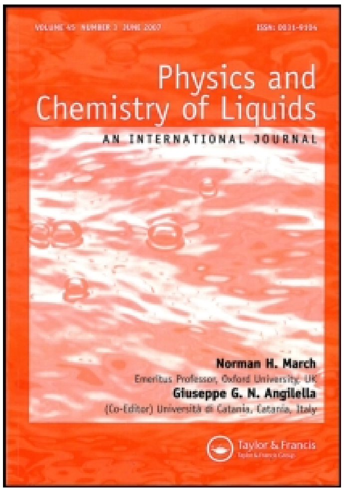

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D. C. Champeney[a]; H. Comert[a]
[a] School of Mathematics and Physics, University of East Anglia, Norwich, UK

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Transference Numbers and Activity Coefficients of Solutions of KCl and NaCl in Glycerol Using Concentration Cells

D. C. CHAMPENEY and H. COMERT

School of Mathematics and Physics, University of East Anglia, Norwich, NR4 7TJ, UK

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Transference numbers and mean ionic activity coefficients of solutions of potassium chloride and sodium chloride in glycerol have been measured at 25°C using concentration cells with silver/silver chloride electrodes. The EMFs of cells with transference, using a liquid junction, were measured at concentrations between 0.001 and 0.5 mol dm^{-3}, and the EMFs of cells without transference were measured using a potassium or sodium amalgam to link the two half-cells, at concentrations in the range 0.05 to 0.5 mol dm^{-3}. Using the Nernst equations, cation transference numbers of 0.479 and 0.417 were deduced respectively for solutions of potassium chloride and sodium chloride in glycerol at a concentration of 0.1 mol dm^{-3}. Activity coefficients for both salts were deduced as a function of concentration up to 0.5 mol dm^{-3}, using independent data on the low concentration transference numbers. The results indicate similarities between the solvent properties of glycerol and water.

KEY WORDS: Glycerol, sodium chloride, potassium chloride, activity coefficient, transference number, concentration cell.

1 INTRODUCTION

The experiments described here were carried out in order to obtain values for the transference numbers and the mean activity coefficients of KCl and NaCl dissolved in glycerol at 25°C. Glycerol is an interesting solvent on account of its high viscosity[1] ($\eta = 0.94$ Pa s at 25°C) and the readiness with which it can be supercooled below its freezing point at 17°C to give much higher viscosities. Experiments[2] on the electrical conductivities of KCl in glycerol solutions at various temperatures have indicated that the Walden product, $\eta\Lambda^{\infty}$, where η is the solvent viscosity and Λ^{∞} the equivalent conductance of the solution extrapolated to zero concentration, is not constant with change of temperature and viscosity; instead a modified Walden rule is obeyed such that

$$\left(\frac{\eta}{\text{Pa s}}\right)^{p}\left(\frac{\Lambda^{\infty}}{\text{S m}^{2}\text{ mol}^{-1}}\right) = K \tag{1}$$

where $p = 0.89$ and $K = 3.19 \times 10^{-5}$. In fact[2] the conductivities of dilute KCl solutions in glycerol, in ethylene glycol, and in water can all be fitted moderately well by Eq. (1), with the above values of p and K. The similarity between these solvents might follow from the facts that all three liquids display intermolecular hydrogen bonding, and have high values of relative permittivity ($\varepsilon_r > 40$) arising from polar molecules. A further test of the similarity or otherwise of these liquids would follow from measurements of transference numbers of the solution. Although a fair amount of data is available for ethylene glycol, see for instance the review by Spiro,[3] less data is available for glycerol.

There are three main experimental methods of obtaining transference numbers, namely, the Hittorf method, the moving boundary method, and the concentration cell method. Although the moving boundary method is generally regarded as being the most accurate method of measuring transference numbers, the concentration cell method has the attraction that it can at the same time yield values for the mean activity coefficient of the solution, and, when applicable, is a simple and rapid technique. The present experiments were undertaken partly, therefore, to determine the reliability and accuracy of the concentration cell method in non-aqueous solutions with a view, perhaps, of using it in later experiments at reduced temperatures with glycerol in the supercooled liquid state.

Fortunately one set of moving boundary data does exist[4] giving the positive ion transference number, t_+, for KCl dissolved in various glycerol-water mixtures, and we have been able to compare this with our value of t_+, obtaining satisfactory agreement. With this established we have continued to measure t_+ for NaCl in glycerol.

2 EXPERIMENTAL DETAILS

2.1 General Outline

The experiment rests upon measuring the electromotive forces, E_{LJ} and E_{AMALG}, of the concentration cells which operate respectively with transference (using a liquid junction) and without transference (using a mercury amalgam electrode to join the two half-cells).

The cells without transference may be represented by the following example:

$$\text{Ag, AgCl}|\text{MCl}(c_1)|M_x\text{Hg} - M_x\text{Hg}|\text{MCl}(c_2)|\text{AgCl, Ag}$$

where c_1 and c_2 are the concentrations in the two half-cells ($c_2 > c_1$), and M stands for K and Na.

The cells with transference are:

$$\text{Ag, AgCl}|\text{MCl}(c_1) \vdots \text{MCl}(c_2)|\text{AgCl, Ag.}$$

The electromotive force of a concentration cell without liquid junction, E_{AMALG}, can be expressed by the relation:

$$E_{\text{AMALG}} = -\frac{2RT}{F}\ln\frac{a_2}{a_1} \tag{2}$$

in which a_1 and a_2 are the mean activities at the concentrations c_1 and c_2.

If the transference number, t, is a constant within the concentration ranged involved, the electromotive force of a cell with liquid junction, E_{LJ}, can be expressed by the equation:

$$E_{\text{LJ}} = -\frac{2tRT}{F}\ln\frac{a_2}{a_1}, \tag{3}$$

t being the transference number of the ion to which the electrodes of the cells are not reversible.

If, however, the transference number is a function of the concentration, in this case Eq. (3) must be replaced by

$$E_{\text{LJ}} = -\frac{2RT}{F}\int_{\text{I}}^{\text{II}} t \,\mathrm{d}\ln a \tag{4}$$

the integration being from concentration I to concentration II.

Combining Eqs (2) and (3) we arrive at an expression for calculating the transference number of the ion directly from electromotive force measurements:

$$t = \frac{E_{\text{LJ}}}{E_{\text{AMALG}}} \tag{5}$$

In Eqs (2) and (3) we adopt the standard convention that E_{LJ} and E_{AMALG} are equal to the open circuit voltage of the electrode immersed in concentration c_2 relative to the elctrode immersed in concentration c_1.

2.2 Materials and Electrodes

Aldrich gold label grade glycerol (99.5 + % pure), potassium chloride (99.99% pure), and sodium chloride (99.999% pure) were used throughout the experiment. On account of the hygroscopic nature of glycerol and the salts, the solutions were made up in a glove-box under the flow of argon gas purified by a BOX rare gas purifier Mk 3. Solutions of salts in glycerol were made by weight using a balance inside the glove-box, and the solutions wee kept sealed and stirred at about 40°C for between 24 and 48 hours depending on the concentration of the solution.

The potassium and sodium amalgams, containing approximately 0.02 wt % of the alkali metal, were prepared by electrolysis. Aldrich gold label mercury (99.999% pure) or triple distilled mercury from our own laboratory formed the cathode of a cell in which 1 M KOH or NaOH (analar) was the electrolyte. Electrical contacts were made through two platinum wires in glass sheaths which were immersed in the hydroxide solution and mercury respectively, the hydroxide lying above the mercury. After passing a current of 50 mA for the required time, depending on the amount of mercury, the amalgam was run off through a fine capillary tube, fitted at the bottom of the vessel, to free it from the scum and transferred into another evacuated vessel where the amalgam was stored in vacuum until used. Freshly made amalgam was used for each experiment, prepared about one hour beforehand. Experiments with 0.01 wt % of alkali metal showed no dependence of E.M.F. on amalgam concentration, as found also by other authors.[5]

Silver–silver chloride electrodes were prepared by electrolysis, guided by the reviews by Bailey,[6] Bates,[7] and Durst.[8] Silver wire of 0.5 mm diameter was sealed into lead glass tubing, leaving about 10 mm of wire projecting. After cleaning in acetone, distilled water, 50% nitric acid, and again with distilled water, the silver wire was electrolyzed as anode in analar 0.1 M HCl solution, the other electrode being a platinum wire. A current density of about 0.2 mA cm^{-2} was passed for about 60 min., giving a charge density of about 0.7 C cm^{-2}. The potentials of the electrodes were intercompared in 0.1 M KCl solution. In a batch of 10 such electrodes it was almost always possible to choose a pair which gave an EMF of less than 0.05 mV in magnitude. Some pairs of electrodes gave an EMF which changed after use and/or after storage in distilled water for several days, giving EMF up to about 1 mV. However, the results quoted in this paper were obtained using two selected pairs of electrodes each of which gave, throughout, an EMF of less than 0.05 mV.

2.3 Apparatus and Experimental Procedure

The cell used for experiments without transference was similar to that employed by Harned.[9] With about 160 g of amalgam, and 1 mm diameter capillaries tapered to a diameter of 0.22 mm at their lower ends a flow time of about 3 minutes was obtained.

The cell used for measurements with transference consisted of a U-tube with outlet and three-way stopcock. The three-way stopcock permitted the separation of the solutions in the limbs of the tube until the measurement was about to be made. When the two solutions were at the same level in the two limbs of the U-tube, connection between them was made by opening the stop-cock. The high viscosity of the glycerol meant that problems of diffusion were much less than is the case with aqueous solutions.

The procedure was as follows. After filling the cells in the glove-box and placing both types of cell in a water bath which was maintained at 25 ± 0.01°C, the electrodes were placed in the cell without transference and the whole allowed to equilibrate for one hour. The amalgam flow was then initiated, and readings were taken as rapidly as possible throughout the 3 minutes period of flow, and an average taken over the central two minute period. The electrodes were then removed from this cell and placed in the cell with transference, each electrode being immersed in the liquid of the same concentration as before. The liquid junction was then formed and the EMF observed until it was steady to within ±0.1 mV over a period of 30 minutes. In some cases this meant waiting for a time of about an hour, whilst in other cases a period of 10 or 15 minutes was sufficient.

At each concentration a repeat experiment was performed using fresh solution and amalgam, and using the same electrodes but with the electrodes placed in the opposite concentration from that of the first experiment. In this way spurious EMF's due to the electrodes being not identical would tend to cancel out.

The cells had resistances up to about 10 MΩ, and the cell EMF was measured using a Schlumberger-Solarton 7065 digital voltmeter which had an input resistance of greater than 100 GΩ.

3 RESULTS

3.1 Transference Numbers

The potential of the concentration cell was determined twice for each pair of solutions used. Table 1 gives the averaged EMF's measured for

Table 1 The measured EMFs of the various cells.

Salt	c_1/mol dm^{-3}	c_2/mol dm^{-3}	E_{LJ}/mV	E_{AMALG}/mV	t_+
KCl	0.001	0.01	52.78	83.96	0.629
KCl	0.005	0.05	50.55	99.21	0.510
KCl	0.010	0.10	47.09	97.84	0.481
KCl	0.050	0.50	47.11	98.46	0.478
NaCl	0.001	0.01	45.49	89.23	0.510
NaCl	0.005	0.05	42.68	99.44	0.429
NaCl	0.010	0.10	41.19	99.65	0.413
NaCl	0.050	0.50	42.06	99.98	0.421

the various cells. An analysis of the spread of readings obtained on repetition leads to random uncertainties of 0.4(6) mV and 0.8(7) mV on E_{LJ} and E_{AMALG} respectively. However, the deviations from average of E_{LJ} and E_{AMALG} were correlated, and the random uncertainty in the ratio E_{LJ}/E_{AMALG} was 0.002(9).

The estimation of systematic errors, due for instance to any element of irreversibility in the system, is very difficult to estimate directly, and we rely instead on a comparison of our value for t_+ in KCl calculated from Eq. (5), with a value obtained using the moving boundary method. Erdey Gruz *et al.*[4] measured values of t_+ for 0.01 mol dm^{-3} solutions of KCl in glycerol–water mixtures up to 99.8 mol% glycerol, at which mixture they obtained $t_+ = 0.476$ at 25°C. From this a simple extrapolation of their data gives no significantly different value in pure glycerol. This is within 1% of our values for solutions in the range 0.01 to 0.5 mol dm^{-3}, and we conclude that the concentration cell method is satisfactory in glycerol solutions over this concentration range at the 1% accuracy level.

At concentrations below 0.01 mol dm^{-3} we see that the ratio E_{LJ}/E_{AMAL} rises appreciably, whereas moving boundary experiments on for example ethylene glycol and methanol[3] and on water lead to no such large increases in value of t_+. However, it is well known[9] that the amalgam electrode when used with aqueous solution gives erroneous values at concentrations below about 0.05 mol dm^{-3} and we assume that this is also the case in glycerol solutions below about 0.01 mol dm^{-3}.

Taking it that Eq. (5) is valid at concentrations of 0.01 mol dm^{-3} and above, and assuming t_+ is constant we calculated an average value of $t_+ = 0.479 \pm 0.003$ for KCl in glycerol over the concentration range 0.01 to 0.5 mol dm^{-3}. Likewise for NaCl in glycerol we obtained a value of $t_+ = 0.417 \pm 0.004$ over the concentration range 0.01 mol dm^{-3} to 0.5 mol dm^{-3}.

3.2 Activity Coefficients

Values of the mean activity coefficient γ ($= a/c$) can be deduced from our measurements of E_{LJ} using Eq. (3) if assumptions are made about the dependence of t_+ on concentration and if it is assumed that γ is given by a modified Debye-Huckel formula at low concentrations. We consider these assumptions in turn.

The variation of t_+ with concentration for solutes dissolved in various organic solvents has been reviewed for instance by Spiro.[3] Because our measured value of t_+ for KCl in glycerol is close to 0.5 we have assumed that its variation with concentration is negligible, an assumption which is borne out by the data on KCl solutions in methanol and ethylene glycol quoted by Spiro. For the NaCl in glycerol solutions, with $t_+ = 0.417$ at $c = 0.1$ mol dm^{-3}, one would expect a small change in t_+ with concentration. A rough indication of the magnitude of this change may be obtained from the following Debye-Huckel formula (in S.I. units):

$$t_+ = t_+^0 + \frac{(t_+^0 - 0.5)}{\eta\Lambda^\infty}\left(\frac{2e^6N_0^3c}{9\pi^2\varepsilon_0\varepsilon_r kT}\right)^{1/2} \tag{6}$$

In this equation t_+^0 is the limiting value of t_+ at zero concentration, Λ^∞ is the limiting conductance of the solution at zero concentration, η is the solvent viscosity, e is the magnitude of the electron charge, N_0 is the Avogadro constant, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity of the solvent at absolute temperature T, and k is the Boltzmann constant. This equation predicts a decrease in t_+ of 0.006 between zero concentration and 0.1 mol dm^{-3}. Since this equation is only expected to be strictly true in the limit of low concentrations an independent value of t_+^0 for NaCl in glycerol has been obtained from conductance measurements on dilute KCl and NaCl solutions: assuming a value of $t_+^0 = 0.479$ for KCl in glycerol the conductance data lead to the value $t_+^0 = 0.42(1)$ for NaCl in glycerol. The resulting effect of this small change in t_+ on the calculated activity coefficient is negligible, and we have assumed the average value $t_+ = 0.417$ at all concentrations.

In aqueous solutions at low concentrations the following extended Debye-Huckel formula is often found[9] to be a good approximation for $\ln \gamma$,

$$\ln \gamma = -\frac{e^3(2N_0c)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r kT)^{3/2}} + Ac \tag{7}$$

where A is an empirical constant. In view of the fact that the electrical conductivity of KCl in glycerol solutions[2] is well represented by the

Table 2 Activity coefficients of KCl and NaCl in glycerol solutions.

c/mol dm^{-3}	$-\ln\gamma$ (KCl)	$-\ln\gamma$ (NaCl)
0.001	0.091 ± 0.005	0.093 ± 0.005
0.005	0.188 ± 0.005	0.199 ± 0.005
0.010	0.251 ± 0.01	0.273 ± 0.01
0.050	0.439 ± 0.03	0.510 ± 0.03
0.100	0.643 ± 0.04	0.653 ± 0.04
0.500	0.830 ± 0.06	0.850 ± 0.06

unmodified Debye-Huckel-Onsager equation up to a concentration of about 0.005 mol dm^{-3}, it is reasonable to take Eq. (7), with the extra flexibility given by the parameter A, as a good approximation at least up to a concentration of 0.01 mol dm^{-3}. Knowing the values of E_{LJ} and t_+ for the 0.001 mol dm^{-3}/0.01 mol dm^{-3} concentration cell we can deduce the value of A using Eqs (3) and (7), and thence calculate ln γ at the concentrations 0.001 mol dm^{-3} and 0.005 mol dm^{-3}. From the values of ln γ at low concentrations, the values at higher concentrations follow directly from the measured values of E_{LJ} using Eq. (3). The results are given in Table 2 and in Figures 1 and 2. The uncertainties in ln γ, quoted in Table 2, reflect the fact that the calculation of ln γ magnifies the uncertainties in E_{LJ} and t_+, and is moreover cumulative as one works up to the higher concentrations.

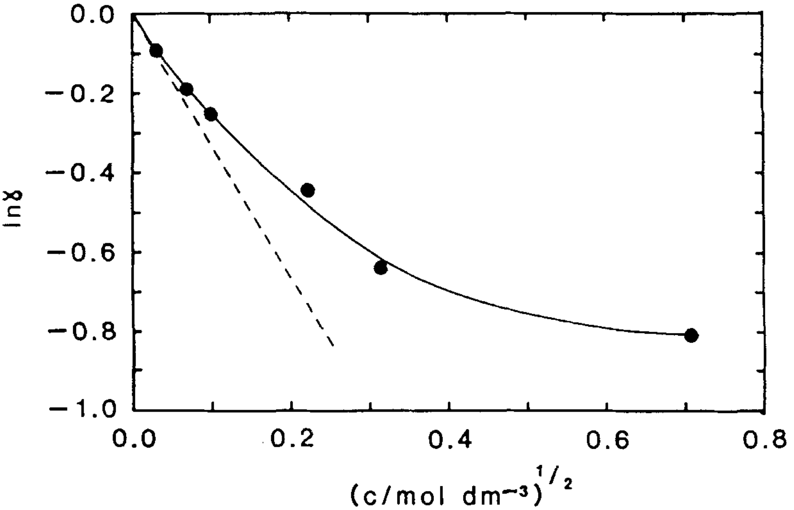

Figure 1 The dependence of ln γ on $c^{1/2}$ for KCl dissolved in glycerol. The dashed line gives the limiting Debye-Huckel behaviour, Eq. (7) with $A = 0$.

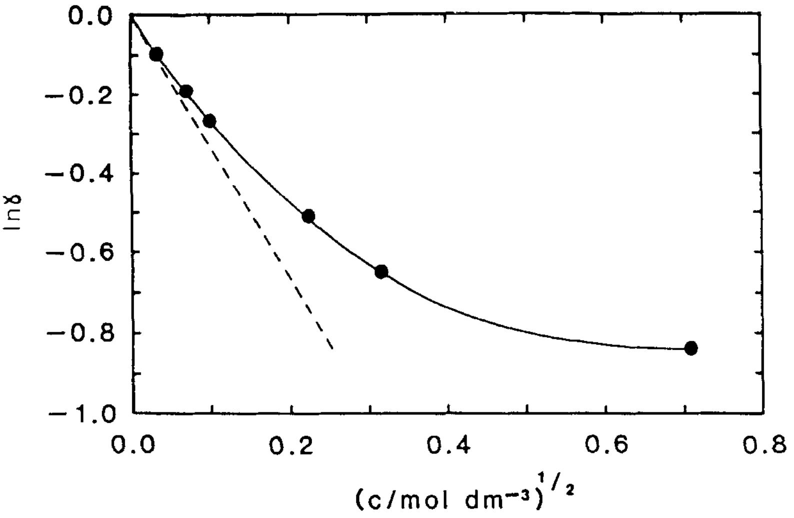

Figure 2 The dependence of ln γ on $c^{1/2}$ for NaCl dissolved in glycerol. The dashed line gives the limiting Debye–Huckel behaviour, Eq. (7) with $A = 0$.

4 CONCLUSIONS

Experiments based on concentration cells have been used to determine transference numbers of solutions of KCl and NaCl in glycerol at concentrations near 0.1 mol dm^{-3}, and also to derive activity coefficients for these solutions at concentrations up to 0.5 mol dm^{-3}.

The transference numbers are rather similar to the corresponding values in aqueous solution[10] with $t_+ = 0.479$ and 0.490 respectively for KCl in glycerol and water, and $t_+ = 0.417$ and 0.396 respectively for NaCl in glycerol and water.

The activity coefficients for KCl and NaCl in glycerol are very similar to each other at concentrations up to 0.5 mol dm^{-3} and approach the Debye–Huckel values below about 0.001 mol dm^{-3}. In these respects the results are qualitatively similar to those in aqueous solution, summarized for instance by Harned and Owen.[9] In aqueous solutions the activity coefficient for NaCl begins to show a significant excess over that of KCl at concentrations more than 1 mol dm^{-3}; our data in glycerol shows an indication of a difference in the opposite direction but this difference is comparable with our experimental uncertainty.

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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