where ($\bar{V}_2 - V_2^\circ$) is the volume change associated with the mixing process, ($\partial P/\partial T$) can be calculated from the thermal expansion and the isothermal compressibility coefficients of chlorocyclohexane, and Δ is the slope of experimental $R(\partial \ln x_2/\partial \ln T)$ vs. $-R \ln x_2$ plot, except for N_2, O_2, and CH_4 whose values were taken from the literature (*12*) as they lead to results in better agreement with the experimental ones.

In Table III, experimental and calculated results of $10^4 x_2$ at 298.15 K, and the partial molal volumes of the gases obtained from equation (*12*), are shown.

Registry No. H_2, 1333-74-0; D_2, 7782-39-0; N_2, 7727-37-9; O_2, 7782-44-7; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; VF_4, 75-73-0; SF_6, 2551-62-4; CO_2, 124-38-9; chlorocyclohexane, 542-18-7.

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Received for review June 27, 1986. Accepted July 8, 1987. We are grateful to Comisión Asesora de Investigación Cièntifica y Tècnica (Madrid) for financial help (Proyecto 1877/82).

Transference Number Measurements in Aqueous Solutions at 25 °C. 3. Lithium Bromide

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Transference numbers for aqueous solutions of LiBr at 25 °C are determined by employing the direct moving-boundary method. Due to the hygroscopic character of this electrolyte, the value of the concentration for each of the solutions studied, with its most probable error included, is obtained from its experimental density. The corrected ionic transference numbers are optimized on the basis of their sum which must equal 1 at each concentration. From the "best" transference numbers thus obtained, C_{best} values are calculated which allow the direct determination of experimental values for such transference numbers that would be coincident with these best ones. The extrapolation to zero concentration of these transference numbers is done by using the 1963 Fuoss and Onsager equation and from such limiting values, $T_\pm^0$, the limiting equivalent conductance for the lithium ion, is also obtained. The density-concentration relationship found for these aqueous solutions of LiBr is also presented.

Introduction

In solutions of hygroscopic electrolytes, the knowledge of their concentration is usually accompanied by a high lack of precision that prevents an accurate calculation of the electrolyte magnitudes which depend on these concentrations as well as a rigorous analysis of their variation with that concentration. Nevertheless, in the case of transference numbers, this situation is not very problematic. In fact, if we take into account that this ionic parameter can be independently obtained for each of the ions present in the solution plus the fact that the sum of the transference numbers for all of these ions must equal 1 (from the definition of the transference number), we have an easy way to optimize the results and thus to minimize the errors derived from the use of that concentration value.

In the present paper we illustrate this assertion by presenting the transference numbers for both Li^+ and Br^- ions in aqueous solutions of LiBr at 25 °C. The hygroscopic character of the LiBr does not permit the preparation of their solutions by the most accurate method of weighing both solvent and solute, but instead uses stock solutions whose concentrations have to be determined by titration. The possibility of optimizing the value of such concentrations on the basis of the transference numbers obtained makes possible the obtainment of more precise values for other thermodynamic parameters of this electrolyte.

Experimental Section

***Chemicals*.** LiBr, Merck "suprapur", was heated in vacuo at 150 °C for 72 h before use. $(C_2H_5)_4NBr$, Carlo Erba for polarography, was used without any previous manipulation but dried by means of a dry nitrogen stream before use. $KOOCCH_3$, Merck analytical reagent grade, was recrystallized twice from a saturated solution with ethanol, dried in an oven at 110 °C for 24 h, and stored in a desiccator. Sodium salt was used instead of the lithium salt because the latter was not available; nevertheless it is well-known (*1*) that the use of the former salt does not introduce any error into the experimental determination of the transference numbers.

***Solutions. Determination of Their Concentrations*.** The following electrolyte solutions were prepared by weighing and correcting to vacuo both conductivity-grade water ($\kappa_0 = 5 \times 10^{-7}$ ohm^{-1} cm^{-1}) and the solute.

LiBr solutions, due to the hygroscopic character of the electrolyte, must be prepared from stock solutions which were obtained as follows: LiBr, after heating to vacuo, was added to a small known quantity of conductivity-grade water, determining by difference the weight of salt added and estimating the concentration of the solution thus prepared (which we will call "initial solution"). From this initial solution, "stock solutions" at different concentrations were prepared by taking portions of it and adding to them different quantities of conductivity-grade water. The concentration of each one of these stock solutions was determined from the value of its experimental density by substituting it into the expression

$$d = (0.997055 \pm 3.4 \times 10^{-5}) + (0.00726 \pm 2.6 \times 10^{-5})p \qquad (1)$$

Table I. Summary of Observed and Corrected Transference Numbers for LiBr in Water at 25 °C

C, M	current, mA	$(T_+)_{obsd}$	$(T_-)_{obsd}$	$10^4\Delta T_{vol}$	$10^4\Delta T_{sol}$	$(T_+)_{cor}$	$(T_-)_{cor}$
0.015 529 ± 0.000 59	1.25–1.35	0.3232_9		1.7	1.1	0.3232_2	
	0.71–0.76		0.6795_0	1.7	2.2		0.6798_9
0.020 129 ± 0.000 61	1.22–1.73	0.3143_7		2.3	0.8	0.3142_3	
	0.80–0.91		0.6647_7	2.3	1.7		0.6651_7
0.030 927 ± 0.000 65	1.82–2.31	0.3201_5		3.4	0.6	0.3198_6	
	1.01–1.51		0.6818_9	3.4	1.2		0.6823_6
0.043 984 ± 0.000 70	3.55–3.76	0.3157_2		4.9	0.4	0.3152_7	
	1.84–2.11		0.6782_8	4.9	0.9		0.6788_6
0.069 411 ± 0.000 79	4.91–4.95	0.3175_9		7.7	0.3	0.3168_5	
	2.82–2.93		0.6910_3	7.7	0.6		0.6918_7
0.100 238 ± 0.000 91	4.75–5.01	0.3156_7		11.1	0.2	0.3145_8	
	3.31–3.41		0.6945_8	11.1	0.5		0.6957_4

(where p represents weight percent of salt). From the least-squares method, this equation was obtained by adjusting density–concentration data reported in the literature (*2*). In this equation the values of the confidence interval for a 95% confidence for the adjusted parameters are included. The method of determining the concentration of the solution from its density value led us to more precise results than other analytical methods (volumetric, conductometric, etc.) also used.

From a portion of each one of the stock solutions, whose composition in weight was very precisely determined by weighing, the "leading solutions" used to measure the ionic transference numbers for LiBr were prepared. From the knowledge of the exact amount of water added, the percentage concentration of these work solutions, together with the value of its most probable error, was calculated. Finally, their densities were measured.

As the concentrations of the LiBr solutions have used as normality (in equiv dm^{-3}) in the calculation of transference numbers, the percentage concentration was first translated to molality and then to normality by means of the Robinson and Stokes equation (*3*)

$$\frac{C}{m} = \frac{d}{1 + 10^{-3}mM_2} \tag{2}$$

where d is the experimental density value of the solution.

***Apparatus*.** The apparatus used for the direct moving-boundary technique as well as the falling-boundary cell employed have been described in a previous paper (*4*). In all the runs a silver anode was placed in the closed compartment and a silver bromide cathode in the open one. All measurements were carried out at 25.00 °C.

The densities of the different solutions were measured by employing a digital densimeter DMA-60 Anton Parr, which permits the obtainment of values with an accuracy of 10^{-6}. The temperature of the sample inside the densimeter was kept constant at 25.00 ± 0.003 °C by an ultrathermostat unit, Heto 02 PG 623.

Results and Discussion

In Table I the summary of the observed and corrected transference numbers is presented for both Li^+ and Br^- ions at each molar concentration employed, together with the current interval selected for the experimental measurements. The value of the molar concentrations for the LiBr solutions used, which is presented in the first column of this table, includes the value of its most probable error although the calculation of the transference numbers was done by using only the mean value of the interval presented. As can be seen, the most probable error that accompanies each concentration value here presented is somewhat large (up to 4% approximately) and affects the third significant figure of its value. For this reason, less precise transference number values are expected. Nevertheless, the fact that we are measuring such parameter for both the cation and the anion of the electrolyte allows an easy optimization of the results.

Table II. Summary of Both "Best" Cation Transference Number and "Best" Concentration for LiBr in Water at 25 °C

C, M	$\sum(T_\pm)_{cor}$	$(T_+)_{best}$	$10^4\Delta C$, M	C_{best}, M
0.015 529 ± 0.000 59	1.0031_2	0.3222_2	−0.48	0.01548_1
0.020 129 ± 0.000 61	0.9794_0	0.3208_4	4.23	0.02055_3
0.030 927 ± 0.000 65	1.0022_2	0.3191_6	−0.68	0.03086_0
0.043 984 ± 0.000 70	0.9941_3	0.3171_3	2.59	0.04424_3
0.069 411 ± 0.000 79	1.0087_1	0.3141_1	−5.98	0.06881_3
0.100 238 ± 0.000 91	1.0103_2	0.3113_6	−10.21	0.09921_7

For the volume correction (*5*) $\Delta V_\pm$ was calculated from the expression

$$\Delta V_\pm = \bar{V}(\mathrm{AgBr}) - \bar{V}(\mathrm{Ag}) - T_+(\mathrm{LiBr})\Phi(\mathrm{LiBr}) \tag{3}$$

where $\bar{V}$ represents molar volume (29.01 and 10.27 cm^3 mol^{-1} for AgBr and Ag, respectively) and Φ apparent molar volume. The values of this last parameter for the LiBr solutions were calculated from the equation proposed by Harned and Owen (*6*)

$$\Phi = \frac{1000}{Cd_0}(d_0 - d) + \frac{M}{d_0} \tag{4}$$

in which d_0 and d are, respectively, the densities of both the pure solvent (0.997 047 g cm^{-3}) and the solutions at concentration C, M being the molecular weight of LiBr (86.85). This volume correction, ΔT_{vol} (shown in Table I), must be subtracted from the value of the observed transference number in the case of the cation runs, but added to it in the case of the anion runs.

For the solvent correction (*5*) the specific conductivity for LiBr solutions was determined from the value of its equivalent conductance, Λ, which was calculated at each concentration, in ohm^{-1} cm^2 equiv^{-1}, from

$$\Lambda = 116.82 - 86.98C^{1/2} + 41.30C \log C \qquad \text{(at 25 °C)} \tag{5}$$

because the value of the product κa in all cases was greater than 0.2, κ being the Debye parameter. This solvent correction, which is always added to the observed transference number, is also shown in Table I.

Both cation and anion corrected transference numbers, after both solvent and volume corrections were applied, are presented in Table I. Their sums at each concentration of LiBr studied are presented in Table II. As can be seen these sums are not exactly equal to the theoretical unit value but their discrepancies can easily be minimized by obtaining the "best" values of $T_\pm$ (*5*). These "best" values at each LiBr concentration employed are also summarized in Table II for the cation only.

Generally the sum of both corrected transference numbers differs from unity. Such observed discrepancy is still being attributed to small errors in some of the following: the calibration of the cell employed; the value of the standard resistor used in the circuit; the volume or solvent corrections; the knowledge of the concentration of LiBr leading solution (*7*). In the present case, the lack of precision in the knowledge of the LiBr solution concentration (obtained through an indirect way) must be considered as the only factor responsible for the large discrepancies observed (differences up to 2%). This assertion can be easily understood if we pay attention to the different magnitudes involved in the calculation of the transference number

$$(T_\pm)_{\text{obsd}} = CvF/i_\pm t_\pm = CvF/q_\pm \tag{6}$$

and their corresponding errors. By taking into account that

$$(T_\pm)_{\text{cor}} = (T_\pm)_{\text{obsd}} \mp \Delta T_{\text{vol}} + \Delta T_{\text{sol}} \tag{7}$$

and that the errors in both the volume and the solvent corrections can be neglected, the error that appears in the corrected transference numbers is the same as in the observed ones, i.e.

$$\Delta(T_\pm)_{\text{cor}} = \Delta(T_\pm)_{\text{obsd}} \tag{8}$$

Let us analyze the extent of the errors for the magnitudes that appear in eq 6. All of them, except the concentration (whose value is not known exactly, but falls within a rather wide interval) are determined with an accuracy better than one part in one thousand, so the main error must arise, as mentioned before, from the LiBr concentration value used.

An attempt to calculate this concentration error can be done by considering the numerical values of the errors involved. By differentiating eq 6 for both the cation and the anion and rearranging adequately their sum, we can write

$$\Delta(T_+)_{\text{cor}} + \Delta(T_-)_{\text{cor}} = 1 - \sum(T_\pm)_{\text{cor}} = \left(\frac{\Delta v}{v} + \frac{\Delta F}{F}\right)\sum(T_\pm)_{\text{obsd}} + \frac{\Delta C}{C}\sum(T_\pm)_{\text{obsd}} - \left[\frac{\Delta q_+}{q_+}(T_+)_{\text{obsd}} + \frac{\Delta q_-}{q_-}(T_-)_{\text{obsd}}\right] \tag{9}$$

from which equation can be calculated the correction, ΔC, that we have to apply to the concentration value, C, which has been used until now, to obtain a "best" concentration value. This C_{best} concentration substituted in eq 6 and 7 directly leads to experimental values for the corrected transference numbers that are coincident with the "best" transference numbers finally found. Thus, this new value of such "best" concentration of LiBr, C_{best}, can be obtained from

$$C_{\text{best}} = C + \Delta C \tag{10}$$

The values of the interval confidence used here are 1.6 C equiv^{-1} (*8*) for the Faraday constant, ΔF; 1.9 × 10^{-4} cm^3 (the mean value obtained by us in this work) for the volumes of calibration, Δv; and values that correspond to the amount of electricity which flows through the cell, $\Delta q_\pm$, were calculated for each of the ions at different concentrations by taking into account all the runs carried out. The values of ΔC are shown in Table II together with C_{best} values. As can be observed, these C_{best} values are maintained in the concentration interval previously calculated, except in the case of the 0.1 M solution.

This procedure of concentration optimization should allow us to obtain better values for the concentration-dependent properties of hygroscopic electrolytes. If the desired parameter is hard-dependent on the concentration of the electrolyte, it will be necessary to have an accurate knowledge of this variable. In this way, based on the measurement of the transference numbers, it is possible to have at our disposal a more precise value than that obtained by any other analytical method.

Table III. Experimental Densities for LiBr Aqueous Solutions at 25 °C

C_{best}, M	p, wt%	d_{expt}, g cm^{-3}
$0.015\,48_1$	0.134 72	0.998 03
$0.020\,55_3$	0.178 80	0.998 32
$0.030\,86_0$	0.268 28	0.999 00
$0.044\,24_3$	0.384 32	0.999 82
$0.068\,81_3$	0.596 71	1.001 41
$0.099\,21_7$	0.858 83	1.003 34

The behavior of these "best" transference numbers with the concentration of LiBr is the same as has been observed for other 1:1 electrolytes, i.e., the cation transference number decreases when the concentration of the electrolyte increases. The calculation of the limiting value when the "best" concentration of salt approaches zero was done by means of the 1963 Fuoss and Onsager equation (*9*), this value being $T^0(\text{Li}^+) = 0.3318$ with $a = 4.4$ Å (a, distance of closest approach cation–anion).

By considering that $\lambda^0 = T^0\Lambda^0$ and applying this equation to both the cation and the anion, we can write, after dividing one into another

$$\lambda^0(\text{Li}^+) = \lambda^0(\text{Br}^-)[T^0(\text{Li}^+)/T^0(\text{Br}^-)] \tag{11}$$

that connects the limiting values of the ionic conductances with those of the transference numbers for both ions. From this relationship the conductance of lithium ion was calculated as equal to $\lambda^0(\text{Li}^+) = 38.83$ ohm^{-1} cm^2 equiv^{-1} by taking the value of $\lambda^0(\text{Br}^-) = 78.20$ ohm^{-1} cm^2 equiv^{-1} from the literature (*10*). Thus the equivalent conductance is equal to 117.03 ohm^{-1} cm^2 equiv^{-1} for LiBr.

Finally, the experimental densities measured here (whose values are presented in Table III) were fitted against the "best" concentration values (expressed as weight percent) by using a least-squares method. The linear relationship found was

$$d = (0.99702 \pm 1.4 \times 10^{-5}) + (0.00735 \pm 3 \times 10^{-5})p \tag{12}$$

which is in good accordance with the previous one obtained from literature data.

Registry No. LiBr, 7550-35-8; Li$^+$, 17341-24-1.

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Received for review January 30, 1987. Accepted July 6, 1987.