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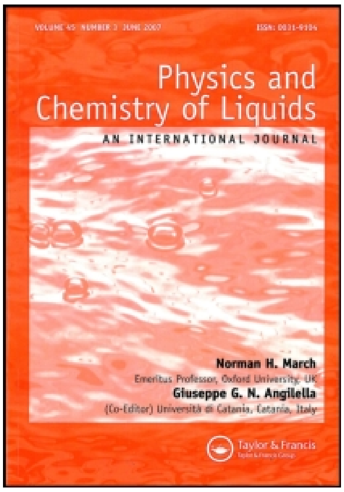

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MOBILITY OF NICKEL IONS IN ETHYLENE GLYCOL AND GLYCEROL AT 25°C

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The electrical conductivities of solutions of nickel chloride in ethylene glycol and glycerol have been measured at 25°C at concentrations within the range 0.001 to 0.5 mol dm^{-3}. The results are consistent with the Debye–Hückel–Onsager theory at low concentrations, and values of the molar conductivity at infinite dilution have been obtained by extrapolation. Values for the ionic conductivity of the doubly charged nickel ion are deduced, for these solvents, using previously measured values for the chlorine ion, whence the ion mobilities of nickel in ethylene glycol and glycerol have been calculated. The results indicate that, as in aqueous solutions, this doubly charged ion has a lower mobility than singly charged ions of the same radius, but that the effect is more marked in ethylene glycol and even more so in glycerol.

KEY WORDS: Debye–Hückel–Onsager theory, nickel ion mobility.

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INTRODUCTION

Ethylene glycol (EG) and glycerol are interesting among non-aqueous solvents because, like water, they are both hydrogen bonded liquids with a high value of relative permittivity. It is thus natural to look for similarities in behaviour between these solvents and water. Previous experiments have provided values for the ion molar conductances and mobilities of potassium, sodium, lithium and chlorine ions in EG[1,2] and in glycerol[3]. That work shows that the variation of molar ion conductance with ion radius in these solvents follows the same general pattern as in aqueous solution, but that the value of the product of molar ion conductance with solvent viscosity (the Walden product) increases in the solvent order water, EG, glycerol.

As yet there seems to be no published data on the molar ion conductances of divalent ions in these solvents, and the present experiments were undertaken to find out whether solutions of 2:1 salts in EG and glycerol show similarities with the aqueous solutions in the same way that the 1:1 salts did.

A nickel salt was chosen because nickel is a convenient element to use in neutron diffraction studies of solvation in solution, on account of the possibility of using the isotopic substitution method to obtain information on the solvent coordination around the nickel ion. This technique has been successfully[4,5,6] applied to aqueous

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solutions of nickel salts, and recent work in this laboratory[7] has applied it also to nickel salts dissolved in ethylene glycol.

EXPERIMENTAL

The glycerol used as solvent was Aldrich 99.5+ % pure and its measured conductivity was 9.49×10^{-9} S cm^{-1}. Aldrich anhydrous gold label EG, 99+% pure was employed, having a conductance of 5.94×10^{-7} S cm^{-1}. Anhydrous $NiCl_2$ from BDH, 98+% pure, was used to prepare solutions in EG. For the solutions in glycerol Aldrich gold label $NiCl_2$ $6H_2O$, quoted as 99.999% pure, was heated to 120°C under vacuum for about 20 hours to produce the brown anhydrous salt. The loss in weight on drying confirmed that more than 98% of the water had been removed. All solutions were prepared and sealed into conductance cells in a glove box filled with BOC high purity (99.998%) Argon. For each solvent two different sets of solutions were prepared by weight dilution. Concentrations have been calculated taking the solution density as equal to that of pure solvent, an approximation which is estimated to have negligible effect on the extrapolated conductance at infinite dilution. The conductance cells had platinized platinum electrodes, and were calibrated using aqueous KCl solutions. The impedance of the cells was measured using a Wayne Kerr model B905 Automatic Precision Bridge. It was found, for these aqueous solutions, that the frequency variation of the resistance across the cell between 1 and 10 kHz was less than 0.3%. Conductancies were measured at 25°C (±0.005°).

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RESULTS

The solutions in both solvents were green, as is the case with aqueous solutions. All measurements in both pure solvents and solutions showed a dominantly resistive impedance between 10 Hz and 10 kHz. For the EG solutions the change in the resistance over this frequency range was less than 0.1% and the conductance values were calculated from readings at 10 kHz.

With glycerol as solvent the effects of electrode polarization were shifted to lower frequencies, and conductancies were calculated from readings at 100 Hz, the variation in resistance between 10 Hz and 1 kHz being less than 0.1%. All conductance values were corrected for the solvent contribution, thus correction being at most 5% (in the most dilute solutions).

The molar conductances of solutions of $NiCl_2$ in glycerol and EG are given in Tables 1 and 2.

In the limit of very dilute concentrations, the conductance of 2:1 electrolytes is given by Debye–Hückel–Onsager (DHO) law as:

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

Table 1 Molar conductance of $NiCl_2$-ethylene glycol solutions of various concentrations at 25°C.

c (mol/m^3)	Λ $(mS\ mol^{-1}\ m^2)$
100.10	0.675
50.00	0.756
20.00	0.859
10.01	0.934
4.99	1.015
3.033	1.068
2.004	1.109
1.001	1.155

Table 2 Molar conductance of $NiCl_2$-glycerol solutions of various concentrations at 25°C.

c $(mol\ m^{-3})$	$\Lambda(\mu S\ mol^{-1}\ m^2)$
499.40	11.09
100.00	21.40
49.94	24.16
41.27	25.66
9.995	29.69
4.156	33.85
0.998	35.74

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where Λ^0 is the limiting conductance at zero concentration and A and B the parameters of the DHO theory. In SI units these parameters are given by

$$A = \frac{z_1 z_2 e^3 q (2N\nu z)^{1/2}}{12\pi(1 + q^{1/2})(\varepsilon_0 \varepsilon_r kT)^{3/2}}$$

and

$$B = \left(\frac{2N^3 e^6 \nu^3 z^3}{9\pi^2 \varepsilon_0 \varepsilon_r kT\eta^2}\right)^{1/2}$$

where

$$q = \left[2z\left(\frac{t_1}{z_1} + \frac{t_2}{z_2}\right)\right]^{-1}$$

$$z = \tfrac{1}{2}(z_1 + z_2)$$

and

$$\nu = z_1 \nu_1 = z_2 \nu_2$$

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e being the proton charge, N the Avogadro constant, ε_0 the permittivity of vacuum, ε_r the relative permittivity of the solvent, k the Boltzmann constant, T the absolute temperature, η the viscosity of the solvent, $z_i(>0)$ the charge number of ion type i, v_i the stoichiometric number and t_i the transport number of ion type i.

In Figures 1 and 2 we show the graphs of experimental values of the conductance against $c^{1/2}$ for glycerol and EG, respectively. It can be seen in both figures that

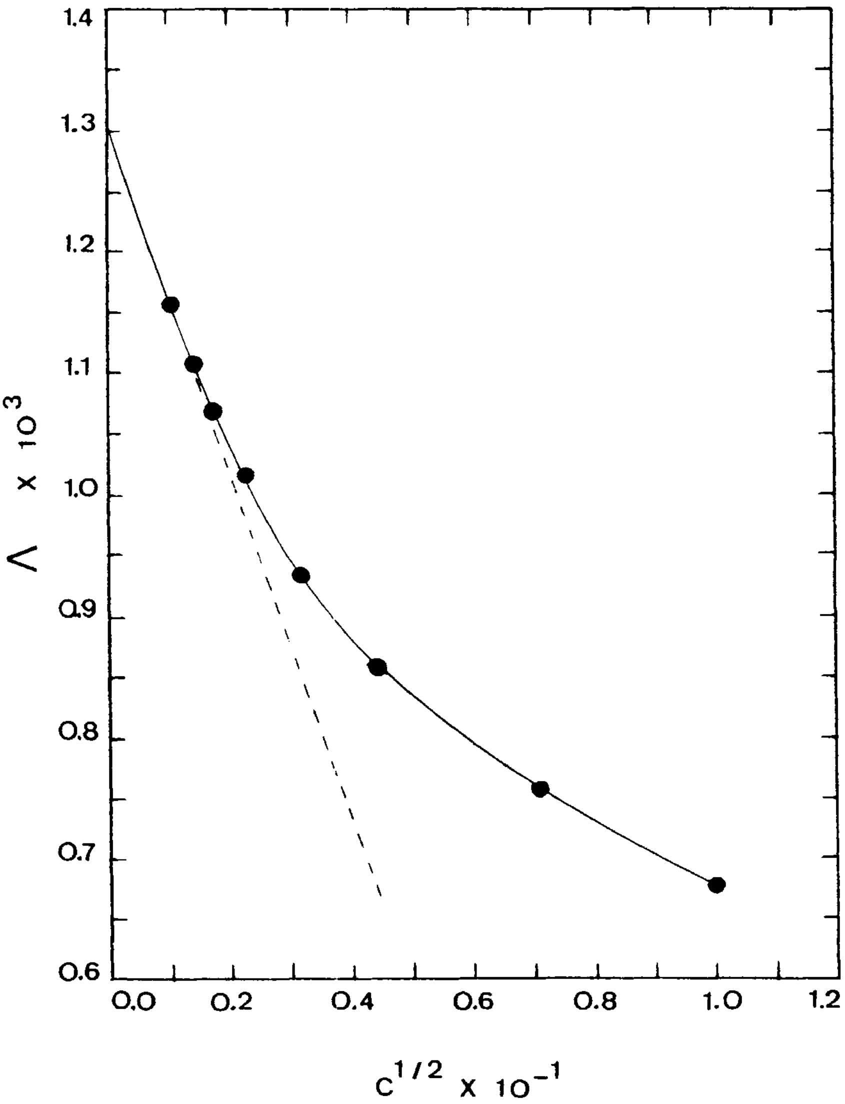

Figure 1 Plot of molar conductivity Λ (S m^2 mol^{-1}) against the square root of the concentration c (mol m^{-3}) for $NiCl_2$ in Ethylene Glycol at 25°C. The dashed line is calculated from the limiting DHO equation.

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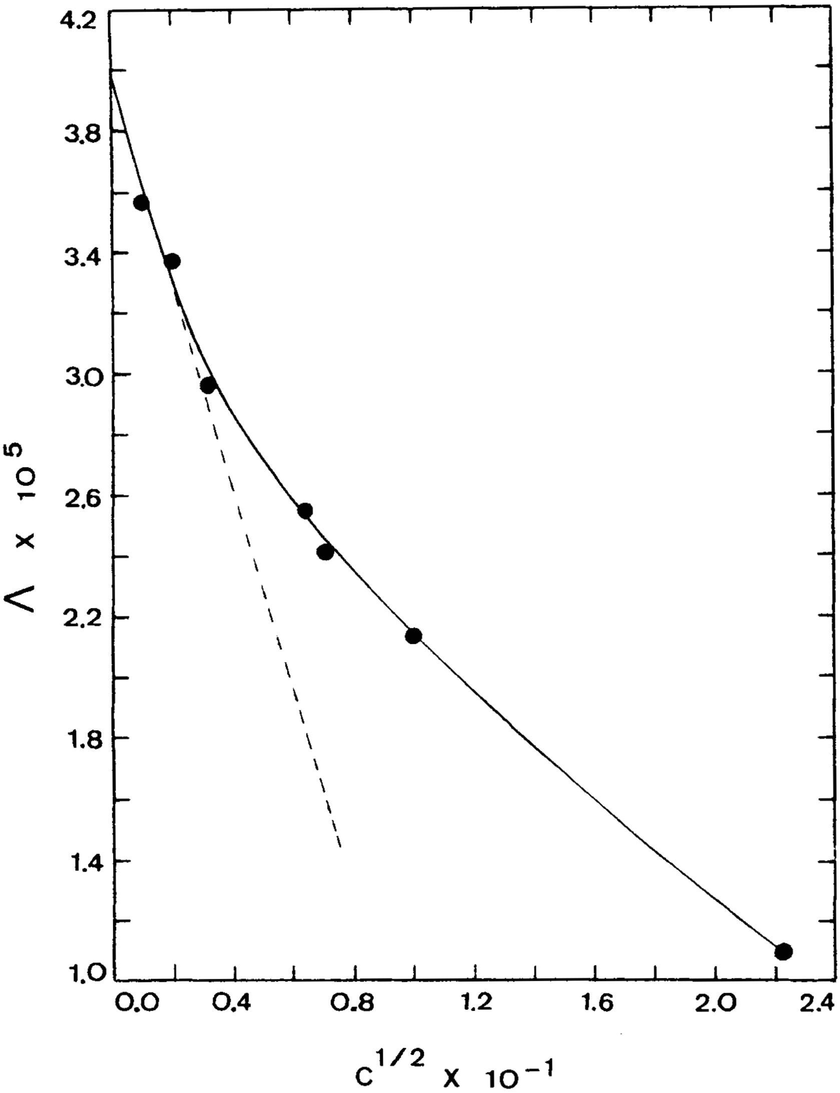

Figure 2 Graph of molar conductivity Λ (S m^2 mol^{-1}) against the square root of the concentration c (mol m^{-3}) for $NiCl_2$ in Glycerol at 25°C. The dashed line is calculated from the limiting DHO equation.

conductance values, at concentrations below 0.01 mol dm^{-3}, converge to the DHO asymptote shown as a dashed line. By fitting Eq. (1) to the low concentration data we have determined the values of Λ^0 using the least squares procedure developed by Marquardt[8]. The values obtained were $\Lambda^0 = 39.7 \times 10^{-6}$ S m^2 mol^{-1} for glycerol and $\Lambda^0 = 1.31 \times 10^{-3}$ S m^2 mol^{-1} for EG. By using these Λ^0 values together with the previously determined ionic molar conductance of the chlorine ion, we can deduce the conductance values for the nickel ion. With $\lambda^0(Cl^-) = 1.74 \times 10^{-5}$ S m^2 mol^{-1} in

Glycerol[3] and $\lambda^0(\mathrm{Cl}^-) = 0.5073 \times 10^{-3}$ S m^2 mol^{-1} in EG[1] we deduce the following ionic molar conductances and transference numbers at infinite dilution for the Ni^{2+} ion: in glycerol, $\lambda^0(\mathrm{Ni}^{2+}) = 4.90 \times 10^{-6}$ S m^2 mol^{-1} and $t^0(\mathrm{Ni}^{2+}) = 0.12$, whilst in EG $\lambda^0(\mathrm{Ni}^{2+}) = 2.95 \times 10^{-4}$ S m^2 mol^{-1} and $t^0(\mathrm{Ni}^{2+}) = 0.22$.

DISCUSSION

We consider first the fit of the data to the limiting DHO equation. Strictly one can only expect the limiting law to be well obeyed when $\kappa a \leq 1$ where κ is the Debye–Hückel parameter,

$$\kappa = \left(\frac{2\nu z N e^2 c}{\varepsilon_0 \varepsilon_r k T}\right)^{1/2}$$

and where a is some minimum distance of approach between positive and negative ion centres. Putting notionally $a = 0.3$ nm we find that $\kappa a = 0.1$ when $c = 1.8$ mol m^{-3} in the EG and glycerol solutions, and when $c = 3.4$ mol m^{-3} in aqueous solutions. However it can be seen from Figures 1, 2 and 3 that in fact the data for EG and glycerol depart from the DHO values more slowly with increase in concentration than is the case with water. To illustrate this, if we choose a concentration such that $\Lambda_{\mathrm{DHO}}/\Lambda^0 = 0.7$ then we find that at this concentration $\Lambda/\Lambda_{\mathrm{DHO}}$ is equal to 1.13 for water, and equal to 1.06 for EG and glycerol. However there are no features in the concentration dependence to suggest that the values of Λ^0 obtained by extrapolation, for EG and glycerol, are in error by more than about 1% due to ion association, or to suggest that the salt is not fully dissociated in the limit of infinite dilution.

The most striking feature of our data is the smallness of the ionic molar conductivities of Ni^{2+} in EG and glycerol in comparison with the values for other ions. If we define an ionic mobility μ_i by $\mu_i = v_k/F_i$ where v_i is the ion speed produced by a force F_i, then μ_i is related to the ionic molar conductivity λ_i by

$$\lambda_i = N z_i^2 e^2 \mu_i,$$

so that to compare the mobilities of ions of different charges it is sufficient to compare the values of λ_i/z_i^2. In Table 3 we compare the mobility of Ni^{2+} with that of Cl^- at infinite dilution, in water, EG, and glycerol. However since the crystal ionic radii are rather different[10], 0.08 nm and 0.17 nm respectively for Ni^{2+} and Cl^-, we also give in Table 3 a comparison of the mobilities of Ni^{2+} and Li^+, the lithium crystal ionic radius being approximately 0.09 nm. A value for $\lambda^0(\mathrm{Li}^+)$ in aqueous solution of 3.86 mS m^2 mol^{-1} has been used, from the compilation by Horvath[11].

The reduction in mobility associated with reduction in ion radius and increase in ion charge is usually attributed to the effects of solvation caused by the increased electric field gradients near the ion. If this is so then the data in Table 3 mean that the effects of solvation around Ni^{2+} ions increase in the solvent order water, EG, glycerol. This order corresponds both to an increase in solvent molecular size and also to an increase in the number of hydroxyl groups per solvent molecule, so that

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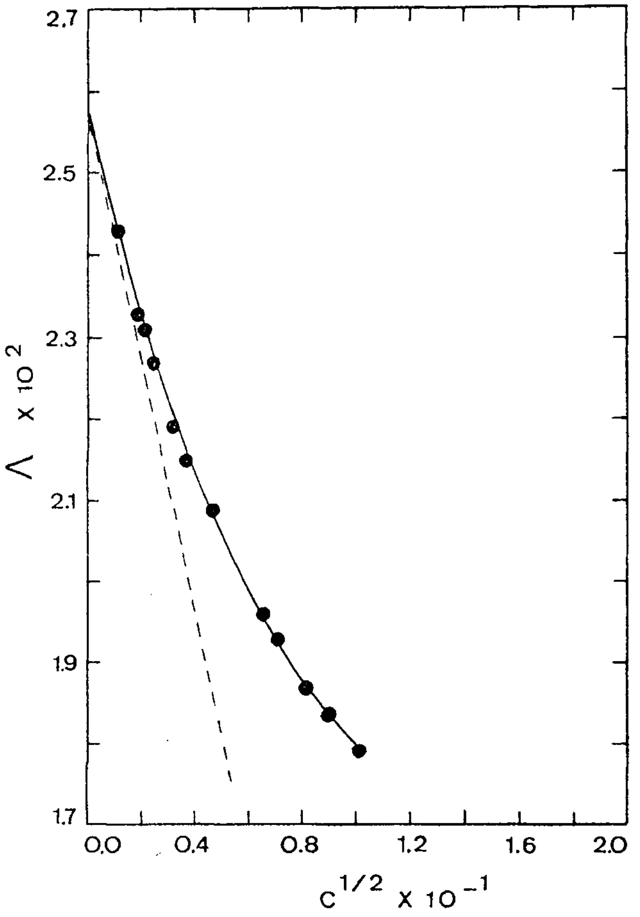

Figure 3 Graph of molar conductivity Λ (S m^2 mol^{-1}) against the square root of the concentration (mol m^{-3}) for $NiCl_2$ in water at 25°C. The dashed line is calculated from the limiting DHO equation. The data is that of Stokes *et al.*[9] yielding Λ° ($NiCl_2$) = 25.87 mS m^2 mol^{-1}: their measurements of the corresponding transference number yielded λ° (Ni^{2+}) = 10.61 mS m^2 mol^{-1} and λ° (Cl^-) = 7.63 mS m^2 mol^{-1}.

the mobility data suggests progressively larger and longer lived solvation complexes around the Ni_{2+} ion in the solvent order water, EG, glycerol.

It is interesting to correlate the ion mobility data with recent neutron scattering data[7] on the structure around Ni^{2+} ions in solutions in EG. The configuration which best matches the neutron scattering results is a bidentate configuration with three EG molecules forming a first coordination shell around the Ni^{2+} ion. A large, long lived solvation complex of this type would, at least qualitatively, explain the low ion mobility. The even lower relative mobility of Ni^{2+} in glycerol would lead one to expect likewise a well developed, stable, solvation structure in this case.

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Table 3 The ionic mobility of Ni^{2+} at infinite dilution compared with those of Cl^- and Li^+ in three solvents at 25°C.

Solvent	$\frac{\mu(Ni^{2+})}{\mu(Cl^-)}$	$\frac{\mu(Ni^{2+})}{\mu(Li^+)}$
Water	0.35	0.68
EG	0.15	0.35
Glycerol	0.07	0.15

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