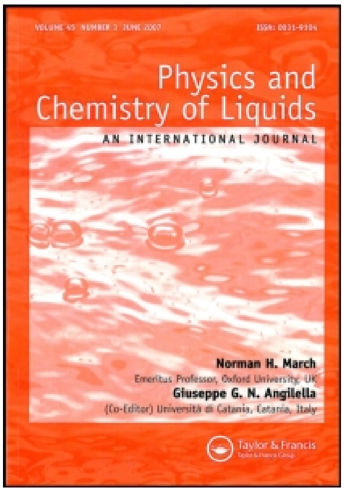

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Transference Numbers and Activity Coefficients of Some Alkali Metal Halide Solutions in Ethylene Glycol, Using Concentration Cells

M. C. Blanco[a][b]; D. C. Champeney[a]; M. Kameche[a][c]
[a] School of Physics, University of East Anglia, Norwich, UK [b] Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Santiago de Compostela, Spain [c] Département de Physique, Université de Tlemcen, Tlemcen, Algeria

To cite this Article Blanco, M. C. , Champeney, D. C. and Kameche, M.(1989) 'Transference Numbers and Activity Coefficients of Some Alkali Metal Halide Solutions in Ethylene Glycol, Using Concentration Cells', Physics and Chemistry of Liquids, 20: 2, 93 — 103

To link to this Article: DOI: 10.1080/00319108908036396

URL: http://dx.doi.org/10.1080/00319108908036396

Phys. Chem. Liq., 1989, Vol. 20, pp. 93–103
Reprints available directly from the publisher
Photocopying permitted by license only

TRANSFERENCE NUMBERS AND ACTIVITY COEFFICIENTS OF SOME ALKALI METAL HALIDE SOLUTIONS IN ETHYLENE GLYCOL, USING CONCENTRATION CELLS

M. C. BLANCO*, D. C. CHAMPENEY and M. KAMECHE**

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

(Received 11 August 1988)

The reliability of the concentration cell method for determining cation transference numbers has been tested using solutions of LiCl, NaCl, KCl, NaBr and LiBr in ethylene glycol at 25°C. Concentrations in the range 0.0005 to 0.5 mol dm^{-3} were used. Our transference numbers have been compared with those deduced from previous data on moving boundary and conductivity experiments. Good agreement between both sets of values has been found in most of the solutions, but significant discrepancies appear in the cases of NaBr and LiCl. The mean activity coefficients have been calculated from the EMF data and the transference numbers.

KEY WORDS: Hydrogen bonding, concentration cells.

INTRODUCTION

The properties of hydrogen bonded solvents having high relative permittivities are of interest because these properties can be compared with those of water, the most important such solvent, and because theories attempting to explain the behaviour of electrolyte solutions can be better tested if data on non-aqueous as well as aqueous solutions is available. Methanol and ethanol are obvious candidates for comparison with water, but their relative permittivities of 32.7 and 24.6 respectively at 25°C are rather low compared with the value of 78.3 for water, and the same is true of the higher monohydric alcohols. Ethylene glycol is of special interest, however, because its relative permittivity of 40.7 at 25°C is one of the highest amongst the common alcohols. It is remarkable also that the partial ionic molal volumes of alkali metal halides dissolved in ethylene glycol are quite close to the corresponding values in water, a result not displayed by the corresponding solutions in methanol or ethanol[1].

The present experiments have the general aim of finding out the extent to which concentration cells can provide data on the properties of electrolyte solutions in alcohols such as ethylene glycol, and the particular aim of giving values for the transference numbers and mean ionic activity coefficients of KCl, NaCl, LiCl, KBr,

---

* Permanent address: Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Santiago de Compostela, Spain.

** Université de Tlemcen, Départment de Physique, Tlemcen, Algeria.

and NaBr dissolved in ethylene glycol. Previous work[2] has included a determination of the cation transference number, t_+, of KCl in ethylene glycol using the moving boundary technique, from which transference numbers in dilute solution for other alkali metal halides were deduced using conductivity data. We are not aware of any previous measurements on ethylene glycol using concentration cells, or of determinations of activity coefficients for these solutions.

METHOD

The concentration cell method for determining transference numbers and activity coefficients is well known, and relies on the standard formulae giving the EMF, E_{LJ}, of a concentration cell with transference (i.e. with a liquid junction), and the EMF, E_{AM}, of a concentration cell without transference (i.e. using an amalgam to link the two half-cells). For a 1:1 electrolyte, and assuming electrodes reversible to the anion these formulae are, in S.I. units, as follows:

$$E_{AM} = \frac{-2RT}{F} \ln\left(\frac{c_2\gamma_2}{c_1\gamma_1}\right) \tag{1}$$

$$E_{LJ} = \frac{-2RT}{F} \int_1^2 t_+(c) d \ln(c\gamma) \tag{2}$$

$$\approx -\frac{2RTt_+}{F} \ln\left(\frac{c_2\gamma_2}{c_1\gamma_1}\right). \tag{3}$$

In these equations the sign convention is such that E_{LJ} or E_{AM} is the EMF of the electrode in the half-cell at concentration c_2 relative to that of the electrode in the half-cell at concentration c_1. $t_+(c)$ is the transference number of the cation at concentration c, γ is the mean ionic activity coefficient, and R, F, and T are the gas constant, the Faraday constant and the absolute temperature respectively. Equation (3) is based on the approximation that $t_+(c)$ can be replaced by the constant average value t_+ over the concentration range c_1 to c_2.

In principle t_+ for each cell can be found by measuring the ratio E_{LJ}/E_{AM} and using Eqs. 1 and 3, whilst $\ln \gamma$ can be deduced by assuming that in a dilute solution ($c \lesssim 0.001$ mol dm^{-3}) the value of $\ln \gamma$ is given by the Debye-Huckel approximation, and deducing values stepwise at higher concentrations by substituting values of E_{LJ} and t_+ into Eq. (3). Cells were chosen with the molalities in the two half-cells having a ratio of 10:1, the molality m_1 of the more dilute half-cell being chosen to give a molar concentration, c_1, of 0.0005, 0.001, 0.005, 0.01, or 0.05 mol dm^{-3}.

Experiments with KCl dissolved in ethylene glycol showed that the cell with $c_1 = 0.05$ mol dm^{-3} gave a ratio E_{LJ}/E_{AM} equal to 0.476. This is consistent with the moving boundary value, at infinite dilution, of $t_+^0 = 0.477$, since when t_+ is near 0.5 the concentration dependence is expected to be very small. However the cells using lower concentrations gave values of the ratio E_{LJ}/E_{AM} which were unphysically high: this behaviour is just that found in aqueous solutions, when the amalgam electrodes are found to give non-ideal behaviour at concentrations below about 0.05 mol dm^{-3}. The problem then arises of finding an alternative method of finding t_+ for the more dilute cells when using salts other than KCl.

One approach is to use our ratio E_{LJ}/E_{AM} to determine t_+ for the most concentrated cell, with $c_1 = 0.05$ mol dm^{-3}, and to use values of t_+^0 deduced from the moving boundary value for KCl in combination with conductivity data for the salts used, as in Appendix 5.12.4 of Spiro[3]. Values of t_+ at intermediate concentrations are then determined by interpolation assuming that t_+ varies linearly with $c^{1/2}$.

Another approach, which has the attraction of making the concentration cell method self contained, is to measure E_{LJ} in a cell with c_1 and c_2 equal to 0.0005 and 0.001 mol dm^{-3} respectively. If one assumes that at these concentrations ln γ is given by the following Debye–Huckel (DH) formula (for a 1:1 electrolyte)

$$\ln \gamma = \frac{-e^3(2N_0c)^{1/2}}{8\pi(\varepsilon_0\varepsilon_r kT)^{3/2}}, \tag{4}$$

then one can deduce $t_+(\approx t_+^0)$ for this cell using Eq. (3). In Eq. (4), e, N_0, ε_0, ε_r and k represent respectively the magnitude of the electron charge, the Avogadro constant, the permittivity of vacuum, the relative permittivity of the solvent, and the Boltzmann constant. Once again the value of t_+ at intermediate concentrations can be found by linear interpolation versus $c^{1/2}$.

These two methods of obtaining t_+^0 were in good agreement for the salts KCl, NaCl and KBr, but lead to significant discrepancies for NaBr and LiCl. We discuss these differences later in conjunction with a further discussion of the applicability of the Debye–Huckel formula at low concentration. In all the salts measured the variation of t_+ with concentration was sufficiently small that the error in replacing Eq. (2) by Eq. (3) and using an average value of t_+ was neglible.

EXPERIMENTAL

The KCl, NaCl, KBr, NaBr, LiBr and Hg were Aldrich gold label quoted as 99.999% pure. The Ethylene Glycol used as solvent was Aldrich 99.5% pure. All the solutions were prepared using an electronic balance located inside a glove box filled with BOC high purity (99.998%) Argon. The range of concentrations studied was from 5×10^{-1} to 5×10^{-4} mol dm^{-3}. The most concentrated solution was prepared from alkaly halide powder, which in the case of LiCl was dried at 130°C for 1½ hours. The mixture of the powder with the solvent was later stirred for about twelve hours. The other solutions were prepared by dilution from the concentrated one.

Silver wires of 0.5 mm diameter and 10 mm length, cleaned as indicated by Bailey[4], were used to make Ag/AgCl and Ag/AgBr electrodes. They were made by electrolysis in 0.1 M solutions of Analar HCl or HBr using a platinum electrode as the cathode, and a current density at the surface of the silver of about 0.6 mA cm^{-2}. The charge density was about 3 C cm^{-2}, and after preparation the electrodes were stored in distilled water.

The EMF of electrode pairs was checked before use in 0.01 M KCl or KBr aqueous solutions, and pairs were chosen which displayed a potential difference less than 0.1 mV throughout the whole period of the experiments. In order to cancel out this difference, the electrodes were interchanged in each cell, and the average of both EMF readings was taken as the final EMF value of the cell, within an uncertainty of 0.5 mV. The EMF values were measured using a solartron 7065 digital voltmeter which has an input resistance greater than 100 GΩ.

The cells with transference employed were

$$Ag/AgCl|MX(m_1):MX(m_2)|AgCl/Ag$$

In order to avoid problems of bubbles and leakage at taps in mobile liquids such as ethylene glycol, which can dissolve grease, we designed a cell in which the junction was made without using any tap. The characteristics of the cell are schematized in Figure 1. It contains two tubes, A and B, of 1.1 cm diameter and 10 cm length each. Inside each tube is inserted one electrode which is not shown in the figure. The tubes A and B are joined by two U shaped branches, C and E. The branch C equalises the pressures in the various limbs when the tops are sealed with rubber bungs, thus avoiding unwanted level differences. The branch E is a capillary tube (2 mm diameter) which reduces diffusion when the cell is working.

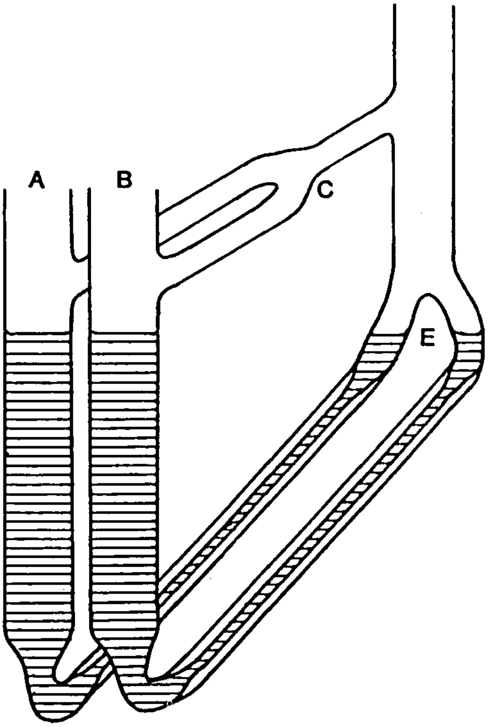

Figure 1 A schematic diagram of the liquid junction cell. The liquid junction is formed by rotating the cell in a clockwise direction.

The working procedure was as follows. The cell was filled with the solutions, whilst in the glove box, through the A and B tubes, holding it in an inclined position to keep separate both solutions. The electrodes were then inserted, the cell was sealed with rubber bungs, and the assembly was put inside a water bath at 25.00 ± 0.01°C. When the system reached this temperature, the junction of the solutions was produced by a simple inclination of the cell. The EMF of the cell was followed, until it was constant, for about 30 minutes. This took between one and a half and three hours, depending on the concentrations of the cell.

Flowing amalgam cells of the type

$$\mathrm{Ag/AgX|MX(m_1)|MHg|MX(m_2)|AgX/Ag}$$

were employed. The design was similar to that used by Harned[5], and the flow of the amalgam was 1 g s^{-1} for about three minutes. The cells were filled with solution and then sealed under an Argon atmosphere in the glove box.

Alkali metal amalgam concentrations were 0.02% by weight in the case of Na and K and 0.003% by weight for Li, as has been recommended[6,7]. The amalgams were prepared by electrolysis of NaOH, KOH or LiOH 1M solutions, making use of the mercury as the cathode. A current of 50 mA was passed during the required time, using a platinum anode. Freshly made amalgam was used for each experiment, and in the case of sodium and potassium it was stored under vacuum for about half one hour before using. Lithium amalgam, however, is much more difficult to control becuase the high reactivity of this metal. Therefore, special conditions, with the previous deoxygenation of the LiOH solutions and the maintenance of a N_2 atmosphere in the amalgam's preparation flask, were employed. Moreover, the amalgam was not stored but it was transferred directly into the reservoir of the cell, keeping the N_2 flow until the experiment was finished.

The EMF of the cell was followed during the period of flow, and found to be steady within 0.1 mV during the central 2 minutes of flow; an average over this central period was then taken.

RESULTS

Some of the transference numbers t_+ were calculated by taking the ratio between the EMF of the cell with transference (E_{LJ}) and that of the cell without transference (E_{AM}) i.e.,

$$t_+ = \frac{E_{LJ}}{E_{AM}} \tag{5}$$

The results are summarized in Table 1.

According to Spiro[3], transference numbers close to 0.5 change little with the concentration. The transference number at infinite dilution, t_+^0, for KCl ethylene glycol solutions has been already determined using the moving boundary method[2]; the result was $t_+^0 = 0.4765$. This value agrees satisfactorily with our transference

Table 1 EMF and transference numbers of KCl, NaCl, KBr, NaBr, LiCl in ethylene glycol at 25°C. The molalities were chosen so as to correspond to the nominal concentrations 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5 mol dm^{-3}

	$m_2(mol\,kg^{-1})$	$m_1(mol\,kg^{-1})$	$-E_{LJ}(mV)$	$-E_{AM}(mV)$	t_+
KCl	0.44930	0.0898	47.76	100.40	0.476
	0.08980	0.00895	48.06	99.11	(0.485)
	0.04425	0.00415	49.26	98.62	(0.500)
	0.00895	0.00089	51.48	93.79	(0.549)
	0.00089	0.00044	16.34		0.479
NaCl	0.44938	0.04390	36.60	100.85	0.363
	0.09008	0.00896	37.57		
	0.04390	0.00437	38.75		
	0.00896	0.00099	40.51		
	0.00099	0.00043	13.00		0.381
KBr	0.44912	0.04469	47.34	99.50	0.476
	0.08986	0.00890	48.48		
	0.04469	0.00444	49.78		
	0.00890	0.00088	52.03		
	0.00088	0.00044	16.19		0.474
NaBr	0.44915	0.04312	37.90	105.43	0.359
	0.08662	0.00859	38.46		
	0.04312	0.00429	39.24		
	0.00859	0.00085	42.12		
	0.00085	0.00043	(14.00)		(0.410)
LiCl	0.17331	0.01721	27.80	99.00	0.281
	0.03445	0.00343	29.67		
	0.01721	0.00171	30.55		
	0.00343	0.00034	32.03		
	0.00034	0.00017	(14.07)		(0.412)

number determined from the most concentrated cell ($t_+ = 0.476$) but disagrees somewhat with the other t_+ values. This disagreement is almost certainly due to the E_{AM} values being erroneous at concentrations below about 0.05 mol dm^{-3}, as has been found also in aqueous solutions[8]. In Table 1 calculated value of t_+ which are believed to be erroneous are placed in brackets.

In dilute solutions the mean activity coefficient can be calculated using the DH Eq. (4), and then the transference number can be calculated using the Nerst Eq. (3) for a

Table 2 Cation transference numbers at infinite dilution of KCl, KBr, NaCl, NaBr and LiCl in ethylene glycol at 25°C. Doubtful figures are placed in parentheses.

Method	t^0_+ (KCl)	t^0_+ (NaCl)	t^0_+ (KBr)	t^0_+ (NaBr)	t^0_+ (LiCl)
Concentration Cell	0.479	0.382	0.474	(0.413)	(0.420)
Moving Boundary[3] and Conductance	0.4766	0.3798	0.4812	0.3842	0.2939

Table 3 Mean activity coefficients of KCl, NaCl, KBr, NaBr, LiCl in ethylene glycol at 25°C

$\sqrt{c}(mol\ m^{-3})^{1/2}$	$-\ln\gamma(KCl)$	$-\ln\gamma(NaCl)$	$-\ln\gamma(KBr)$	$-\ln\gamma(NaBr)$	$-\ln\gamma(LiCl)$
1.000	0.10	0.10	0.10	0.09	0.09
2.230	0.21	0.22	0.21	0.18	0.20
3.162	0.30	0.31	0.30	0.24	0.27
7.070	0.51	0.51	0.56	0.49	0.45
10.000	0.64	0.65	0.65	0.54	0.56
22.360	0.88	0.86	0.94	0.76	0.82

cell with transference. We have employed a cell with concentrations of $c_2 = 0.001$ mol l^{-1} and $c_1 = 0.0005$ mol l^{-1}. Table 1 shows the transference numbers obtained for very dilute cells, calculated in this way, for the various systems we have studied. It can be appreciated that the transference number of K^+ in KCl ($t_+ = 0.479$) is very close to the one ($t_+ = 0.476$) we previously found for this ion in the most concentrated cell. This is what is to be expected for a correctly operating cell[3]. In the same table we give the cation transference numbers for solutions of NaCl, KBr, NaBr and LiCl based on data from the corresponding cells.

In order to compare our results with other existing data[3] we have calculated the transference numbers of the various systems at infinite dilution. This has been carried out by a simple linear extrapolation of the results at low and high concentrations. The results are given in Table 2 where for comparison we have also given the values of the transference numbers from the conductance and moving boundary methods. As can be seen there is good agreement between the obtained t_+^0 for both methods in the case

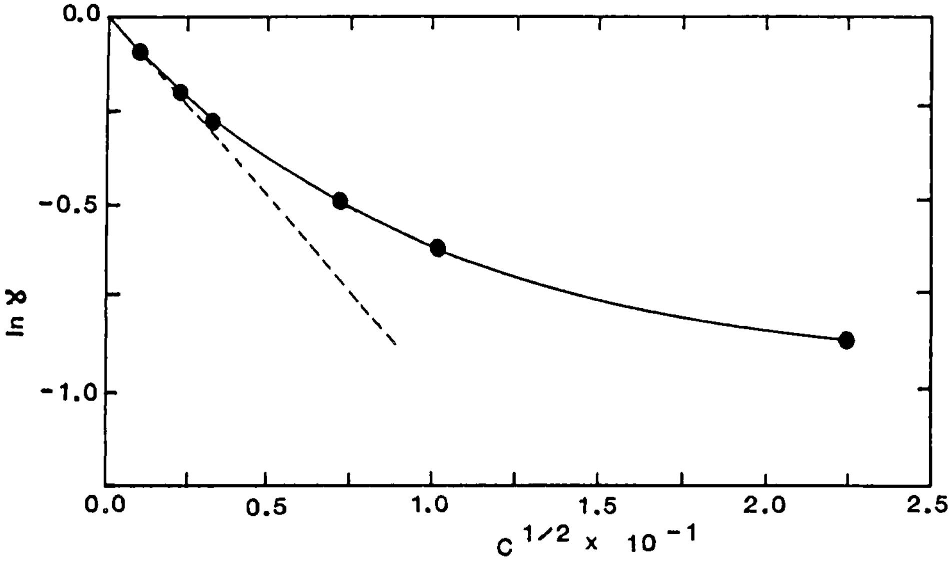

Figure 2 Graph showing the dependence of the activity coefficient on concentration for KCl in ethylene glycol solutions. The full curve is a smooth fit to the data points; the dashed line is calculated from the DH formula. The concentration, c, is in mol m^{-3}.

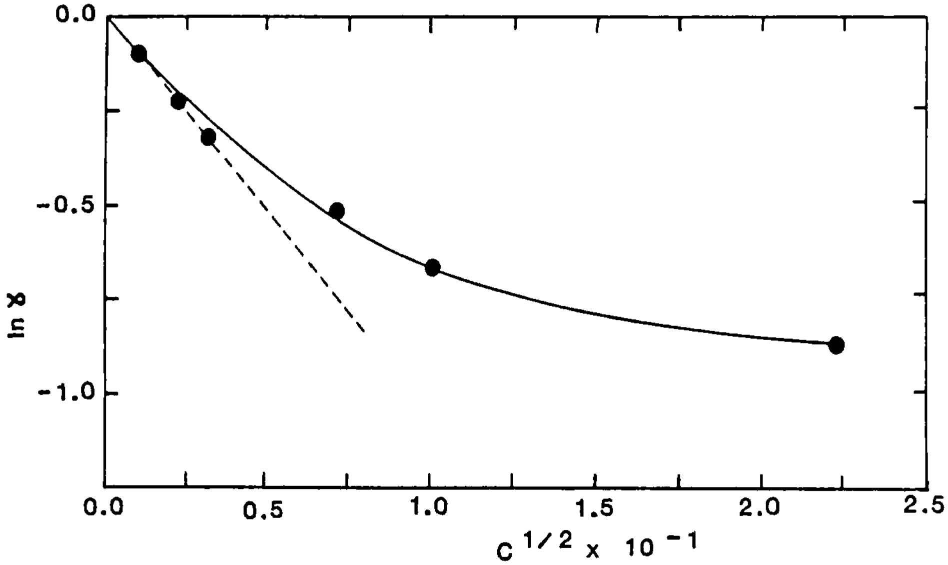

Figure 3 As for Figure 1, but for NaCl in ethylene glycol solutions.

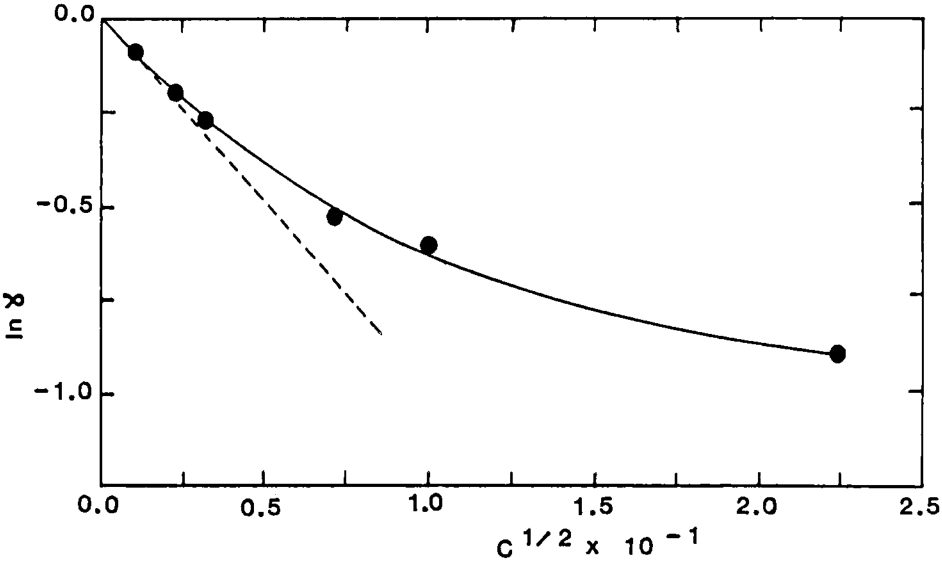

Figure 4 As for Figure 1, but for KBr in ethylene glycol solutions.

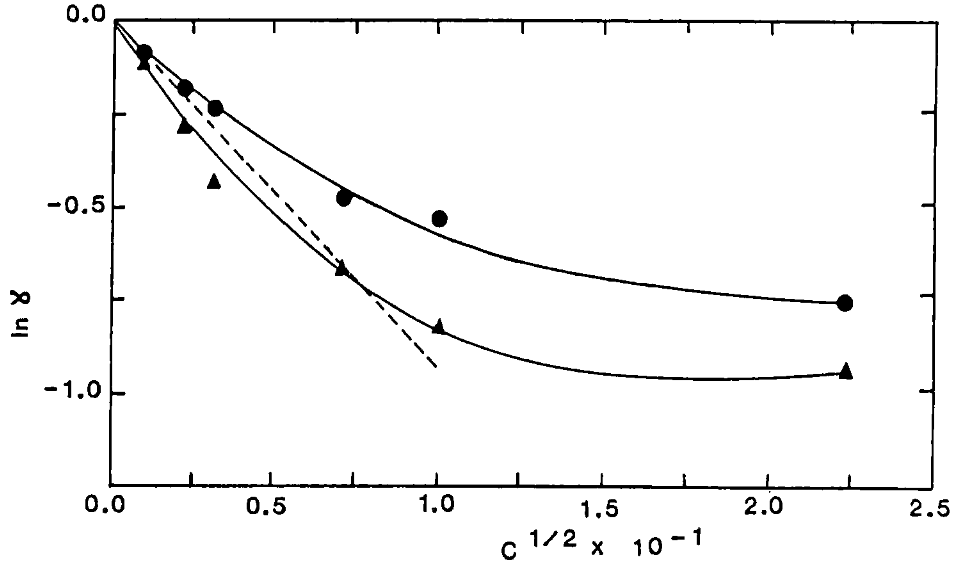

Figure 5 Graphs showing apparent dependence of the activity coefficient on concentration for solutions of NaBr in ethylene glycol. The concentration, c is in mol m^{-3}. See text for the meanings of the two graphs.

of KBr, KCl and NaCl, although some differences exist for NaBr and LiCl. By using the t_+ from our concentrated cell and the t_+^0 from the boundary method it is possible, making an interpolation, to obtain the t_+ values at intermediate compositions. By using then the EMF data from our transference cells, it is possible, with the use of the Eqs. (3) and (4), to obtain the mean activity coefficient for each concentration. These values are shown in Table 3. In Figures 2–6 we have plotted ln γ against $c^{1/2}$ for each system studied. Concentrations in mol dm^{-3} were calculated from molalities in mol kg^{-1} using the partial molal volume data of Zana[1]; the effect of the solution density differing from solvent density was negligible except at the highest concentrations. In these figures, the broken line represents the predictions of the DH theory, while the continuous line gives the ln γ values obtained. It can be seen that when $c \leq 0.001$ mol dm^{-3} the ln γ values agree quite well with the Debye-Huckel theory, whilst at higher concentrations the experimental values are greater than the theoretical ones, as is the case in aqueous solutions. We can alternatively use also the t_+^0, obtained from the extrapolated concentration cell t_+ values, to calculate mean activity coefficients. With KCl, NaCl and KBr the results are the same as before. However with NaBr the graph for ln γ obtained using our t_+^0 lies below the Debye-Huckel graph at low concentrations, as shown in Figure 4, and we conclude that this value of t_+^0 is false. With LiCl a similar situation exists, with the graph based on an extrapolated value of t_+^0 lying even lower, as in Figure 6. We conclude that values of t_+^0 can be correctly deduced from EMF measurements in very dilute concentration cells for KCl, NaCl and KBr, but that in the cases of NaBr and LiCl the EMF values in very dilute concentration cells must have been false. In Figures 5 and 6 we regard the upper graphs as the correct ones.

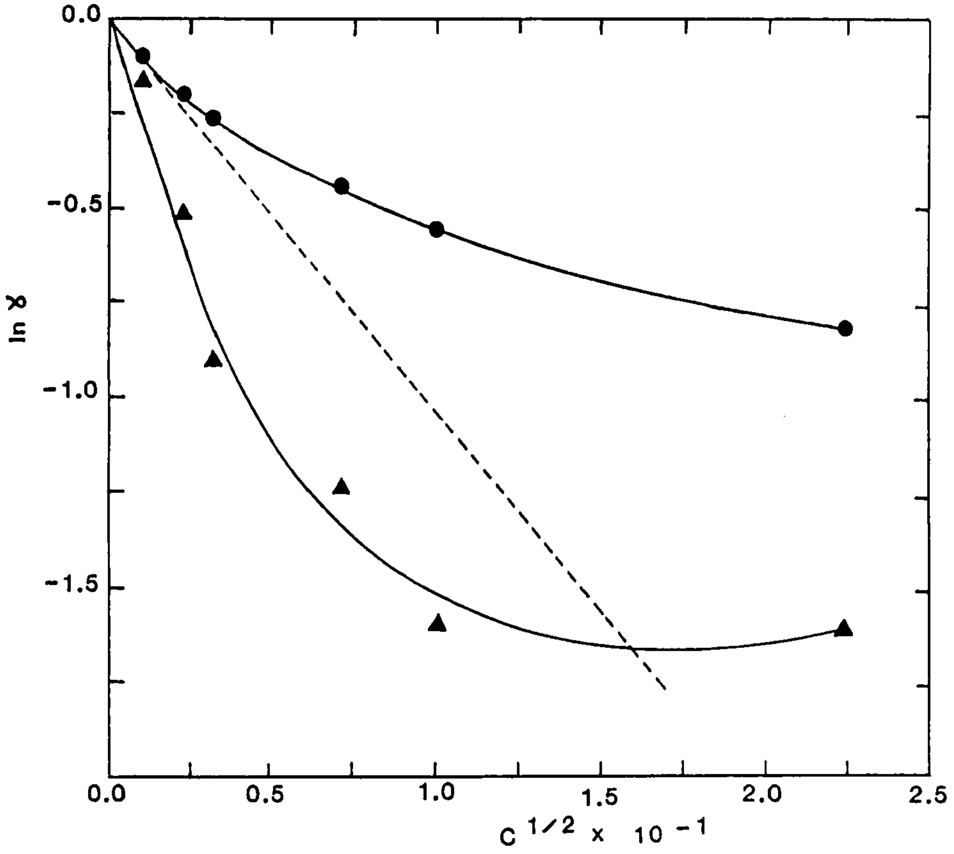

Figure 6 As for Figure 5, but for LiCl in ethylene glycol solutions.

CONCLUSION

We have shown that concentration cells can be used to yield transference numbers for several solutions of alkali metal halides in ethylene glycol. The standard method, involving the measurement of EMFs with and without a liquid junction, yields transference numbers at a concentration of about 0.1 mol dm^{-3} for the salts KCl, NaCl, KBr, NaBr and LiCl. An alternative method, based upon liquid junction EMFs only, yields transference numbers at concentrations of about 0.001 mol dm^{-3} for the salts KCl, NaCl and KBr which agree with those derived from conductance and moving boundary data; this alternative method fails however for NaBr and LiCl.

Values for the mean activity coefficients of the ions in all these solutions have also been deduced from the data. In the case of NaBr and LiCl this necessitated using transference numbers deduced from conductivity data at low concentrations, but with the other salts the results could be obtained solely from concentration cell data.

Acknowledgements

M. C. Blanco is grateful to the Spanish Consejo Superior de Investigaciones Cientificas and to the British Council for the provision of a Research Fellowship. M. K. wishes to thank the Algerian Ministry of Higher Education for financial support.

References

1. R. Zana and E. B. Yeager, *Modern Aspects of Electrochemistry No. 14.* (Ed. J. O'M. Bockris, B. E. Conway and R. E. White), Chapter 1 (Plenum Press, New York and London, 1982).
2. M. C. Santos and M. Spiro, *J. Phys. Chem.*, **76**, 712 (1972).
3. M. Spiro, *Physical Chemistry of Organic Solvent Systems* (Ed. A. K. Covington and T. Dickinson), Chapter 5 (Plenum Press, London and New York, 1973).
4. P. L Bailey, *Analysis with Ion-Selective Electrodes* (Heyden, 1980).
5. H. S. Harned, *J. Am. Chem. Soc.*, **51**, 416 (1929).
6. D. A. MacInnes and K. Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915).
7. H. S. Harned and F. E. Swindells, *J. Am. Chem. Soc.*, **48**, 126 (1926).
8. H. Armbruster and J. L. Crenshaw, *J. Am. Chem. Soc.*, **56**, 2525 (1934).