Ionic Molar Conductivities in Solutions of KCl, NaCl and LiCl in Glycerol at 25°C

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IONIC MOLAR CONDUCTIVITIES IN SOLUTIONS OF KCl, NaCl AND LiCl IN GLYCEROL AT 25°C

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Conductivities of solutions of KCl, NaCl and LiCl in glycerol at 25°C have been measured for concentrations in the range 0.0005 to 0.5 mol dm^{-3}, and values of molar conductivity at infinite dilution obtained by extrapolation. Using previously measured transference numbers for KCl dissolved in glycerol, values of ionic molar conductivities at infinite dilution have been deducted for K$^+$, Na$^+$, Li$^+$ and Cl$^-$ ions. Values of ionic Walden products are calculated and compared with those in aqueous and other alcoholic solutions, the values for glycerol being the largest so far measured.

1 INTRODUCTION

We describe here an experimental study of the conductivities of solutions of KCl, NaCl and LiCl in glycerol at 25°C and at concentrations in the range 0.0005 to 0.5 mol dm^{-3}. Since the cation transference number of KCl in glycerol has previously been measured both by the moving boundary technique[1] and by the concentration cell method[2] and the cation transference number of NaCl in glycerol has been measured by the concentration cell method[2], it follows that ionic conductivities in the low concentration limit can now be deduced for K$^+$, Na$^+$, Li$^+$ and Cl$^-$ if the independent migration of ions is assumed. In this paper we compare the resulting values with those in aqueous solution and with those in alcoholic solutions.

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

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glycerol is nearly a thousand times greater than that of water. An analysis of our results shows that in many respects this is the case.

2   EXPERIMENTAL

The glycerol used as solvent was Aldrich 99.5 + % pure having a measured conductivity of 9.29×10^{-9} S cm^{-1}. The KCl, NaCl and LiCl were Aldrich gold label quoted as 99.999 % pure. All solutions were prepared inside a glove-box filled with BOC high purity (99.998 %) Argon, and the conductance cells were filled and sealed inside the glove-box as previously described[3]. The impedance of the cell was measured using a Wayne Kerr model B905 automatic Precision Bridge allowing measurements at frequencies ranging from 100 Hz to 10 kHz.

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_2 Pt Cl$_6$ solution to which traces of lead acetate were added, as recommended by Jones and Bollinger[4].

The cell was placed inside a copper container whose temperature was kept constant at 25.000 ± 0.005°C by placing it in a thermostated water bath. The cell constant was determined using 0.1 M and 0.01 M KCl aqueous solutions, with the conductance values given by Jones and Bradshaw[5]. The frequency dependence between 1 and 10 kHz was checked in these aqueous solutions and the results indicated that at 10 kHz the residual effect of electrode polarisation was less than 0.2%.

3   RESULTS

Our experiments using glycerol as solvent showed that the effects of the electrode capacitance were shifted to lower frequencies than in experiments in aqueous solutions. The cell impedance in most solutions was purely resistive between 100 Hz and 10 kHz, with a change in resistance over this frequency range of less than 0.2%. In the most dilute solutions, however, and in the nominally pure glycerol, the cell resistance appeared to increase slightly (~ 0.5%) over the frequency range 100 Hz to 10 kHz. However in these cases the cells had a resistance of over 1 MΩ, and this increase was attributed to error in the measuring circuit at high frequencies. The figures adopted were these at 100 Hz and 1 kHz which agreed to better than 0.1%. All conductances were corrected by subtracting the solvent contribution. The molar conductances Λ of KCl, NaCl and LiCl solutions, and the corresponding concentrations in mol dm^{-3}, are given in Table 1 and are plotted versus $c^{1/2}$ in Figure 1. At concentrations up to and including 0.01 mol dm^{-3} the data agree remarkably well with the Onsager limiting law,

$$\Lambda = \Lambda^0 - (A\Lambda^0 + B)c^{1/2}. \tag{1}$$

Table 1 Molar conductivities of KCl, NaCl and LiCl solutions in glycerol at 25°C

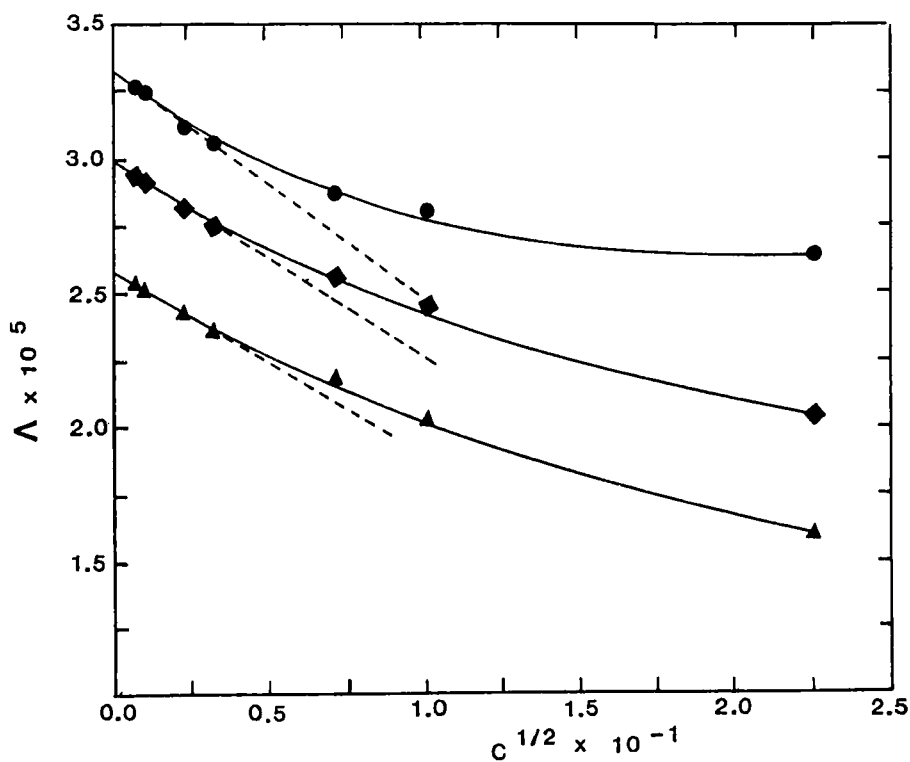| c/mol dm⁻³	Λ (KCl) ($\mu S\ m^2\ mol^{-1}$)	Λ (NaCl) ($\mu S\ m^2\ mol^{-1}$)	Λ (LiCl) ($\mu S\ m^2\ mol^{-1}$)
0.0005	32.62	29.34	25.27
0.001	32.43	29.06	25.00
0.005	31.12	29.11	24.12
0.01	30.47	27.33	23.45
0.05	28.60	25.41	21.69
0.1	27.92	24.32	20.14
0.5	26.18	20.18	15.85

Figure 1 Graphs of molar conductivity versus the square root of the concentration for various salts in glycerol at 25°C. The units of Λ are S m² mol⁻¹ and the units of c are mol m⁻³. ● KCl, ◆ NaCl, ▲ LiCl. The dashed lines are calculated from the limiting Onsager equation.

Table 2 Molar conductivities at infinite dilution and Walden products of KCl, NaCl and LiCl in glycerol at 25°C.

Salt	$\Lambda^0/\mu S\ m^2\ mol^{-1}$	$\Lambda^0\eta/\mu N\ S\ s\ mol^{-1}$
KCl	33.3	30.3
NaCl	29.9	27.2
LiCl	25.7	23.4

In equation (1) Λ^0 is the limiting conductance at zero concentration and A and B are the usual Onsager coefficients given, in S.I. units, by

$$A = \frac{N_A^{1/2}e^3}{12(1 + 2^{1/2})\pi(\varepsilon_0\varepsilon_r kT)^{3/2}}$$

$$B = \left[\frac{2e^6N_A^3}{9\pi^2\varepsilon_0\varepsilon_r kT\eta^2}\right]^{1/2},$$

N_A is the Avagadro constant, e the proton charge, ε_0 the permittivity of vacuum, ε_r the relative permittivity of the solvent, k is Boltzmann's constant, T the absolute temperature, and η is the solvent viscosity. Values for Λ^0 were determined by fitting the data for $c \leq 0.01$ mol dm^{-3} to Eq. (1), using an iterative procedure, with the values $\varepsilon_r = 42.7$ and $\eta = 0.91$ Pa s for pure glycerol[6,7]. The results, together with the Walden product, $\Lambda^0\eta$, are shown in Table 2.

Ionic molar conductances at infinite dilution, λ^0, can now be deduced if a figure for the cation transference number at infinite dilution, t_+^0, for one of the salts is known. For KCl in glycerol the moving boundary[1] and concentration cell[2] methods have given values of $t_+ = 0.476$ and 0.479, and we adopt a value of $t_+^0 = 0.478$, the dependence of t_+ on concentration being assumed very small for values of t_+ near to 0.5. The resulting ionic molar conductivities are given in Table 3, together with the corresponding Walden products, $\lambda^0\eta$. A check on the consistency of the data is provided by the value $t_+^0 = 0.423$ for NaCl in glycerol, based on concentration cell data[2], which compares with the value 0.418 calculated from the figures in Table 3: we regard the difference as lying within the combined uncertainties of the two sets of experiments.

Table 3 Ionic molar conductivities at infinite dilution and Walden products for K^+, Na^+, Li^+, and Cl^- in glycerol at 25°C.

Ion	$\lambda^0/\mu S\ m^2\ mol^{-2}$	$\lambda^0\eta/\mu N\ S\ s\ mol^{-1}$
K^+	15.9	14.5
Na^+	12.5	11.4
Li^+	8.3	7.5(5)
Cl^-	17.4	15.8

4 DISCUSSION OF RESULTS

It is noticeable that the Onsager equation fits quite well up to $c \sim 0.01$ mol dm^{-3}. This contrasts with the behaviour in aqueous solutions when departures became evident above about 0.001 mol dm^{-3}. With a value of ε_r in glycerol, which is about one half that in water, one would expect departures to become evident at even lower concentrations in glycerol. One can perhaps attribute the surprisingly good fit to the onset of ionic association with increasing concentration, which counteracts the usual departure from the limiting law. This idea has been included in the equation derived by Fuoss[8], and a more detailed analysis of this for KCl in glycerol has been given previously[9]. Whilst the actual validity of the Fuoss model is still in doubt, this analysis does seem to indicate that an extrapolation using Onsager's equation will give values of Λ^0 that are not significantly falsified by association.

There have been previous measurements of Λ^0 for KCl in glycerol at 25°C, but not as far as we know for NaCl or LiCl. The previously reported values for KCl in glycerol at 25°C range from 27.5 μS m^2 mol^{-1} by Accascina and Petrucci[10] to 36.5 μS m^2 mol^{-1} by Heigemann[11]. Erdey-Gruz et $al.$ obtained $\Lambda\eta = 29.0$ μN S s mol^{-1} for a 0.01 mol dm^{-3} solution[12]: on using their value of $\eta = 0.945$ Pa s and using our value for the ratio of the conductivities at zero concentration and at 0.01 mol dm^{-3} we calculate a value $\Lambda^0 = 33.5$ μS m^2 mol^{-1} from their data. From our own laboratory the previous data of Champeney and Ould-Kaddour[13] gave the value $\Lambda^0 = 34.6$ μS m^2 mol^{-1}.

The scatter in these values presumably reflects differences in the purity of the glycerol used in each case. Some of the scatter might well be attributed to different levels of water content, since 1% by weight of water reduces the viscosity, and thus increases Λ^0, by about 20%, but the effect of other impurities is less easy to estimate. In absolute terms we must realistically allow that our values for Λ^0 could all be subject to a systematic error up to about $\pm 4\%$. However since we used the same stock of glycerol throughout and prepared the solutions under similar conditions we believe that the random errors between values for different salt solutions are below the 0.3% level. Aside from the overall uncertainty arising from the glycerol purity, we believe that differences between the ionic molar conductivities for the ions in Table 3 are reliable to about ± 0.1 μS m^2 mol^{-1}.

Table 4 Values of the viscosity and relative permittivity of various solvents at 25°C.

Solvent	$10^4\eta/Pa\ s$	ε_r
Water	8.90	78.3
Methanol	5.45	32.7
Ethanol	10.78	24.6
Ethylene glycol	168.4	40.7
Glycerol	9100	42.7

In comparing the ionic conductivities of solutions in glycerol with those in other solvents it is convenient to evaluate the Walden product, so as to allow approximately for the effect of the high viscosity of glycerol, and the results are shown in Figure 2 for aqueous solutions and some of the lower alcohols. Two features are apparent. Firstly, the ratios between the Walden products for different ions are approximately the same in water, ethylene glycol 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 three 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. One might wonder whether this is related to the high viscosity of glycerol and whether a modified Walden rule in which $\Lambda\eta$ increases somewhat with increase in viscosity applies. Whilst the data for glycerol, ethylene glycol and water are described approximately by the rule
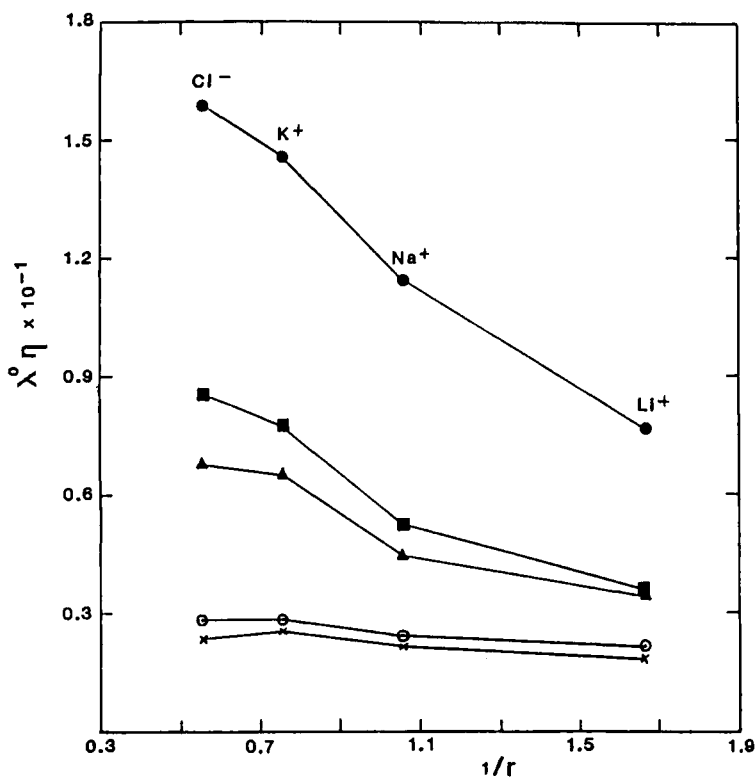
$$\eta^{0.89}\Lambda^0 = \text{constant,}$$

Figure 2 Graphs showing the dependence of ionic Walden product on the reciprocal of the ionic radius for various solvents. The units of $\lambda^\circ\eta$ are μN S s mol^{-1}, and those of the radius r are Angstroms. ● glycerol, ■ ethylene glycol, ▲ water, ○ methanol, × ethanol. Values for non-aqueous solvents other than glycerol are taken from Spiro[14], aqueous values from Horvath[15].

the data for methanol and ethanol do not fit this, as is apparent from Figure 4 of Ref. 13. Alternatively it appears 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 mono-alcohols are similar to each other, water and ethylene glycol have similar values, and glycerol, with three hydroxyl groups in the molecule, lies on its own. A useful check of this hypothesis would be made by measurements in 1,2 propane diol, but such data does not appear to be available at present.

References

1. T. Erdey-Gruz, L. Majthényi and I. Nagy-Czako, *Acta. Chim. Acad. Sci. Hung*, **53**, 29 (1967).
2. D. C. Champeney and H. Comert, *Phys. Chem. Liq.*, **18**, 43 (1988).
3. M. C. Blanco, D. C. Champeney and M. Kameche, in press.
4. G. Jones and D. M. Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).
5. G. Jones and B. C. Bradshaw, *J. Am. Chem. Soc.*, **55**, 1799 (1933).
6. D. W. Davidson and R. H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951).
7. Y-M. Chen and A. J. Pearlstein, *Ind. Eng. Chem. Res.*, **26**, 1970 (1987).
8. R. M. Fuoss, *J. Phys. Chem.*, **82**, 2427 (1978).
9. D. C. Champeney and F. Ould-Kaddour, *Phys. Chem. Liq.*, **16**, 239 (1987).
10. F. Accascina and S. Petrucci, *La Ricerca Scientifica*, **29**, 1640 (1959).
11. J. Hiegemann, *Ann. Physik*, **25**, 337-58 (1936).
12. T. Erdey-Grúz, E. Kugler and L. Majthenyi, *Electrochim Acta*, **13**, 947 (1968).
13. D. C. Champeney and F. Ould-Kaddour, *Mol. Phys.*, **52**, 509 (1984).
14. M. Spiro, *Physical Chemistry of Organic Solvent Systems*, Ed. A. K. Covington and T. Dickinson, Chapter 5 (Plenum Press, London and New York, 1973).
15. A. L. Horvath, *Handbook of Aqueous Electrolyte Solutions* (Ellis Horwood, Chichester, 1955).