Conductance of Solutions of Alkali-Metal Halides in Glycerol

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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 and at other temperatures from (3.37 to 42.24) °C in the case of KCl and NaCl. 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. The values for glycerol were the largest so far measured. The limiting ion conductivities, λ^∞, obtained from experimental data were compared with those calculated applying the Boyd−Zwanzig theory. A modified Walden rule, $\Lambda^\infty\eta^p = \text{constant}$, is suggested as applicable in glycerol, the exponent p being less than unity and having a value down to 0.9. Finally, the temperature dependence of the Walden product for NaCl− and KCl−glycerol solutions is discussed.

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 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.

Since previous experiments have provided values for the cation transference number of KCl in glycerol,[1] 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,[2] where these workers have tested the Debye−Hückel−Onsager (DHO) equation in the limit of low concentration and found that this equation fits quite well up to $c \sim 0.01$ mol dm^{-3}. However, there was a lack of conductance data on electrolytes in glycerol at temperatures other than 25 °C; therefore, it seemed very interesting to provide data for such a highly viscous solvent over as large a temperature range as possible. In a previous paper,[3] the ionic mobility in glass-forming mixtures of sodium chloride and glycerol was studied. Experiments resulted in the conclusion that the ion mobility displays a very smooth and regular variation with temperature, and there seems at first inspection to be no evidence for a change in the character of ion motion between the low- and high-viscosity regions. In the present paper, we report conductance data for KCl and NaCl in glycerol at 25 °C and other temperatures to test the Walden product, as there are indications of a less direct nature, based on the rule, which do suggest a change in the ionic transport mechanism as the glycerol is cooled.

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 the values predicted by the Boyd−Zwanzig theory.

2. Experimental Section

2.1. Materials. Aldrich gold label grade glycerol, 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 7.4×10^{-9} S cm^{-1} at 23.9 °C, this value not being 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. All solutions were prepared by mass. The solution concentrations were initially calculated in terms of mole fraction of solute x and converted to a molar basis c in moles per cubic decimeter of solution, using the density data previously described.[4]

2.2. Apparatus. 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, as recommended by Jones and Bollinger.[5] The cells were filled under a 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

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10.1021/je000044n CCC: $19.00

(10^{-7} Torr). The experimental details are described elsewhere.[3,4]

The experiments were carried out at 25 °C for all the salts and at various temperatures from 42.24 to 3.37 °C for KCl and NaCl.

2.3. Procedure. 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 equation

$$\sigma/x = Gl/ax = k_cG/x$$

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.[6] The experiments on (σ/x) involved making several measurements, which were manipulated arithmetically to achieve one result ($\sigma/x = kcG/x$). The effect on this final result of the uncertainties in each of the measurements was as follows. The average uncertainty in determining mole fractions due to weighing with the Sartorius balance was at the most 1%. Possible uncertainties in G were associated with the instrument, and the accuracy 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 accuracy of 0.1 Ω^{-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%. When studying the temperature dependence of σ/x, the uncertainty due to the inhomogeneity of the temperature across the conductance cells was ±0.01 °C and the uncertainty due to the thermocouple/NPL thermometer calibration (outside the cryostat in a thermostated oil bath) was 0.05 °C between 21 and 27 °C, and 0.1 °C between 27 °C and 50 °C, thus giving a total uncertainty in the temperature of the order 0.12−0.14 °C (between 0 and 50 °C).

3. Results and Discussion

3.1. Primary Results of Data Analysis. The Onsager limiting equation describing the concentration dependence of the molar conductivity is given by

$$\Lambda = \Lambda^{\infty} - (A\Lambda^{\infty} + B)c^{1/2} \qquad (1)$$

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

$$A = \frac{N_A^{\ 1/2}e^3}{12(1 + 2^{1/2})\pi(\epsilon_0\epsilon_r kT)^{3/2}}$$

$$B = \left[\frac{2e^6N_A^{\ 3}}{9\pi^2\epsilon_0\epsilon_r kT\eta^2}\right]^{1/2}$$

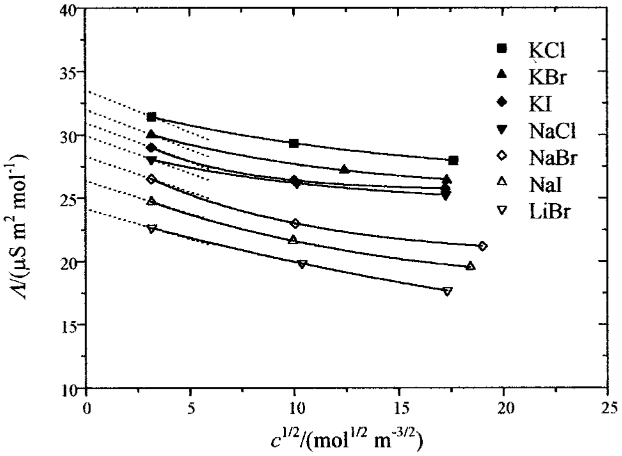

Figure 1. Graphs of molar conductivity versus the square root of the concentration for various salts in glycerol at 25 °C. The dotted lines are calculated from the limiting Onsager equation.

Table 1. Molar Conductance, Λ, of Alkali-Metal Halide Salts As a Function of Molar Concentration *c* at 25 °C

salt	c/(mol dm^{-3})	$\Lambda/(\mu$S m^2 mol^{-1})	$\Lambda^{\infty}/(\mu$S 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	

N_A is the Avogadro constant, e is the proton charge, ϵ_0 is the permittivity of vacuum, ϵ_r is the relative permittivity of the solvent, k is Boltzmann's constant, T is the absolute temperature, and η is the solvent viscosity. The relative permittivity ϵ_r and the viscosity η for glycerol at 25 °C were 40 and 909 mPa s, respectively. When replacing A and B, in eq 1, by their numerical values, the Onsager expression becomes

$$\Lambda/\text{S m}^2\ \text{mol}^{-1} = \Lambda^{\infty} - (0.019922\Lambda^{\infty} + 0.026278 \times 10^{-5})(c/\text{mol m}^{-3})^{1/2} \qquad (2)$$

It can be seen from Figure 1 that the extrapolation to zero solute concentration of Λ is based on three concentration points. From our own laboratory, the previous data of Blanco et al.[2] showed the DHO equation valid up to about 0.015 mol dm^{-3} in glycerol and we calculated values of Λ^{∞} for the salts by adjusting Λ^{∞} in eq 2, so that the limiting slope predicted by the Onsager equation passes through the data point corresponding to our lowest concentration, which is 0.01 mol dm^{-3}. The values of Λ^{∞} obtained through this method, for different salts, are included in Table 1. The analysis with the actual validity of the Onsager model does seem to indicate that this method of extrapolation gives values of Λ^{∞} that are not significantly falsified.

Table 2. Ionic Molar Conductance, λ^∞, and Walden Products, $\lambda^\infty\eta$, of Alkali-Metal Halide Ions in Glycerol (Present Work), in Water,[7] in Methanol, and in Ethylene Glycol,[8] at 25 °C

	$\lambda^\infty/(\mu\mathrm{S\ m^2\ mol^{-1}})$			
ion	glycerol[a]	water[b]	methanol[c]	ethylene glycol[d]
$\mathrm{Na^+}$	12.5	50.1×10^2	45.2×10^2	31.0×10^1
$\mathrm{K^+}$	16.1	73.5×10^2	52.5×10^2	46.2×10^1
$\mathrm{Li^+}$	8.3	38.6×10^2	39.6×10^2	21.1×10^1
$\mathrm{Cl^-}$	17.5	76.3×10^2	52.3×10^2	50.7×10^1
$\mathrm{Br^-}$	15.9	78.1×10^2	56.4×10^2	49.8×10^1
$\mathrm{I^-}$	14.4	76.8×10^2	62.7×10^2	46.0×10^1

	$\lambda^\infty\eta/(\mu\mathrm{S\ m^2\ mol^{-1}\ Pa\ s})$			
ion	glycerol[a]	water[b]	methanol[c]	ethylene glycol[d]
$\mathrm{Na^+}$	11.3	4.46	2.46	5.22
$\mathrm{K^+}$	14.6	6.54	2.86	7.78
$\mathrm{Li^+}$	7.5	3.43	2.16	3.55
$\mathrm{Cl^-}$	15.9	6.79	1.76	8.54
$\mathrm{Br^-}$	14.4	6.95	3.07	8.38
$\mathrm{I^-}$	13.1	6.83	3.41	7.75

[a] $\eta/\mathrm{Pa\ s} = 909 \times 10^{-3}$. [b] $\eta/\mathrm{Pa\ s} = 0.8903 \times 10^{-3}$. [c] $\eta/\mathrm{Pa\ s} = 0.544 \times 10^{-3}$. [d] $\eta/\mathrm{Pa\ s} = 16.84 \times 10^{-3}$.

3.2. 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 $\lambda^\infty_{\mathrm{K^+}}$ and $\lambda^\infty_{\mathrm{Na^+}}$ have been computed using the equations

$$\lambda^\infty_{\mathrm{K^+}} = t^\infty_{\mathrm{K^+}}\Lambda^\infty_{\mathrm{KCl}}$$

$$\lambda^\infty_{\mathrm{Na^+}} = t^\infty_{\mathrm{Na^+}}\Lambda^\infty_{\mathrm{NaCl}}$$

and the known transference numbers at infinite dilution $t^\infty_{\mathrm{K^+}} = 0.479$ in KCl and $t^\infty_{\mathrm{Na^+}} = 0.417$ in NaCl at 25 °C,[1] the dependence of t_+ on concentration being assumed very small for values of t_+ near to 0.5 mol dm^{-3}. The value $\lambda^\infty_{\mathrm{Cl^-}}$ has been calculated using Kohlrausch's law of independent migration of ions

$$\lambda^\infty_{\mathrm{Cl^-}} = \Lambda^\infty_{\mathrm{KCl}} - \lambda^\infty_{\mathrm{K^+}} \tag{a}$$

$$\text{or } \lambda^\infty_{\mathrm{Cl^-}} = \Lambda^\infty_{\mathrm{NaCl}} - \lambda^\infty_{\mathrm{Na^+}} \tag{b}$$

Knowing $\lambda^\infty_{\mathrm{K^+}}$, $\lambda^\infty_{\mathrm{Na^+}}$, and $\lambda^\infty_{\mathrm{Cl^-}}$, we can then compute the values $\lambda^\infty_{\mathrm{Br^-}}$, $\lambda^\infty_{\mathrm{I^-}}$, and $\lambda^\infty_{\mathrm{Li^+}}$ for each ion, for example,

$$\lambda^\infty_{\mathrm{Br^-}} = \Lambda^\infty_{\mathrm{KBr}} - \lambda^\infty_{\mathrm{K^+}} \tag{a}$$

$$\text{or } \lambda^\infty_{\mathrm{Br^-}} = \Lambda^\infty_{\mathrm{NaBr}} - \lambda^\infty_{\mathrm{Na^+}} \tag{b}$$

taking always, as the best value of $\lambda^\infty_\pm$, the average of the two values obtained by methods a and b. The resulting ionic conductances are given in Table 2, along with data for these ions in water[7] and methanol and ethylene glycol.[8]

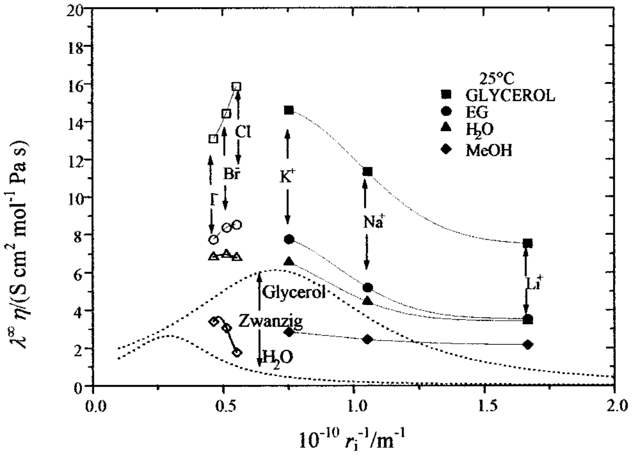

Figure 2. Graphs showing the dependence of limiting ionic Walden product on the reciprocal of the ionic radius for ions in various solvents at 25 °C.

3.3. 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:

$$\lambda^\infty_\pm\eta = A' r_i^{\,3}/(r_i^{\,4} + B')$$

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, r_i is the crystallographic ionic radius, and the other symbols have their usual meaning.[3,4] The theory accordingly suggests that $\lambda^\infty_\pm\eta$ passes through a maximum of $27^{1/4}A'/4B'^{1/4}$ at $r_i = (3B')^{1/4}$.

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 $\lambda^\infty_\pm\eta$ were respectively 4.2[9] and 40 and 1.1267×10^{-9} s in glycerol.[3] We have used the experimental single-ion molar conductance of the alkali-metal and halide ions in glycerol at 25 °C, combined with the viscosity value $\eta = 909$ mPa·s of pure glycerol, to compare experimental and theoretical ionic behavior. The resulting conductance–viscosity products for these ions in glycerol are given in Figure 2 along with data[10] of these ions in other solvents as a function of ionic crystallographic radii r_i. 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_i^{-1}, the maximum calculated value of λ^∞ is not in agreement with experiment. The use of the perfect "slippage" condition increased $(\lambda^\infty_\pm\eta)_{\max}$ 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 $(\lambda^\infty_\pm\eta)$ differs considerably according to the sign and the charge of an ion. It appears also from our data in Figure 2 that the solvents group together according to the number of hydrogen bonds which can be formed per solvent molecule. Thus, the values for the monoalcohols are similar to each other, water and ethylene glycol have similar values, and glycerol, with three hydroxyl groups in the molecule,[11] lies on its own.

In comparing the ionic conductances of solutions in glycerol with those in other solvents, two features are apparent. First, the ratios between the Walden products 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

Table 3. Density, d_0, Molar Concentration, c, Viscosity, η, and Molar Conductance at Infinite Dilution, Λ^∞, of KCl and NaCl in Glycerol at Various Temperatures

t/°C	d_0/(kg dm^{-3})	c/(mol dm^{-3}) KCl/NaCl	η/(Pa·s)	Λ^∞/(μS m^2 mol^{-1})
42.24	1.2468	0.3106/0.2973	0.242	146.0/125.8
37.98	1.2495	0.3112/0.2979	0.327	107.1/93.7
34.70	1.2516	0.3118/0.2984	0.416	87.2/78.2
29.35	1.2550	0.3126/0.2992	0.632	57.0/51.8
22.26	1.2595	0.3137/0.3004	1.155	33.0/30.2
17.72	1.2624	0.3144/0.3010	1.761	23.3/20.0
13.15	1.2653	0.3152/0.3017	2.762	15.8/13.4
9.16	1.2678	0.3158/0.3023	4.207	10.3/8.9
3.37	12715	0.3167/0.3032	8.107	5.8/4.1

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.

3.4. Test of a Modified Walden Relation. Accurate values for the viscosity η of pure glycerol exist above 0 °C,[12] and if we combine these with our readings of Λ^∞ between 3.37 and 42.24 °C, for KCl and NaCl, to form the Walden products, we obtain results given in Table 3. To calculate Λ^∞ at various temperatures from our measured values of σ/x, we have used a glycerol density $d_0(t)$ at temperatures calculated from

$$d_0/(\mathrm{kg.m}^{-3}) = 1273.7 - 0.637(t/°\mathrm{C})$$

the equation being a least-squares fit to the data between 0 and 100 °C given by Newman.[13] This equation also provides a good representation of the density data[14] for pure glycerol down to about −85 °C. A least-squares fit to the viscosity data of glycerol between 0 and 100 °C,[12] to an empirical power law formula[15] gave

$$\ln_e\{\eta/(\mathrm{Pa\ s})\} = -8.1229 + 0.167\{1000/(T/\mathrm{K})\}^{3.2}$$

This equation allows the calculation of the viscosity $\eta(T)$ to form Walden products at various temperatures. The calculations of Λ^∞ from σ/x also involve knowing the ratio Λ^∞/Λ_x, where Λ_x is the molar conductivity at mole fraction x. We have used the values $\Lambda^\infty/\Lambda_x = 1.189$ when $x = 22.43 \times 10^{-3}$ for KCl and $\Lambda^\infty/\Lambda_x = 1.186$ when $x = 21.49 \times 10^{-3}$ for NaCl.

We note that our values of Walden product increase as the temperature is lowered and the viscosity is increased. This is in qualitative agreement with other experiments,[8,16] in which the viscosity of the solution has been increased by the addition of a second solvent. These various authors have suggested a modified Walden rule, $(\Lambda^\infty\eta)^p$ = constant, as applicable in these cases, the exponent p being less than unity and having values down to about 0.7. Writing

$$(\Lambda^\infty\eta/\mathrm{S\ m^2\ mol^{-1}\ Pa\ s})(\eta/\mathrm{Pa\ s})^{p-1} = K \qquad (3)$$

a plot of $\ln_e(\Lambda^\infty\eta)$ versus $\ln_e(\eta)$, and a least-squares fit to our data on glycerol in Figures 3 and 4 between 3.37 and 42.24 °C give, respectively, for KCl and NaCl, $\{K = (3.982 \pm 0.0279) \times 10^{-5}, p = (0.915 \pm 0.006)\}$ and $\{K = (3.362 \pm 0.159) \times 10^{-5}, p = (0.906 \pm 0.004)\}$, and this best fit is shown as straight lines in the figures. One can see that the conductivities of dilute KCl and NaCl solutions in glycerol, in ethylene glycol, and in water can all be fitted moderately well by this modified Walden rule, with the above values of p and K. If one uses eq 3 to extrapolate to a viscosity value equal to that of water at 25 °C, we find a value only 11% higher than that of water at 25 °C. Although this close agreement is probably fortuitous, it does suggest that the high Walden product in glycerol is related to its high viscosity rather than any other specific solvation effects.

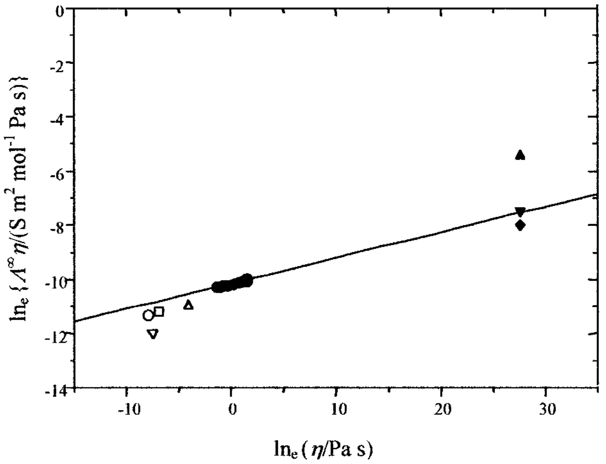

Figure 3. Graph of $\ln_e(\Lambda^\infty\eta)$ versus $\ln_e(\eta)$ to test the modified Walden relation for KCl in glycerol: ●, glycerol between 3.37 and 42.24 °C (present work); □, water at 25 °C;[7] ○, water at 100 °C; ▽, methanol at 25 °C; △, ethylene glycol at 25 °C.[8] At the right of the diagram are points calculated on the assumptions that the viscosity of glycerol is 10^{12} Pa s at respectively −82.4 °C (▲), −85.76 °C (▼), and −88.9 °C (◆). The full line is a least-squares fit to the glycerol data between 3.37 and 42.24 °C.

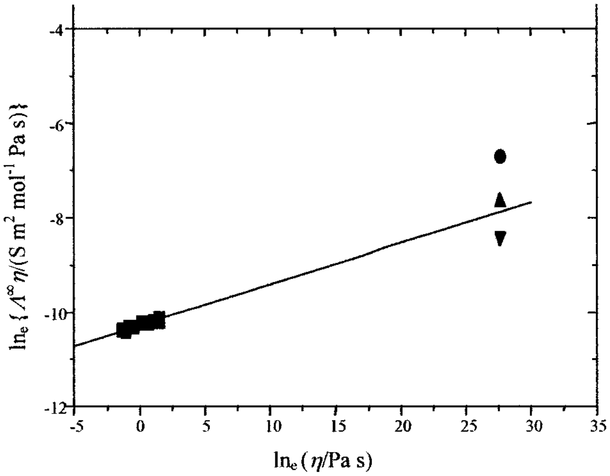

Figure 4. Graph of $\ln_e(\Lambda^\infty\eta)$ versus $\ln_e(\eta)$ to test the modified Walden relation for NaCl in glycerol between 3.37 and 42.24 °C. At the right of the diagram are points calculated on the assumptions that the viscosity of glycerol is 10^{12} Pa s at respectively −83.6 °C (●), −85.32 °C (▲), and −86.74 °C (▼). The full line is a least-squares fit to the glycerol data between 3.37 and 42.24 °C.

It would be very interesting to test eq 3 at low temperatures, but reliable viscosity data for pure glycerol appreciably below 0 °C seem to be not available. Alternatively, one can make a rough estimate using the rule[17] that the viscosity of supercooled liquids reaches a value of approximately 10^{12} Pa s at the glass transition temperature, T_G. If T_G is defined, somewhat imprecisely, as the temperature at which measurements on macroscopic phenomena indicate relaxation times of order 1 min to 1 h, then it seems a reasonable guess that T_G for glycerol probably lies between −83 and −88 °C; our values of dielectric relaxation times[3] give for instance at −82.13 °C a value ι_0 = 1 min while ι_0 = 1 h at −88.36 °C. Our low-temperature conductivity data for KCl and NaCl allow Walden products to be calculated at various assumed values of T_G, and some of these are included in Figures 3 and 4, for trial values of

Table 4. Ionic Molar Conductance, λ^∞, of Ions K^+, Na^+ and Cl^- in Glycerol at Various Temperatures.

	$\lambda^\infty/(\mu S\ m^2\ mol^{-1})$		
t/°C	K^+	Na^+	Cl^-
42.24	69.9	51.1	73.8
37.98	51.3	37.8	54.3
34.70	41.8	32.0	44.8
29.35	27.3	21.0	29.5
22.26	15.8	12.6	17.2
17.72	11.2	8.3	11.8
13.15	7.6	5.4	7.9
9.16	4.9	3.6	5.2
3.37	2.8	2.0	2.9

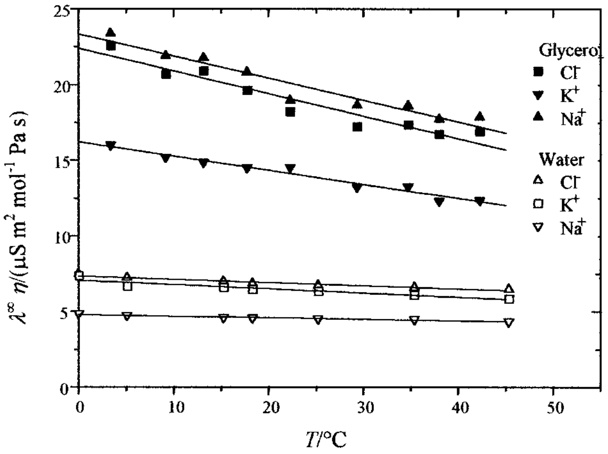

Figure 5. Graphs showing the variation of the ionic Walden product with temperature for glycerol (present work) and water.[18]

T_G between −82 and −88 °C. The results, despite the uncertainty in T_G, suggest that the Walden product for KCl and NaCl will continue to increase all the way down to the glass transition, reaching values in the range 10^{-4} to 10^{-3} S m² mol⁻¹ Pa s. It is suggested that, at temperatures just above the glass transition, the Walden product will probably be an order of magnitude larger than that in ordinary liquids. This is tentatively attributed to hydrogen bonding and network formation.

An additional test is to look at the temperature dependence of the Walden product ($\lambda_\pm^\infty\eta$) for the individual ions K^+, Na^+, and Cl^-. This is done by plotting the products ($\lambda_\pm^\infty\eta$) against the temperature (T) for these ions. Data on the variation of transference numbers with temperature are very scarce. We used the data on aqueous solutions[18] which show that the transference number for the chloride ion in KCl at infinite dilution increased by a factor 1.2% when the temperature was raised from 0 °to 40 °C. Here, we shall assume that $t_{K^+}(KCl) = 0.479$ and $t_{Na^+}(NaCl) = 0.417$ are invariant with temperature in the range 0−40 °C, on the basis of the assumption of the slow increase observed for $t_{Cl^-}(KCl)$ in aqueous solutions. The small change in transference number, t, is unimportant for the purpose of examining trends in ionic mobility with temperature.

Having settled upon the values of the transport numbers $t_{K^+}(KCl)$ and $t_{Na^+}(NaCl)$, one can use them in conjunction with the molar conductances at infinite dilution of KCl and NaCl to calculate ionic molar conductances of K^+, Na^+, and Cl^-. The results are given in Table 4. Figure 5 shows the temperature dependence of the Walden product for K^+, Na^+, and Cl^- in glycerol, along with data of these ions in water.[18] Each of the ions shows approximately the same variation of the product ($\lambda_\pm^\infty\eta$) with temperature. It should be noted, however, that with these ions the variation of ($\lambda_\pm^\infty\eta$) with temperature is only of the order of 30% over the range 0−50 °C in the two liquids.

4. Conclusion

Experiments on the electrical conductivities of solutions of NaCl and KCl in glycerol at various temperatures indicate that the Walden product, $\eta\ \Lambda^\infty$, is not consistent with a change of temperature and viscosity; instead a modified Walden rule is obeyed such that $\eta^p\Lambda^\infty = K$. In fact the conductivities of dilute NaCl and KCl in glycerol, in ethylene glycol, and in water can all be fitted moderately well with the above rule. 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, indicating that in these solvents the same conductive transport mechanism of ions occurs. The similarity between these solvents might follow from the facts that all three liquids display hydrogen bonding and have high values of relative permittivity arising from polar molecules.

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Received for review February 7, 2000. Accepted July 26, 2000.

JE000044N