are the molar conductances of the ions present at infinite dilution, F is Faraday's constant, K_B is Boltzmann's constant, and the other symbols are defined as before. Theoretical values of A in Eq. (3) were calculated with $\eta_0 = 0.909$ Pa·s, $\epsilon_r = 42$, and $T = 298.15$ K. Conductance data measured in this laboratory gave the following values of $10^5 A^{\infty}/S \cdot m^2 \cdot mol^{-1}$: KCl, 3.44; NaCl, 3.08; KI, 3.27; KBr, 3.29; NaBr, 2.92, and of $10^5 \lambda_{\pm}^{\infty}/S \cdot m^2 \cdot mol^{-1}$: K^+ , 1.644; Na^+ , 1.286; Cl^- , 1.794; Br^- , 1.815; I^- , 1.535.

The viscosity data are given in Table II in terms of the Jones–Dole parameter $(\eta_r - 1) c^{-1/2}$. We assumed the validity of the Falkenhagen and Vernon expression, and we plotted $(\eta_r - 1) c^{-1/2}$ values against $c^{1/2}$. The plots are given in Fig. 3, and the slope of the plots gives the B-coefficients.

A summary of all the results obtained (V_{ϕ}^{∞} , A_{theor} , B_{exp}) for NaCl, KCl, KBr, and KI glycerol solutions is given in Tables III and IV, where for comparison we have also included in Table IV, data in other solvents [3, 16].

The fit of the viscosity data to the Jones–Dole equation shows good linearity over the whole concentration range studied for the salts KBr, KI, and KCl, whereas in NaCl the data show two linear regions, one to about

Table II. Jones–Dole Parameter $(\eta_r - 1) c^{-1/2}$ of Alkali-Halides in Glycerol as a Function of Concentration c at 25°C

c (mol · m ⁻³)	$(\eta_r - 1) c^{-1/2}$ (dm ^{3/2} · mol ^{-1/2})	c (mol · m ⁻³)	$(\eta_r - 1) c^{-1/2}$ (dm ^{3/2} · mol ^{-1/2})
KCl			
102.17	-0.00025	397.50	-0.0132
149.33	-0.0043	496.21	-0.0111
199.63	-0.0059	499.37	-0.0100
204.81	-0.0058	588.11	-0.0102
249.31	-0.0071	643.96	-0.0136
334.15	-0.0090		
KBr			
99.56	-0.0193	295.58	-0.0337
100.73	-0.0181	380.42	-0.0374
155.16	-0.0244	442.30	-0.0402
199.26	-0.0260	493.46	-0.0446
NaCl			
10.30	0.0557	307.73	0.2405
49.83	0.1003	315.28	0.2512
99.56	0.1451	370.00	0.2658
143.43	0.1716	383.75	0.2829
149.38	0.1731	410.52	0.3041
200.05	0.1918	498.81	0.3354
238.07	0.2060	526.61	0.3460
KI			
100.91	-0.0070	391.21	-0.0635
208.97	-0.0321	426.83	-0.0868
310.96	-0.0502	574.88	-0.0869
315.18	-0.053		

0.37 mol · dm⁻³ and then a second region beyond this concentration. This phenomenon of a second linear region has been reported for KI in glycerol [1, 17] and KI in methanol [18] and was attributed to ion pairing. Within the uncertainty of our measurements, our viscosity data for KI in glycerol showed only one linear region. The values of A are very small, thereby indicating very weak ion-ion or solute-solute coulombic interactions. The B-coefficient is found to be positive or negative, and the low and negative values obtained for K⁺, Cl⁻, Br⁻, and I⁻ indicate that the interactions between these ions and glycerol molecules are very weak and the size of hydrodynamic entities are very small and close to the bare ion. The situation

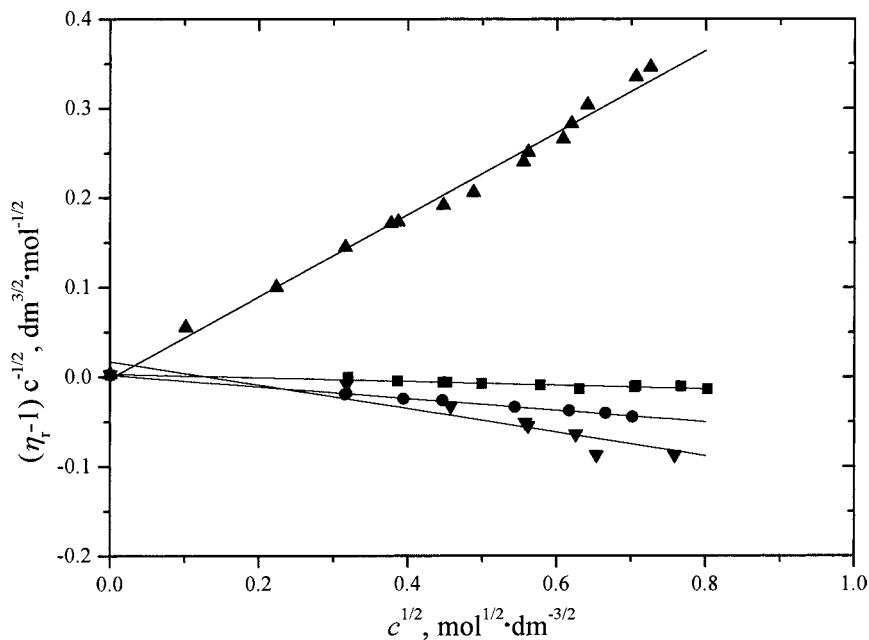


Fig. 3. Classical Jones-Dole viscosity plot for various salts in glycerol at 25°C: (▼) KI, (●) KBr, (■) KCl, (▲) NaCl.

is different in the case of the Na^+ ion, which has a high positive B value suggesting strong ion-solvent interactions.

The B-coefficients of alkali-halides in various solvents can be compared. The results in glycerol and Kaminsky's data in water indicate that in both solvents potassium chloride exhibits slightly negative B-coefficients and is therefore a weak structure breaker. The negative B-coefficients for potassium iodide and potassium bromide suggest they are structure

Table III. Apparent Molar Volumes at Infinite Dilution V_ϕ^∞ Obtained with the Aid of the Theoretical Limiting Slope ($V_\phi^\infty = V_\phi - 0.17\sqrt{c}$), and Jones-Dole Coefficients A (Theoretical) and B (Experimental), for Various Salts in Glycerol at 25°C

Electrolyte	V_ϕ^∞ ($\text{cm}^3 \cdot \text{mol}^{-1}$)	A ($\text{dm}^{3/2} \cdot \text{mol}^{-1/2}$)	B ($\text{dm}^3 \cdot \text{mol}^{-1}$)
KI	44.5	0.0036	-0.178 ± 0.004
KBr	32.9	0.0028	-0.107 ± 0.031
KCl	24.0	0.0030	-0.016 ± 0.004
NaCl	13.6	0.0034	0.463 ± 0.016

Table IV. Apparent Molar Volumes at Infinite Dilution V_{ϕ}^{∞} and Viscosity B-Coefficients for Various Salts in Glycerol, along with Data in Water and in Ethylene Glycol at 25°C

Electrolyte	$V_{\phi}^{\infty}; 10^{-3} \times B \text{ (cm}^3 \cdot \text{mol}^{-1}\text{)}$		
	Glycerol	Water	Ethylene Glycol
NaCl	(13.6; 0.463)	(16.4; 0.0793)	(21.0; —)
KCl	(24.0; -0.016)	(26.5; -0.014)	(30.0; —)
KBr	(32.9; -0.107)	(33.7; -0.039)	(35.9; —)
KI	(44.5; -0.178)	(45.4; -0.0755)	(46.6; 0.0327)

breakers in both solvents, and the effect is more pronounced in glycerol than in water. NaCl and NaBr in glycerol exhibit large, positive B values and suggest a considerable enhancement of structure making in this solvent. The only available B value ($0.0327 \text{ dm}^3 \cdot \text{mol}^{-1}$) for potassium iodide in ethylene glycol indicates that the B-coefficients become increasingly negative in the solvent order, ethylene glycol, water, glycerol, suggesting that the extent of association should be least in ethylene glycol and most pronounced in glycerol. One should also note that a reduction in viscosity associated with a reduction in the ion radius and an increase in the ion charge is usually attributed to the solvation sphere hypothesis [19, 20].

We observe that the trends of the two transport process properties (B and V_{ϕ}^{∞}) with ion size are quite opposite to one another in both solvents; as the partial molar volumes at infinite dilution (V_{ϕ}^{∞}) decrease from KI to KBr to KCl to NaCl, the B-coefficients increase.

For an electrolyte the B-coefficient of the Jones–Dole equation is formed by the independent contributions of the cation and the anion. To split the measured B-coefficients into ionic contributions B_+ and B_- , we relied on the assumption that the cation and the anion of KCl behave identically in solution. Measurements of the limiting equivalent ionic conductance in this laboratory gave the following values, $\lambda_{\text{K}^+}^{\infty} = 16.4 \mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$, and $\lambda_{\text{Cl}^-}^{\infty} = 17.9 \mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-2}$ for the ions K^+ and Cl^- in glycerol at 25°C. This compares with previous data [10] of $\lambda_{\text{K}^+}^{\infty} = 15.9 \mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-2}$, and $\lambda_{\text{Cl}^-}^{\infty} = 17.4 \mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-2}$. Their results show the limiting ionic conductance of K^+ and of Cl^- at 25°C, approximately the same in glycerol, in water, and in some of the lower alcohols. Furthermore, the value of B for KCl is virtually zero ($B_{\text{KCl}} = -0.016 \pm 0.004 \text{ dm}^3 \cdot \text{mol}^{-1}$) indicating that the salt in glycerol is “closest to being neither a net structure-breaker nor a structure-maker.” On this basis we decided to extend the subdivision based on $B_{\text{K}^+} = B_{\text{Cl}^-}$, taken from Kaminsky [16], to the B-coefficient in glycerol. The

Table V. Ionic Jones–Dole B-coefficients in Glycerol and in Water at 25°C Obtained with the Splitting Method ($B_{K^+} = B_{Cl^-}$)

Ion	B_{ion}^{\pm} ($dm^3 \cdot mol^{-1}$)	
	Glycerol	Water
Na ⁺	0.471 ± 0.002	0.086
K ⁺	−0.008 ± 0.003	−0.007
Cl [−]	−0.008 ± 0.003	−0.007
Br [−]	−0.090 ± 0.030	−0.032
I [−]	−0.170 ± 0.005	−0.069

ionic B values obtained through this splitting method, at 25°C, are summarized in Table V along with data in water. Other values were obtained by utilizing the additivity principle [21].

The division of B-coefficients into individual ionic values is a rather arbitrary process, their being no quantity analogous to transport numbers as used in conductivity assignments (Section 3.3). If the B-coefficients of given ions or given electrolytes in various solvents are compared, we observe that they have some relation to the molar volumes, V_{ϕ}^{∞} , of the solvents. Taking, for example, the solvents: glycerol ($V_{\phi}^{\infty}/cm^3 \cdot mol^{-1} = 44.5$), water ($V_{\phi}^{\infty}/cm^3 \cdot mol^{-1} = 45.4$), and ethylene glycol ($V_{\phi}^{\infty}/cm^3 \cdot mol^{-1} = 46.6$), and an electrolyte such as potassium iodide, the corresponding B/ $dm^3 \cdot mol^{-1}$ values are −0.178, −0.075, and 0.033, respectively, at 25°C. Thus, glycerol having the smallest molar volume V_{ϕ}^{∞} also generally exhibits the smallest B-coefficient.

At this point it must be emphasized that a quantitative theory of the B-coefficient is needed to elucidate the points raised, and the derivation of B remains an open question. According to Einstein, the presence of large kinetic entities in a liquid enhances the viscosity η ,

$$\eta = \eta_0(1 + 2.5\nu)$$

where η_0 is the solvent viscosity and ν is the volume fraction occupied by the spherical particles; ν must be taken to include the volume of any solvent immobilized on the surface of the particle. This volume fraction ν is expressed by

$$\nu = c\bar{V}$$

where c is the concentration in $mol \cdot dm^{-3}$ and \bar{V} is the molar volume of the solute including attached solvent in $dm^3 \cdot mol^{-1}$. Einstein's theory would be

successfully used to describe the viscosity of electrolyte solution theory if \bar{V} is assumed to be equal to the partial molar volume of the solvated solute V_ϕ^∞ . At higher concentrations the $A\sqrt{c}$ term in the Jones–Dole expression is very small in comparison with the Bc term; it can be safely neglected and since $v = cV_\phi^\infty$, we finally obtain the expression,

$$B \text{ (Einstein)} = 0.25[V_\phi^\infty / (\text{dm}^3 \cdot \text{mol}^{-1})]. \quad (4)$$

Since experiments (Section 3.1) have provided values for the partial molar volumes, V_ϕ^∞ , they were put into Eq. (4).

Clark's calculations, which take into account both hydrodynamic and electrostatic interactions, yield an ionic B-coefficient, in SI units, of the form,

$$B_{\text{ion}} \text{ (Clark)} = \left[S_H r^3 + S_D \frac{e^2(\epsilon_s - \epsilon_\infty) \tau}{4\pi\epsilon_0\eta_0\epsilon_s(3\epsilon_s + 2)r} \right] N_A \quad (5)$$

where: S_H (sticking) = $10\pi/3$, $S_D = 5/12$ for a sphere which is wetted by the medium, and S_H (slipping) = $4\pi/3$, and $S_D = 2/3$ for a sphere which is not wetted. Subscripts H and D refer to hydrodynamic disturbances and dielectric relaxation. r is the radius of a rigid sphere carrying a charge e , τ is the dielectric relaxation time, and ϵ_s and ϵ_∞ are the static low- and high-frequency permittivities, with the other symbols defined as before. The values of ϵ_s and ϵ_∞ , η_0 , and τ required in order to compute values of B-coefficient using Eq. (5) were in glycerol 40, 4.2, 0.909 Pa·s, and 1.12×10^{-9} s, respectively. The predicted B-coefficients at 25°C obtained using Eqs. (4) and (5) are shown in Table VI, where for comparison we have also included data for aqueous solutions. The data include the values for salts involving large hydrophobic ions, e.g., tetraalkylammonium iodides in glycerol and water at 25°C [3]. Included in Table VI are the experimental partial molar volume, V_ϕ^∞ , in $\text{cm}^3 \cdot \text{mol}^{-1}$, that are involved in the relationship of the B-coefficient in Eq. (4). A dash in columns 3 and 4 means that V_ϕ^∞ is not available for a satisfactory estimation of B.

The experimental values of the B-coefficients of 1:1 electrolytes consisting of small ions (i.e., not large hydrophobic ones) obtained by a rearrangement of the Jones–Dole expression at 25°C are generally smaller than $0.1 \text{ dm}^3 \cdot \text{mol}^{-1}$. For many salts they are considerably smaller, e.g., $B(\text{KCl}, \text{glycerol}) = -0.016 \text{ dm}^3 \cdot \text{mol}^{-1}$. For some salts they are negative, e.g., $B(\text{KI}, \text{glycerol}) = -0.178 \text{ dm}^3 \cdot \text{mol}^{-1}$. For salts involving large hydrophobic ions in glycerol, B-coefficients are commonly larger and almost always negative, e.g., $B(\text{Et}_4\text{NI}, \text{glycerol}) = -0.68 \text{ dm}^3 \cdot \text{mol}^{-1}$, $B(\text{Pr}_4\text{NI}, \text{glycerol}) = -2.9 \text{ dm}^3 \cdot \text{mol}^{-1}$, and $B(\text{Bu}_4\text{NI}, \text{glycerol}) = -1.9$

Table VI. Experimental and Theoretical B-Coefficients (in $\text{dm}^3 \cdot \text{mol}^{-1}$) and Partial Molar Volumes V_ϕ^∞ (in $\text{cm}^3 \cdot \text{mol}^{-1}$) for Salts in Glycerol and Water at 25°C I

Solvent	Partial molar volume V_ϕ^∞	Salt	B (experimental)	B (calculated)	
				Einstein	Clark
Glycerol	13.6	NaCl	0.463	0.034	0.031
	22.5	NaBr	0.360	0.056	0.034
	24.0	KCl	-0.016	0.060	0.032
	32.9	KBr	-0.107	0.082	0.035
	44.5	KI	-0.178	0.110	0.041
	-	Et ₄ NI	-0.680	-	0.130
	-	Pr ₄ NI	-2.90	-	0.171
	-	Bu ₄ NI	-1.90	-	0.211
	Water	16.4	NaCl	0.079	0.041
23.5		NaBr	0.053	0.059	0.073
26.5		KCl	-0.014	0.066	0.065
33.7		KBr	-0.049	0.084	0.067
169.2		Et ₄ NBr	0.343	0.420	0.208
185.3		Et ₄ NI	0.312	0.463	0.102
250.7		Pr ₄ NI	0.843	0.627	0.175
311.9		Bu ₄ NI	1.202	0.779	0.215

$\text{dm}^3 \cdot \text{mol}^{-1}$, while in aqueous solutions B-coefficients are commonly larger and almost always positive, e.g., $B(\text{Et}_4\text{NI}, \text{aq.}) = 0.312 \text{ dm}^3 \cdot \text{mol}^{-1}$, $B(\text{Pr}_4\text{NI}, \text{aq.}) = 0.843 \text{ dm}^3 \cdot \text{mol}^{-1}$, $B(\text{Bu}_4\text{NI}, \text{aq.}) = 1.202 \text{ dm}^3 \cdot \text{mol}^{-1}$, and $B(\text{Et}_4\text{NBr}, \text{aq.}) = 0.343 \text{ dm}^3 \cdot \text{mol}^{-1}$.

The B-coefficients obtained from experimental data are compared with those calculated applying relationships given as Eqs. (4) and (5) for suspensions of spherical particles. Better agreement is achieved when the B-coefficient for aqueous solutions are related to the standard partial molar volumes V_ϕ^∞ , as was the case with large aqueous tetraalkylammonium ions. This is due to the presumption that the major contribution to B arises from the volume of the ion in the solution, as if it were a nonelectrolyte and therefore obeying the Einstein relationship. However, B/V_ϕ for such ions is not constant and deviates from 2.5. Although it is accepted that the larger tetraalkylammonium ions are practically unsolvated, the flexibility of the alkyl chains may cause them to have different shapes in different solvents, leading to departure from the Einstein relation in glycerol.

In Fig. 4, the predicted B-coefficient for perfect "slipping" (full line) and "sticking" (dotted line) boundary conditions obtained using Eq. (5) are

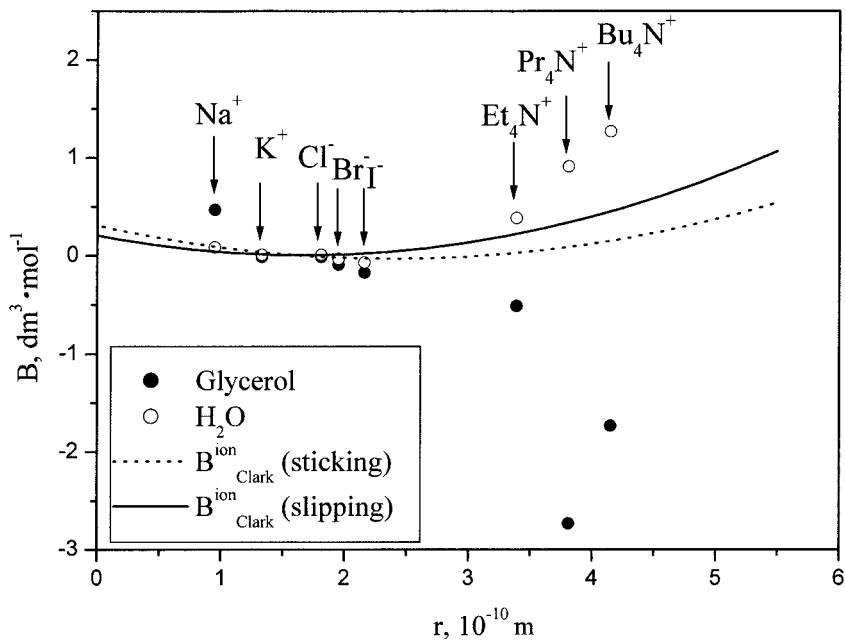


Fig. 4. Ion size dependence of theoretical and experimental values of B-coefficients in glycerol [present work] and in water [3] at 25°C.

compared with the experimental values. The crystallographic radii r used are as follows (in Å): $r(\text{Na}^+) = 0.95$, $r(\text{K}^+) = 1.33$, $r(\text{Cl}^-) = 1.81$, $r(\text{Br}^-) = 1.95$, $r(\text{I}^-) = 2.16$, $r(\text{Et}_4\text{N}^+) = 3.39$, $r(\text{Pr}_4\text{N}^+) = 3.81$, and $r(\text{Bu}_4\text{N}^+) = 4.15$. While in the case of small ions in glycerol, calculated values (positive ones) of B are very low compared to experiment, even when the correction for “slippage” is applied; in water the agreement is generally good. The experimental B -coefficient in glycerol is much larger in the case of Na^+ and this observed maximum for the sodium ion appears to be a real unexplained phenomenon.

3.3. Electrical Conductivity Data

The Onsager limiting equation [22] describing the concentration dependence of the molar conductivity is given by

$$A = A^\infty - (A'A^\infty + B')c^{1/2} \quad (6)$$

A' and B' are the usual Onsager coefficients given, in SI units, by

$$A' = \frac{N_A^{1/2} e^3}{12(1 + \sqrt{2}) \pi (\epsilon_0 \epsilon_r k_B T)^{3/2}}$$

$$B' = \left[\frac{2e^6 N_A^3}{9\pi^2 \epsilon_0 \epsilon_r k_B T \eta_0^2} \right]^{1/2}.$$

All symbols are defined as before. The relative permittivity ϵ_r and the viscosity η_0 for glycerol at 25°C were 40 and 909 mPa·s, respectively. When replacing A' and B' in Eq. (6), by their numerical values, the Onsager expression becomes

$$A/S \cdot \text{m}^2 \cdot \text{mol}^{-1} = A^\infty - (0.019922A^\infty + 0.026278 \times 10^{-5})(c/\text{mol} \cdot \text{m}^{-3})^{1/2}. \quad (7)$$

The molar conductance, A , of some alkali-metal halides salts as a function of molar concentration c at 25°C is given in Table VII. It can be seen from Fig. 5 that the extrapolation to zero solute concentration of A is based on

Table VII. Molar Conductance, A , of Alkali-Metal Halide Salts as a Function of Molar Concentration c at 25°C

Salt	c (mol·dm ⁻³)	A (μS·m ² ·mol ⁻¹)	A^∞ (μS·m ² ·mol ⁻¹)
KCl	0.01	31.43	33.54
	0.10	29.35	
	0.3	27.98	
NaCl	0.01	28.06	29.94
	0.1	26.18	
	0.31	25.25	
KI	0.01	29.00	30.95
	0.1	26.40	
	0.3	25.75	
NaBr	0.01	26.53	28.31
	0.1	23.00	
	0.36	21.20	
NaI	0.1	24.72	26.38
	0.01	21.63	
	0.34	19.54	
LiBr	0.01	22.66	24.18
	0.11	19.85	
	0.3	17.69	
KBr	0.01	30.00	32.02
	0.15	27.20	
	0.3	26.40	

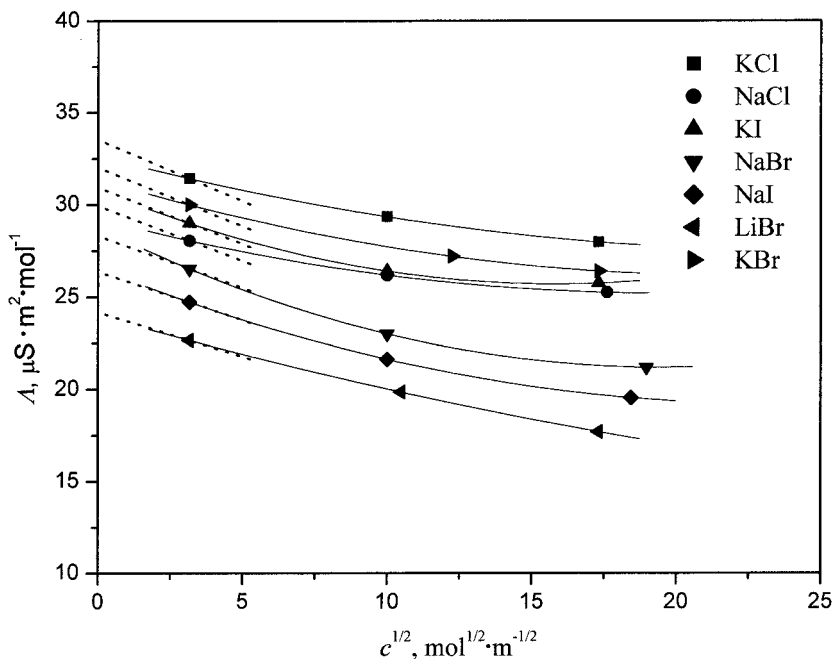


Fig. 5. Plots of molar conductivity versus the square root of the concentration for various salts in glycerol at 25°C. The dotted lines are calculated from the limiting Onsager equation.

three concentration points. The previous data of Blanco et al. [10] showed that the DHO equation is valid up to about $0.015 \text{ mol} \cdot \text{dm}^{-3}$ in glycerol, and we calculated values of Λ^∞ for the salts by adjusting Λ^∞ in Eq. (7), so that the limiting slope predicted by the Onsager equation passes through the data point corresponding to our lowest concentration, which is $0.01 \text{ mol} \cdot \text{dm}^{-3}$. The values of Λ^∞ obtained through this method, for different salts, are included in Table VII. This method of extrapolation with the assumption that the Onsager model is valid gives values of Λ^∞ that are not significantly falsified.

3.3.1. Single Ion Molar Conductivity in Glycerol

Ionic molar conductances at infinite dilution, λ^∞ , can now be deduced provided that accurate values of transference numbers are available at concentrations low enough to permit extrapolation to infinite dilution. For KCl and NaCl in glycerol, the ionic mobilities $\lambda_{\text{K}^+}^\infty$ and $\lambda_{\text{Na}^+}^\infty$ have been computed using the equations,

$$\lambda_{\text{K}^+}^\infty = t_{\text{K}^+}^\infty \times \Lambda_{\text{KCl}}^\infty,$$

$$\lambda_{\text{Na}^+}^\infty = t_{\text{Na}^+}^\infty \times \Lambda_{\text{NaCl}}^\infty,$$

and the known transference numbers at infinite dilution $t_{\text{K}^+}^\infty = 0.479$ in KCl and $t_{\text{Na}^+}^\infty = 0.417$ in NaCl at 25°C [9], the dependence of t_+ on concentration being assumed very small for values of t_+ near 0.5 mol·dm⁻³. $\lambda_{\text{Cl}^-}^\infty$ has been calculated using Kohlrausch's law of independent migration of ions:

$$\lambda_{\text{Cl}^-}^\infty = A_{\text{KCl}}^\infty - \lambda_{\text{K}^+}^\infty, \quad \text{or} \quad (\text{a})$$

$$\lambda_{\text{Cl}^-}^\infty = A_{\text{NaCl}}^\infty - \lambda_{\text{Na}^+}^\infty. \quad (\text{b})$$

Knowing $\lambda_{\text{K}^+}^\infty$, $\lambda_{\text{Na}^+}^\infty$, and $\lambda_{\text{Cl}^-}^\infty$ we can then compute the values $\lambda_{\text{Br}^-}^\infty$, $\lambda_{\text{I}^-}^\infty$, and $\lambda_{\text{Li}^+}^\infty$ for each ion, e.g.,

$$\lambda_{\text{Br}^-}^\infty = A_{\text{KBr}}^\infty - \lambda_{\text{K}^+}^\infty, \quad \text{or} \quad (\text{a})$$

$$\lambda_{\text{Br}^-}^\infty = A_{\text{NaBr}}^\infty - \lambda_{\text{Na}^+}^\infty \quad (\text{b})$$

taking always, as the best value of λ_{\pm}^∞ , the average of the two values obtained by methods (a) and (b). The resulting ionic conductances are given in Table VIII, along with data for these ions in water [23] and in methanol and ethylene glycol [24].

Table VIII. Ionic Molar Conductance, λ^∞ , and Walden Products, $\lambda^\infty\eta$, of Alkali-Metal Halide Ions in Glycerol (Present Work), in Water [23], in Methanol, and in Ethylene Glycol [24] at 25°C

Ion	Glycerol ^a	Water ^b	Methanol ^c	Ethylene Glycol ^d
λ^∞ ($\mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$)				
Na ⁺	12.5	50.1 × 10 ²	45.2 × 10 ²	31.0 × 10 ¹
K ⁺	16.1	73.5 × 10 ²	52.5 × 10 ²	46.2 × 10 ¹
Li ⁺	8.3	38.6 × 10 ²	39.6 × 10 ²	21.1 × 10 ¹
Cl ⁻	17.5	76.3 × 10 ²	52.3 × 10 ²	50.7 × 10 ¹
Br ⁻	15.9	78.1 × 10 ²	56.4 × 10 ²	49.8 × 10 ¹
I ⁻	14.4	76.8 × 10 ²	62.7 × 10 ²	46.0 × 10 ¹
$\lambda^\infty\eta$ ($\mu\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \cdot \text{Pa} \cdot \text{s}$)				
Na ⁺	11.3	4.46	2.46	5.22
K ⁺	14.6	6.54	2.86	7.78
Li ⁺	7.5	3.43	2.16	3.55
Cl ⁻	15.9	6.79	1.76	8.54
Br ⁻	14.4	6.95	3.07	8.38
I ⁻	13.1	6.83	3.41	7.75

^a $\eta = 909 \times 10^{-3} \text{ Pa} \cdot \text{s}$.

^b $\eta = 0.8903 \times 10^{-3} \text{ Pa} \cdot \text{s}$.

^c $\eta = 0.544 \times 10^{-3} \text{ Pa} \cdot \text{s}$.

^d $\eta = 16.84 \times 10^{-3} \text{ Pa} \cdot \text{s}$.

3.3.2. Mobilities of Ions in Relation to Viscosity

The Boyd–Zwanzig theoretical treatment of the solvent dipole relaxation effect is a correction of Stokes' law, and leads to the following expression:

$$\lambda_{\pm}^{\infty} \eta_0 = A'' r^3 / (r^4 + B'')$$

where in SI units,

$$A'' = N_A e^2 / 4\pi (10^7 / w^2)$$

$$B'' = (z_i e)^2 (\epsilon_s - \epsilon_{\infty}) \iota_0 / \{4\pi \epsilon_0 \epsilon_s (2\epsilon_s + 1) \eta\}$$

ι_0 is the dielectric relaxation time of pure glycerol, z_i (> 0) is the charge number of the ion type, w is the speed of light, and the other symbols have their usual meaning. The theory accordingly suggests that $\lambda_{\pm}^{\infty} \eta_0$ passes through a maximum of $27^{1/4} A'' / 4B''^{1/4}$ at $r = (3B'')^{1/4}$.

The limiting high frequency relative permittivity ϵ_{∞} , the static relative permittivity ϵ_s , and the dielectric relaxation time ι_0 , used to compute values of $\lambda_{\pm}^{\infty} \eta_0$ were, respectively, 4.2 [25], 40, and 1.1267×10^{-9} s in glycerol [11]. We have used the experimental single ion molar conductance of the

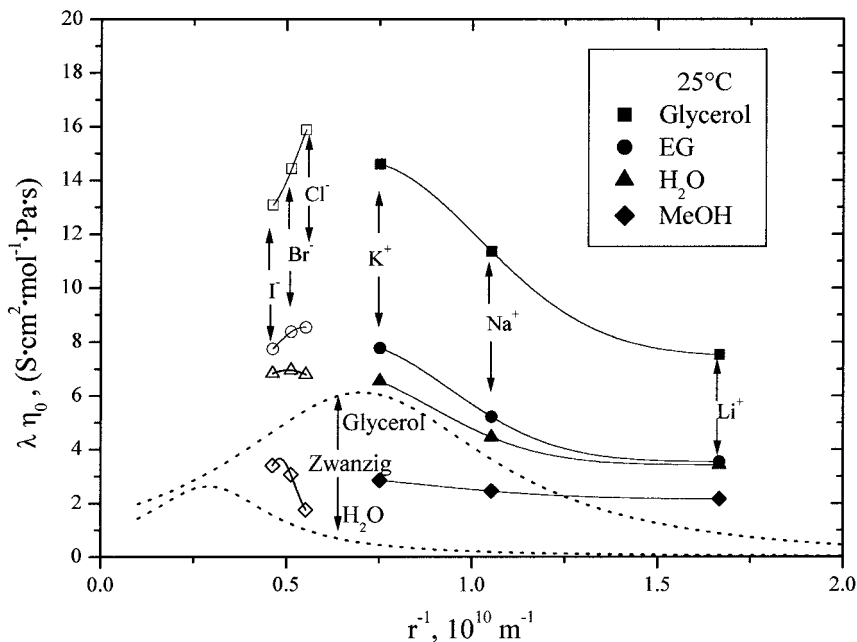


Fig. 6. Plots showing the dependence of limiting ionic Walden product on the reciprocal of the ionic radius for ions in various solvents at 25°C.

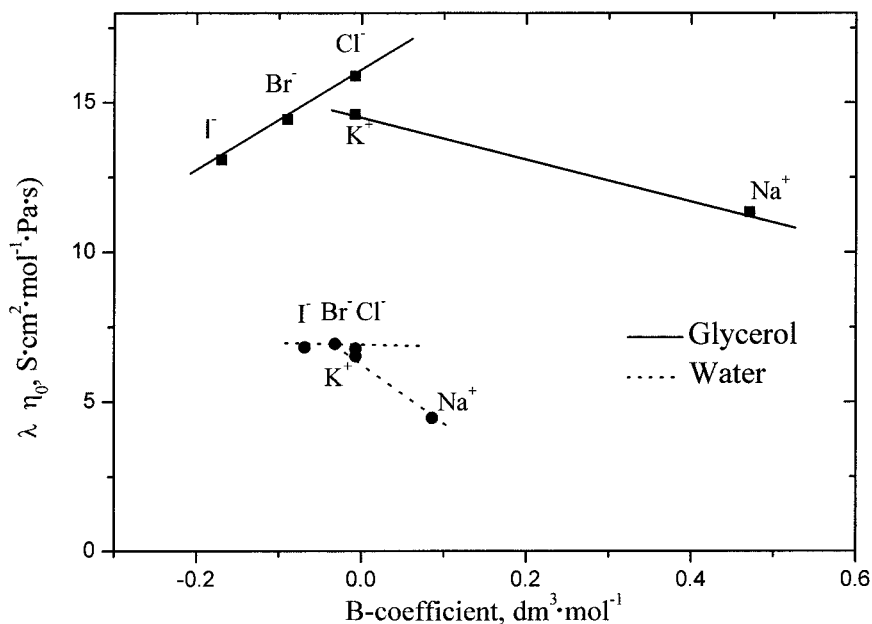


Fig. 7. Walden products for ions in glycerol and in water versus their B-coefficients at 25°C.

alkali-metal and halide ions in glycerol at 25°C, combined with the viscosity value $\eta_0 = 909 \text{ mPa}\cdot\text{s}$ of pure glycerol, to compare experimental and theoretical ionic behavior. The resulting conductance-viscosity products for these ions in glycerol are given in Fig. 7 along with data [26] of these ions in other solvents as a function of ionic crystallographic radii r . The predictions (dotted lines) of the above equation for perfect “slip” conditions in glycerol and water are also given in the figure. Although the addition of the solvent relaxation effect now makes it possible to account for the shape of the Walden product dependence on r^{-1} , the maximum calculated value of λ^∞ is not in agreement with experiment. The use of the perfect “slippage” condition increased $(\lambda_{\pm}^\infty \eta_0)_{\text{max}}$ by 15%; however, no other modification of the Boyd–Zwanzig equation will account for the experimentally observed values of the alkali-metal and halide ions in these solvents. Boyd–Zwanzig’s theory also predicts a common curve for both anions and cations, whereas $(\lambda_{\pm}^\infty \eta_0)$ differs considerably according to the sign and the charge of an ion. It appears also from our data in Fig. 7 that the solvents group together according to the number of hydrogen bonds which can be formed per solvent molecule. Thus, the values for the mono-alcohols are similar to each other, water and ethylene glycol have similar values, and glycerol, with three hydroxyl groups in the molecule [27], lies by itself.

In comparing the ionic conductances of solutions in glycerol with those in other solvents, two features are apparent. Firstly, the ratios between the Walden product for different ions are approximately the same in water, ethylene glycol, methanol and glycerol. This seems to indicate that the mechanisms, whatever they are, which determine the variation of ionic mobility with ionic radius, are the same in these solvents, despite the differences in solvent viscosity and solvent molecular size. The second feature is that the Walden products for glycerol are markedly higher than those for the other solvents.

A comparison of the trends of viscosity B-coefficients with the resulting conductance-viscosity products for the alkali-metal halides ions in glycerol and other solvents need to be explored. One can see that there are similarities between Clark's calculations of B and Zwanzig's calculations of ionic conductivities λ_0 ; theoretical values are always less than the experimental results.

The relationship between the Walden product for ions and their B-coefficients is of interest and is shown for glycerol and water at 25°C in Fig. 7. *Structure-breaking* ions (those with negative B-coefficients) are seen to have higher Walden products than *structure-making* ones.

4. CONCLUSION

We have made V_ϕ studies of partial molar volumes in glycerol solutions of alkali-halides that have yielded reliable infinite dilution values V_ϕ^∞ . The Redlich and Rosenfeld theoretical limiting law was used up to its limits with a high degree of accuracy. Glycerol is found to be one of the few solvents that is similar to water in showing large positive partial molar volumes. Moreover, viscosity studies show that ions with negative B-coefficients are the same in both solvents, although the values of B are larger in glycerol. We consider that the subdivision of the B-coefficients into ionic contributions, proposed for water, can be successfully used in glycerol.

The B-coefficient depends on ion-solvent interactions and is related to the volumes of the ions, but so far in a theoretically inaccessible manner. The existing theories predict B to be always positive, while experimental evidence showed that B could be negative. Although the theories appears to be sound for water, they do not hold when the solvent is changed. For glycerol, this outcome is predictable due to its very low electrostatic character compared to that of water.

We also made studies of ionic conductivities in glycerol solutions of alkali halides that have yielded infinite dilution values at 25°C. The resulting values were compared with those in aqueous solution and with those in alcoholic solutions. Glycerol stands out from other common solvents in

having a Walden product which is higher than that in any other common solvent. However, the ratio of the ionic mobilities of alkali-metal and halide ions is approximately the same in all three solvents (glycerol, water, and ethylene glycol), indicating that in these solvents the same conductive transport mechanism of ions occurs. The similarity between these solvents, despite the differences in viscosity and molecular size, might follow from the fact that all three liquids display hydrogen bonding, and have high values of relative permittivity arising from polar molecules.

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