*J. Chem. Eng. Data* **1998,** *43,* 1004−1008

# Ion−Solvent Interactions of Some Alkali Halides in Glycerol from Density and Viscosity Data

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This paper presents the results of density and viscosity measurements for glycerol solutions of KCl, NaCl, KBr, and KI at 25 °C. The apparent and partial molar volumes ($V_\Phi$ and $V_1$) 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 $B_{K^+} = B_{Cl^-}$, developed for the separation of the *B*-coefficients in aqueous solutions was used in glycerol. The ionic *B*-coefficients are discussed in terms of structure-making and structure-breaking properties of ions in glycerol. A comparison of molar volume data with viscosity data in glycerol shows that, as in aqueous solutions, the salt (NaCl) having the highest B-coefficient exhibits the smallest limiting apparent molar volume $V_\Phi^\infty$. Finally, the similarities of ion−solvent interactions in pure water with those in glycerol and the effects that the solutes seem to have on both solvents are discussed.

## Introduction

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 (Briscoe and Rhinehart, 1942; Crickard and Skinner, 1969; Jenkins et al., 1995). This led us to study the viscometric as well as molar volume properties for glycerol solutions of a few alkali halide 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 process 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 are available.

Glycerol is an obvious candidate because like water it is a hydrogen-bonded liquid (Champeney et al., 1986) and has a large relative permittivity, which makes it a good solvent for ionic salts. Further motivation for the present work has been provided by the existence of experiments on the variation of molar ion conductance with ion radius in glycerol (Blanco et al., 1989). This work shows that the ionic mobilities of alkali halides ions in glycerol follow the same pattern as in aqueous solution, although the absolute values do of course scale approximately with the solvent viscosity.

The Redlich and Rosenfeld linear square root relationship (Redlich and Rosenfeld, 1931) 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 (Jones and Dole, 1929), 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. No less interest has been shown toward the possibility of calculating the ionic contributions of the *B*-coefficient in order to study the behavior of single ions in solution.

## Experimental Section

Commercial glycerol, Aldrich gold label grade, quoted as 99.5+% pure was further distilled under reduced pressure at 140 °C and 0.5 mmHg. Only the middle fraction was used and found to have an electrical conductivity of $7.4 \times 10^{-9}$ S cm$^{-1}$ at 23.9 °C, this value not being appreciably reduced by further distillation. This electrical conductivity was taken as an indication of purity, the lowest value previously reported being (6 to 8) $\times 10^{-9}$ S cm$^{-1}$ by Accascina and Petrucci (1959). The salts (KCl, KBr, NaCl, and KI) used to prepare solutions in glycerol were Aldrich anhydrous gold label, quoted as 99.999% pure. Owing to the hygroscopic nature of glycerol and the salts, solutions preparation and physical measurements such as density and viscosity were 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 density measurements were carried out in the argon thermostat, while those of viscosity in a glass-walled paraffin bath which was in turn in the thermostated argon atmosphere and whose temperature was kept constant within ±0.05 °C throughout a viscosity run.

Measurements with kinematic viscometers are associated with accurate determination of the density, and 25 mL Technico density bottles type B5733 were used. The

10.1021/je9801260 CCC: $15.00

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 weightings 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 ($d_W = 0.997\,075$ g cm$^{-3}$), we calculated the density $d$ of the sample solution using the formulae:

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

Corrections for the buoyancy of air and argon affected the density value in its fifth place. The density measurements carried out for each solution are believed to be precise within 0.05%.

An ASTM 445 Technico Ubbelohde suspended bulb level viscometer, type VHB-590-170F, size 3 C, was used for all viscosity measurements. The advantages and method of use of this type have been fully described elsewhere (Kaminsky, 1955). 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 recalibration 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

$$\eta_r = \frac{\eta}{\eta_0} = \frac{d \cdot t}{d_0 \cdot t_0}$$

where $d$, $d_0$, $\eta$, $\eta_0$, $t$, 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 $t_0$), which were manipulated arithmetically to achieve one result, $\eta/\eta_0$. The effects 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 $\eta$ 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 deg at 25 °C. Thus, the uncertainty in $\eta$ due to ±0.05 °C accuracy 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 $\eta$ (or $\eta_0$) due to the above uncertainties is 0.11%, and the uncertainty in $\eta/\eta_0$ is believed to be of the order of 0.15%.

## Results

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

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

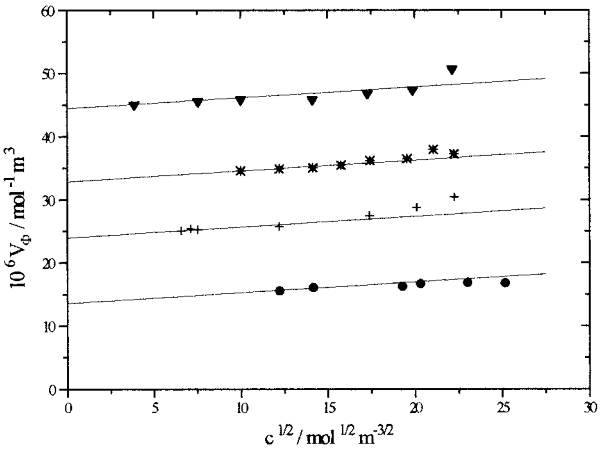

**Figure 1.** Graphs of experimental apparent molar volumes $V_\Phi$ versus the square root of the concentration $c$ for various salts in glycerol at 25 °C: (▼) KI, (*) KBr, (+) KCl, (●) NaCl. The full lines are the calculated theoretical Debye−Hückel limiting slopes.

**Table 1. Partial Molar Volumes $V_\Phi$ and Absolute Densities $d$ of Alkali Halides in Glycerol as a Function of Concentration $c$ at 25 °C**

| $c$/mol m$^{-3}$ | $d$/kg dm$^{-3}$ | $V_\Phi$/cm$^3$ mol$^{-1}$ | $c$/mol m$^{-3}$ | $d$/kg dm$^{-3}$ | $V_\Phi$/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 |
| 148.3171 | 1.2642 | 25.8 | | | |
| | | 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 |

where $V_1$ is the partial molar volume of the solute including attached solvent, $M$ the molar mass of the solute, $M_0$ the molar mass of the solvent, and $x$ the mole fraction of the solute. The values of $V_\Phi$ thus obtained are given in Table 1, 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 (Masson, 1929) is unreliable. We assumed the Redlich and Rosenfeld theoretical equation valid up to 0.05 mol dm$^{-3}$ and extrapolated the $V_\Phi$’s values to infinite dilution with the aid of the following expression

$$V_1 = V_\Phi^\infty + S_{th}\, c^{1/2} + Dc \qquad (1)$$

$$S_{\mathrm{th}} = N^2 e^3 \left(\frac{8\pi w^3}{4\pi \epsilon_0 \epsilon_r}\right)^3 R T^{1/2} \left(\frac{\partial \ln \epsilon_r}{\partial p} - \frac{\beta}{3}\right) \tag{2}$$

where $D$ is an empirical deviation constant, $V_\Phi^\infty$ is the limiting apparent molar volume and is equal to the partial molar volume at infinite dilution $V_\Phi^\infty$, $N$ is Avogadro's constant, $e$ is the proton charge, $\beta$ is the compressibility of the solvent, $R$ is the gas constant, $T$ is the absolute temperature, $p$ is the pressure, $\epsilon_0$ is the permittivity of vacuum, $\epsilon_r$ 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 $\partial \ln \epsilon_r / \partial p = 4.7 \times 10^{-10}$ m$^2$ N$^{-1}$ was calculated from the dielectric-pressure dependence data of Miner and Dalton (1953). Values of the compressibility $\beta$ are also given at 20 °C ($21.1 \times 10^{-11}$ m$^2$ N$^{-1}$) and at 28.5 °C ($21.7 \times 10^{-11}$ m$^2$ N$^{-1}$). At 25 °C a value of $21.4 \times 10^{-11}$ m$^2$ N$^{-1}$ was used in the determination of $S_{\mathrm{th}}$. A common value of 0.17 cm$^3$ mol$^{-1}$ of the limiting slope was used in the determination of apparent molar volumes at infinite dilution $V_\Phi^\infty$, i.e., $V_\Phi^\infty = V_{\Phi_{\mathrm{exp}}} - 0.17c^{1/2}$. The set of full straight lines in Figure 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 extrapolating does not introduce a serious error into the evaluation of $V_\Phi^\infty$ values, but if one extrapolates the high concentrations $V_\Phi$'s to infinite dilution using the linear portion above $c^{1/2} = 15$ mol$^{1/2}$ m$^{-3/2}$, errors up to 5 cm$^3$ mol$^{-1}$ result.

The $A$- and $B$-coefficient were evaluated from Jones and Dole's semiempirical equation in the form

$$(\eta_r - 1)\, c^{-1/2} = A + Bc^{1/2} \tag{3}$$

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 (1932). Their expression of the intercept $A$ is

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

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

$\kappa$ being Debye−Hückel's (D−H) parameter, $\Lambda^\infty$ the molar conductance of the electrolyte at infinite dilution, $\lambda_+^\infty$ and $\lambda_-^\infty$ the molar conductances of the ions present at infinite dilution, $F$ Faraday's constant, $k_B$ Boltzmann's constant, and the other symbols 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 $10^5\Lambda^\infty$/S m$^2$ 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 m$^2$ mol$^{-1}$, K$^+$, 1.644; Na$^+$, 1.286; Cl$^-$, 1.794; Br$^-$, 1.815; I$^-$, 1.535. The $B$-coefficient representing the ion−solvent interaction conditioned by ion size cannot be calculated a priori, despite several theoretical attempts (Einstein, 1906; Clarck, 1975; Ibucki and Nakahara, 1986). The theories predict $B$ to be always positive, while experimental evidences show that $B$ can be negative.

The viscosity data are given in Table 2 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 Figure 3, and the slope of the plots gives the $B$-coefficients.

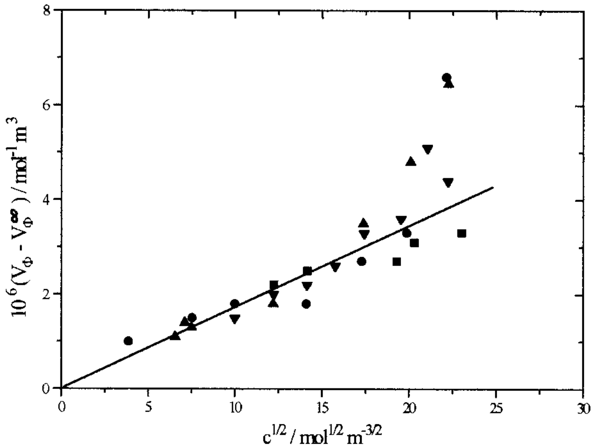

**Figure 2.** Relative apparent molar volumes ($V_\Phi - V_\Phi^\infty$) versus the square root of the concentration $c$ for various salts in glycerol at 25 °C: (▼) KBr, (●) KI, (■) NaCl, (▲) KCl. The full line is the calculated Debye−Hückel limiting slope ($V_\Phi - V_\Phi^\infty = 0.17\sqrt{c}$), common to all the salts studied.

**Table 2. Jones and Dole's 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 | | |

A summary of all the results obtained ($V_\Phi^\infty$, $A_{\mathrm{theor}}$, $B_{\mathrm{exp}}$) for NaCl, KCl, KBr, and KI glycerol solutions is given in Tables 3 and 4, where for comparison we have also included data in other solvents (Millero, 1971; Jenkins and Marcus, 1995).

For an electrolyte the $B$-coefficient of the Jones and Dole equation is formed by the independent contribution 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 conductances in this laboratory gave the following values: $\lambda_{K^+}^\infty = 16.4$ $\mu$S m$^2$ mol$^{-1}$ and $\lambda_{Cl^-}^\infty = 17.9$

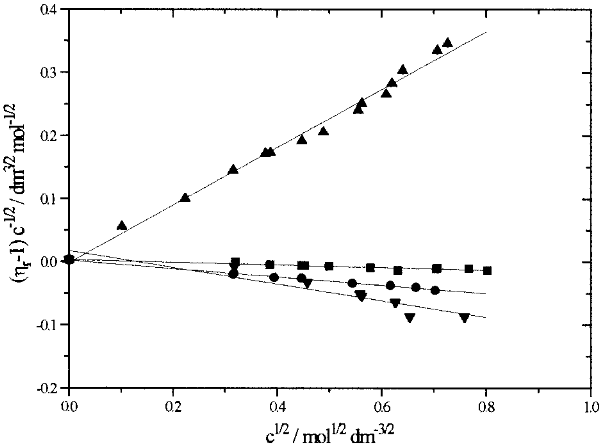

**Figure 3.** Classical Jones and Dole's viscosity plot for various salts in glycerol at 25 °C: (▼) KI, (●) KBr, (■) KCl, (▲) NaCl.

**Table 3. Apparent Molar Volumes at Infinite Dilution $V_\Phi^\infty$ Obtained with the Aid of the Theoretical Limiting Slope ($V_\Phi^\infty = V_\Phi - 0.17\sqrt{c}$), and Jones−Dole's Coefficients *A* (Theoretical) and *B* (Experimental), for Various Salts in Glycerol at 25 °C**

| electrolyte | $V_\Phi^\infty$/cm³ mol⁻¹ | *A*/dm^3/2^ mol^−1/2^ | *B*/dm³ 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 4. Apparent Molar Volumes at Infinite Dilution $V_\Phi^\infty$ and Viscosity *B*-Coefficients for Various Salts in Glycerol, Along with Data in Water and in Ethylene Glycol at 25 °C**

| | ($V_\Phi^\infty$; $10^{-3} \times B$)/cm³ mol⁻¹ | | |
|---|---|---|---|
| solute | 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) |

**Table 5. Ionic Jones−Dole's *B*-Coefficients in Glycerol and in Water at 25 °C Obtained with the Splitting Method ($B_{K^+} = B_{Cl^-}$)**

| | *B*/dm³ mol⁻¹ | |
|---|---|---|
| ion | 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 |

µS m² mol⁻² for the ions $K^+$ and $Cl^-$ in glycerol at 25 °C. This compares with previous data (Blanco et al., 1989) of $\lambda_{K^+}^\infty = 15.9$ µS m² mol⁻², and $\lambda_{Cl^-}^\infty = 17.4$ µS m² mol⁻². Their results show the limiting ionic conductances of $K^+$ and $Cl^-$ 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 ($B_{KCl} = -0.016 \pm 0.004$ dm³ mol⁻¹) indicating that the salt in glycerol is "closest to being neither a net structure-breaker nor a -maker". On these bases we decided to extend the subdivision based on $B_{K^+} = B_{Cl^-}$, taken from Kaminsky (1957), to the *B*-coefficient in glycerol. The ionic *B* values obtained through this splitting method, at 25 °C, are summarized in Table 5 along with data in water. Other values were obtained by utilizing the additivity principle (Dunn, 1968).

## Discussion

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 mol dm⁻³. Above this concentration the data show rapid positive deviations from the D−H values for KCl, KI and KBr, and more slow negative deviation for NaCl. It is also of interest that the magnitude of the volume changes ($V_\Phi^\infty$) in glycerol are quite close to those in ethylene glycol and in water.

The fit of the viscosity data to the Jones and Dole equation shows a 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 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 (Briscoe and Rinehart, 1942; Crickard and Skinner, 1969) and KI in methanol (Krumglaz, 1979) and was attributed to ion pairing. Within the accuracy of our measurements, our viscosity data of 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 is different in the case of $Na^+$ 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 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 dm³ 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 note also a reduction in viscosity associated with reduction in ion radius and increase in ion charge, usually attributed to the solvation sphere hypothesis (Samoilov, 1965; Francks, 1984).

Finally, we observe that the trends of the two transport process properties with ion size are quite opposite to one another in both solvents; as the partial molar volumes at infinite dilution ($V_\Phi^\infty$) decrease from KI to KBr to KCl to NaCl, the *B*-coefficient increases.

## Conclusion

We have made studies of partial molar volumes in glycerol solutions of alkali halides that have yielded reliable infinite dilution values. The Redlich and Rosenfeld theoretical limiting law was used up to the limits set by this law 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 ones in both solvents, though the values of *B* are larger in glycerol. We also consider that the subdivision of the *B*-coefficients into ionic contributions proposed in water can be successfully used in glycerol. The general conclusion is that glycerol and water behave very similarly as solvents for alkyl halides despite the differences in viscosity and molecular size. The similarity is presumably caused by both liquids being hydrogen-bonded and having large relative permittivities.

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Received for review June 2, 1998. Accepted August 11, 1998.

JE9801260