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Transference Number Measurements in Aqueous Solutions at 25 °C. 2. Sodium Bromide

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Transference numbers at 25 °C are measured for different concentrations of NaBr by using both a falling and a rising sheared moving-boundary cell. Both Ag/AgBr and Ag/AgCl electrodes are used with the rising cell, while only Ag/AgBr electrodes are used with the falling one. After different corrections are applied to the observed values, "best" transference numbers are calculated. In all cases, these best values agree perfectly with one another and by applying to them the Fuoss–Onsager and Pitts equations, values at zero concentration, T^0, are obtained. Moreover, electrolytic conductances at 25 °C for NaBr at different concentrations are measured and later extrapolated to null ionic strength by using the 1957 Fuoss–Onsager conductance equation. Individual conductance values are obtained by combining both limiting parameters, T^0 and Λ^0. In the same manner, an adequate value for the adjustable parameter a, distance of the closest approach cation–anion, is obtained from both experimental techniques.

Introduction

Knowledge of numerical values for the individual ionic properties is very important in the study of electrolytic solutions. Generally, such individual knowledge is obtained from the value for the electrolyte, accepting for its unfolding different working hypotheses. Nevertheless, the transference number for an ion can be experimentally determined by a direct method and for this reason such knowledge of ionic property is of great interest.

Longsworth has determined the transference numbers for NaCl in aqueous solutions (*1*). This author found that the chloride anion participates in the electrical charge transport through the solution in higher quantity than the sodium ion (T_-^0(NaCl) = 0.6037). In a recent paper from this laboratory with NaI in aqueous solutions (*2*), a similar value for the iodide ion (T_-^0(NaI) = 0.6055) was also found. This indicates that such a parameter is almost independent of the nature of the halide used, although that anion varies considerably in size (crystallographic radii: 1.81 and 2.20 Å, for Cl^- and I^-, respectively). In consideration of these results we attacked the present work using the bromide ion, having measured the transference numbers for both ions in NaBr (crystallographic radius: 1.96 Å for Br^-) to confirm the behavior previously mentioned for the other sodium halides, which can be justified by accepting for the halide ions the same effective size, that is, the ion size plus its solvation-sheath which move together through the solvent.

Since there are no conductance values in the literature for NaBr in aqueous solutions at 25 °C, these were measured and are presented in this paper. Finally, by combination of these conductance data with our transference numbers, individual limiting ionic conductances for the ions of NaBr in this aqueous medium have been obtained.

Experimental Section

Chemicals and Solutions. NaBr, Merck "Suprapur", was dried in vacuo at 150 °C for 72 h before use. Its purity was tested by elemental analysis with X-ray spectroscopy.

$CdBr_2$, Merck analytical reagent grade, and Analar KIO_3 were recrystallized twice from their saturated aqueous solutions. $KOOCCH_3$, analytical reagent grade from Merck, was recrystallized twice from a saturated ethanol solution. $(C_2H_5)_4NBr$, polarographic grade, was supplied by Carlo Erba and used without any previous manipulation. All chemicals were dried in an oven except KIO_3 which was dried by means of a nitrogen stream.

Conductivity grade water with a specific conductivity, $\kappa_0 = 5.0 \times 10^{-7}$ ohm^{-1} cm^{-1}, was used as solvent. The solutions were prepared by weighing and correcting to vacuo each of the components.

Apparatus. Transference Number Measurements. The apparatus and the moving-boundary technique have been described elsewhere (*3*). Most of the runs were carried out by using a rising-boundary cell with KIO_3 or $CdBr_2$ as following electrolyte for anion or cation runs, respectively. A falling-boundary cell was used to check some of the results. In this case, $KOOCCH_3$ or $(C_2H_5)_4NBr$ was used as following electrolyte for anion and cation runs, respectively. Both types of cells have been previously described (*3*, *4*). The silver or cadmium anodes were obtained by electrolysis on a platinum coil (*5*). The silver chloride or bromide cathodes were made by anodizing electrolytic silver electrodes (*5*). In all cases the electrode placed in the NaBr solution was kept closed.

Conductance Measurements. In conductance measurements the weight of NaBr samples was obtained by using an M5SA Mettler microbalance with an accuracy of 0.001 mg. The cells employed were of the Dagget type with brilliant platinum disk electrodes. They were calibrated by using KCl aqueous solutions (*6*) for which Λ^0 = 149.94 ohm^{-1} cm^2 equiv^{-1} at 25 °C.

The ac conductivity bridge used was a 4666 Leeds & Northrup, supplied by an audio oscillator (1311A General Radio), and a 1232A General Radio tuned amplifier was used as null detector. The values of the resistances measured were plotted against frequency^{-1} to obtain, by extrapolation, their values free from the frequency effect (*7*).

The temperature was kept constant at 25.00 ± 0.003 °C by means of an oil thermostat. The solutions were stirred by a mechanical device immersed in the thermostat, which was provided with mobile magnets to move the stirrers placed inside the cells.

Results and Discussion

Transference Numbers. The experimentally observed transference numbers are summarized in Tables I and II. The main group of such data, measured by using a sheared rising-boundary cell (Table I), was obtained by employing two different types of electrodes.

(***a***) ***Electrodes of Type I.*** First, for both cathodic and anodic runs, an AgBr electrode was used as cathode and an Ag one as anode, the reactions on these electrodes being

$$AgBr \rightarrow Ag + Br^-$$

$$Ag + Br^- \rightarrow AgBr$$

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Table I. Summary of Transference Numbers for NaBr by Using a Sheared Rising-Boundary Cell

C, M	electrode type	current, mA	T_+	T_-	$10^4 \times \Delta T_{vol}$	$10^4 \times \Delta T_{sol}$	$(T_+)_{cor}$	$(T_-)_{cor}$	$\sum(T_\pm)_{cor}$	$(T_+)_{best}$
0.025 00	I	0.95–1.05	0.3836_2		−2.4	0.6	0.3834_4		0.9976_5	0.3843_4
		0.55–0.65		0.6138_7	2.4	1.0		0.6142_1		
0.049 74	I	1.70–1.74	0.3821_6		−4.8	0.3	0.3817_1		0.9983_5	0.3823_4
		0.75–1.35		0.6161_1	4.8	0.5		0.6166_4		
0.075 00	I	2.00–2.15	0.3811_3		−7.2	0.2	0.3804_3		0.9986_4	0.3809_5
		1.40–1.55		0.6174_5	7.2	0.4		0.6182_1		
0.024 99	II	0.80–1.00	0.3838_7		−3.4	0.6	0.3835_9		0.9984_3	0.3841_9
		0.51–0.61		0.6144_2	3.2	1.0		0.6148_4		
0.049 99	II	1.50–1.61	0.3821_0		−6.8	0.3	0.3814_5		0.9978_1	0.3822_9
		0.70–0.75		0.6156_8	6.3	0.5		0.6163_6		
0.074 90	II	1.80–2.01	0.3816_4		−10.2	0.2	0.3806_4		0.9987_7	0.3811_1
		1.45–1.50		0.6171_5	9.4	0.4		0.6181_3		
0.099 79	II	1.91–2.11	0.3802_9		−13.7	0.2	0.3789_4		0.9975_6	0.3798_7
		2.01–2.35		0.6173_6	12.3	0.3		0.6186_2		

Table II. Summary of Transference Numbers for NaBr by Using a Sheared Falling-Boundary Cell with Ag/AgBr Electrodes

C, M	current, mA	T_+	T_-	$10^4 \times \Delta T_{vol}$	$10^4 \times \Delta T_{sol}$	$(T_+)_{cor}$	$(T_-)_{cor}$	$\sum(T_\pm)_{cor}$	$(T_+)_{best}$
0.025 00	1.70–1.80	0.3842_0		−2.4	0.6	0.3840_2		0.9986_8	0.3845_3
	0.80–0.90		0.6143_2	2.4	1.0		0.6146_6		
0.047 70	2.50–3.00	0.3823_8		−4.8	0.3	0.3819_3		0.9979_7	0.3827_1
	2.00–2.20		0.6155_1	4.8	0.5		0.6160_4		

Table III. Summary of the "Best" and Limiting Transference Numbers for NaBr in Water at 25 °C

			T_+^0			a, Å		
C, M	cell type	$(T_+)_{best}$	$(FO)_1$	$(FO)_2$	(P)	$(FO)_1$	$(FO)_2$	(P)
0.024 99	rising	0.3841_9	0.3908	0.3912	0.3907	6.1	4.4	6.1
0.025 00	rising	0.3843_4						
0.025 00	falling	0.3845_3						
0.047 70	falling	0.3827_1						
0.049 74	rising	0.3823_4						
0.049 99	rising	0.3822_9						
0.074 90	rising	0.3811_1						
0.075 00	rising	0.3809_5						
0.099 79	rising	0.3798_7						

The experimental values observed for all of these runs are not influenced by the value of the current of electrolysis employed, so in Table I the values presented for the transference numbers are mean values. In this table, the interval of current of electrolysis employed at the different concentrations of leading solution studied is also indicated.

For the volume correction (*2*, *4*), ΔV was calculated from

$$\Delta V_\pm = \pm[\bar{V}(\mathrm{Ag}) - \bar{V}(\mathrm{AgBr}) + T_+(\mathrm{NaBr})\phi(\mathrm{NaBr})] \qquad (1)$$

The values used for the molar volumes, $\bar{V}$(Ag and AgBr), were 10.3 and 29.0 cm^3 mol^{-1}, respectively, and the apparent partial molar volumes of NaBr were determined from the equation

$$\phi(\mathrm{NaBr}) = 23.48 + 1.760C^{1/2} \qquad (2)$$

in accord with the data compiled by Harned and Owen (*8*).

For the solvent correction (*2*, *4*), the specific conductivity was determined for each concentration studied from the value of its equivalent conductance, Λ, obtained here

$$\Lambda = 128.45 - 89.651C^{1/2} + 47.433C \log C + 312.45C \qquad (3)$$

in ohm^{-1} cm^2 equiv^{-1} at 25 °C. If $\kappa a > 0.2$ (a being the Debye parameter), the linear term in the eq 3 was not considered.

The values of both corrections and the corrected values for $T_\pm$ are presented in Table I, together with their sum at each concentration of NaBr employed. As can be seen, in all cases this sum is less than unity, with differences never greater than 0.3%. By minimizing experimental errors (*2*), "best" values for T were calculated. They are summarized in Table I for the cation only.

(***b***) ***Electrodes of Type II.*** Since the discrepancies from the unity value of the sum for both ionic T_{cor} are important in some of the cases, we considered the necessity of checking up the transference number values reported here, by measuring them in another way. We therefore replaced the previous Ag/AgBr electrodes with Ag/AgCl ones which have been widely used with excellent results in transference number experiments. Thus, we employed as closed electrode an AgCl cathode in cation runs and in anion runs, an Ag anode rounded by an NaCl solution 4 times more concentrated than the NaBr leading solution used, in order to maintain the gravitational stability of the system. The reactions on these closed electrodes are

$$\mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{Cl}^- \text{ (appearing in the NaBr solution)}$$

$$\mathrm{Ag} + \mathrm{Cl}^- \rightarrow \mathrm{AgCl}$$

The results obtained in this new group of experiments are summarized in Table I. As before, no influence on these values was detected with the change of the electrolysis current employed, and so the values presented are also mean values. The corrected ones, after the volume and solvent corrections were applied, as well as their sum and the best cation value at each concentration studied, are shown in Table I. The equations used for these volume corrections are in this case

$$\Delta V_+ = \bar{V}(\mathrm{Ag}) - \bar{V}(\mathrm{AgCl}) + \phi^0(\mathrm{NaCl}) - T_-(\mathrm{NaBr})\phi(\mathrm{NaBr}) \qquad (4)$$

$$\Delta V_- = \bar{V}(\mathrm{AgCl}) - \bar{V}(\mathrm{Ag}) - \phi(\mathrm{NaCl}) + T_-(\mathrm{NaBr})\phi(\mathrm{NaBr})$$

for cathodic and anodic runs, respectively. In these equations

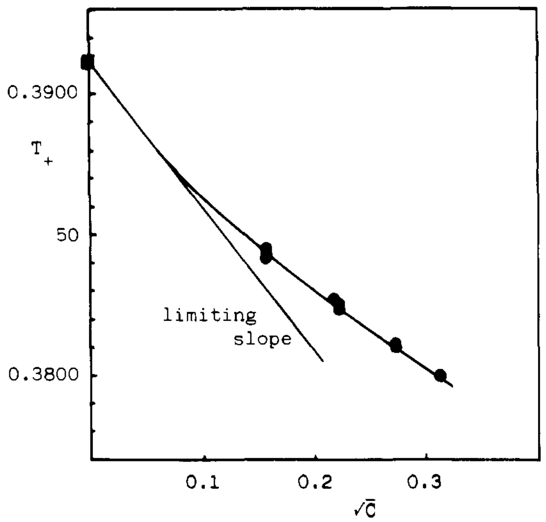

Figure 1. Effect of the concentration of the leading solution on the "best" transference numbers.

the value used for $\bar{V}$(AgCl) was 25.8 cm^3 mol^{-1} and the apparent partial molar volumes for NaCl were calculated from the equation (*8*)

$$\phi(\text{NaCl}) = 16.61 + 2.153C^{1/2} \qquad (5)$$

As can be seen in Table I the use of this type of electrodes leads to the same situation with respect to the sum of T_{cor} values; that is, these sums are less than unity with differences never greater than 0.3%, and the best results finally obtained agree with the previous ones.

A final attempt to prove the validity of these results was made by changing the type of cell employed. In this case, a sheared falling-boundary cell was used and the mean results observed are given in Table II together with the corrected and best cation values. The equation for the volume correction in this case is again eq 1. As in the above situations, the final results obtained agree with one another.

The agreement between all these values found in different ways permits us to accept them as true values for these ions, independently of the discrepancies observed, at each concentration studied, in the sum of both ionic transference numbers.

The summary of all best cation values found is shown in Table III. It can be seen that there exists an influence of the sodium bromide concentration on these transference numbers. Such influence can be better observed by plotting these $(T_+)_{\text{best}}$ against the square root of the concentration (Figure 1). As in the solutions of the other halides, when the concentration of the solution increases, the transference number of the cation decreases and that corresponding to the anion increases. This increase in the anion mobility at the expense of the cation mobility can be justified by changes in the electrophoretic term when the degree of hydration of the ion changes, or as a result of changes in the structure-breaking character of the ions. In fact, if the local viscosity around the anion moves down with respect to the bulk solution and around the sodium ion, its relative mobility has to move up. The behavior shown in Figure 1 is quite often observed in aqueous solutions and can be easily explained through the Debye-Hückel theory. On the basis of the Fuoss-Onsager theory for electrolytic conductance, Stokes (*9*) obtained the known expression

$$T_\pm = \frac{\lambda_\pm}{\Lambda} = \frac{\lambda_\pm^0|Z_\pm|\beta I^{1/2}/(1 + \beta a I^{1/2})}{\Lambda^0 - (|Z_+| + |Z_-|)\beta I^{1/2}/(1 + \beta a I^{1/2})} \qquad (6)$$

that foresees a parabolic dependence between the transference number of an ion and the ionic strength of the medium.

Table IV. Equivalent Conductances for NaBr in Water at 25 °C ($10^7\kappa_0$ = 10.1 ohm^{-1} cm^{-1})

10^4C, M	Λ	$\Delta\Lambda$	Λ^0	a, Å	σ_Λ
0.65195	127.705	-0.021	128.45 ± 0.02	3.9 ± 0.1	0.03
2.11614	127.113	-0.041			
4.61519	126.567	0.016			
5.02454	126.496	0.026			
9.41452	125.757	-0.012			
10.9386	125.552	-0.018			
19.8172	124.674	0.035			
37.8099	123.380	0.048			
67.6185	121.832	-0.034			

For dilute aqueous solutions of 1:1 electrolytes at 25 °C, the eq 6 is reduced to

$$T_\pm = T_\pm^0 + \frac{60.65(T_\pm^0 - 0.5)C^{1/2}}{\Lambda^0} \qquad (7)$$

that defines a linear relationship between the transference number of an ion and the square root of concentration. This limiting slope adjusts properly to the experimental results in Figure 1.

The calculation of the electrophoretic term was made by applying the Fuoss-Onsager (FO) and Pitts (P) equations (*2*) to the best values in Table III. The calculated limiting parameters T_+^0 and a (distance of closest approach cation-anion) are also presented in Table III. The values obtained for T_+^0 from (FO)$_1$ and (P) equations are the same and both differ from the (FO)$_2$ one in about 0.1 unit per cent. The situation is the same with respect to the parameter a except in the amount of the difference among them, which is higher. The value for a obtained from the (FO)$_2$ equation, 4.4 Å, agrees perfectly with those obtained for other sodium halides, so we have accepted that the (FO)$_2$ equation fits the experimental data obtained better.

The value found in this work for the transference number of the bromide ion (T_-^0(NaBr) = 0.6088), similar to the values found previously for the chloride and iodide ions, confirms the hypothesis that the sodium ion approximately carries the same amount of electrical charge through the solution, independently of the halide present in the solution.

***Conductance*.** The values of Λ obtained at each concentration are presented in Table IV together with the theoretical deviation, $\Delta\Lambda$, of these values. The analysis of the change with the concentration of the solution was made by using the 1957 Fuoss-Onsager conductance equation (*10*)

$$\Lambda = \Lambda^0 - SC^{1/2} + EC \log C + JC \qquad (8)$$

valid for 1:1 electrolytes in solvents of high dielectric constant in which no ionic association occurs or is negligible.

The conductance parameters, Λ^0 and a, equal to 128.45 ± 0.02 ohm^{-1} cm^2 equiv^{-1} and 3.9 ± 0.1 Å, respectively, were obtained through a FORTRAN least-squares computer program, the final expression for that conductance being

$$\Lambda = 128.45 - 89.651C^{1/2} + 47.433C \log C + 312.45C$$

with a standard deviation of 0.03. The data of λ^0 for both Br$^-$ and Na$^+$ ions were calculated by combining the Λ^0 and T^0 values obtained here. These ionic contributions are λ^0(Na$^+$) = 50.25 and λ^0(Br$^-$) = 78.20 (in ohm^{-1} cm^2 equiv^{-1}).

The values for the parameter a, obtained from both transference number and conductance measurements, agree adequately with each other, so we can accept the mean value of 4.1 ± 0.3 Å for this adjustable parameter.

Registry No. NaBr, 7647-15-6.

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Speed of Sound in Liquid CCl_3F under Saturated Vapor

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The speed of sound in saturated liquid trichlorofluoromethane has been measured from its triple point temperature (162.7 K) to 458 K by using the pulse echo overlap method. Our data were combined with available density data to obtain the isentropic compressibilities.

Introduction

The experimental data of the speed of sound for CCl_3F under saturated liquid have been represented by a quadratic function of temperature T by Aziz (*1*) and by Chávez et al. (*2*). These equations show a positive curvature and decrease continuously with increasing temperature, and extrapolated for higher temperatures predict a zero sound speed at 570.76 and 539.78 K. However, from the relation of speed of sound W with isentropic compressibility β_s and saturated density ρ_σ

$$W^2 = (\beta_s \rho_\sigma)^{-1} \tag{1}$$

a value of zero is expected for W at the critical temperature $T_c = 471.15$ K (*3*).

In this paper new measurements of the speed of sound from triple point temperature up to near-critical temperature ($T/T_c = 0.97$) are presented. Typical experimental results are depicted in Figure 1. These data show a positive curvature at low temperatures as found previously, an inflection point around 343.5 K, and a negative curvature at higher temperatures with a general trend toward $W = 0$ at T_c. An empirical equation having seven parameters was required to mathematically represent our data within the expected uncertainty and gives a zero speed of sound at T_c.

Experimental Procedure

The speed of sound was measured by using the pulse echo overlap (PEO) method as developed by Papadakis (*4*). This technique and the apparatus are described in an earlier paper (*5*). Measurements were made by using two plane parallel 10-MHz X-cut quartz crystals (2.54 cm in diameter) pressed to the end of a tubular stainless-steel spacer by two electrode springs. The spacer has a length of $d = 9918 \pm 1$ μm. The emitter crystal was forced to vibrate between 3 and 12 MHz by an electrical pulse. The excitation frequency of the crystal was 1/100 or 1/1000 of the triggering repetition frequency of the x axis of the scope. The repetition frequency f is the reciprocal of the round trip travel time of the acoustic pulse through the fluid and it is used to calculate the speed of sound by

$$W = 2df \tag{2}$$

For measurements of speed of sound below room temperatures, it was found that keeping the sample cell in a bath at 162 K for more than an hour did not decrease the temperature of the liquid in the cell below 162.683 K. This constant temperature in the liquid probably arrises because the triple point temperature T_t was attained and some liquid had been solidified. The only datum of the T_t for CCl_3F seems to be that of Osborne et al. (*6*) published in 1941. They define 0 °C = 273.16 K; therefore T_t has to be diminished by 0.01 K according to the actual definition of 0 °C. Taking the correction of the IPTS-48 to IPTS-68 the values of T_{t-48} have to be increased by approximately 0.01 to give $T_{t-68} = 162.68 \pm 0.05$ K which is in good agreement with our measurement.

On the other hand, in the initial run, after measurements above room temperatures to about 434 K, the cell was opened and white solid deposits (probably chlorine) were found on the quartz crsytals and internal walls of the cell. Also the liquid had a light brown color. We believe this was an electrolytic effect at high temperatures. Trying to avoid the former effect we conducted four additional runs as follows. The voltage applied to the emitting crystal was decreased from 130 to 70 V. The excitation frequency was reduced from 1/100 to 1/1000 of the triggering repetition frequency. Then, although the temperature of the liquid was increased to 460 K, no changes in the liquid were observed, and only a very small amount of the white deposits was found in the cell.

The uncertainty in the speed of sound measured with the PEO method is estimated to be less than 0.05%. However, near the critical temperature the signal on the oscilloscope is very small. The right overlapping criteria of the pulse and the remaining echo become difficult to distinguish, and the uncertainty is several times bigger.

In each run, each datum was measured at two or more frequencies, using in total five frequencies between 3 and 12 MHz. From a preliminary analysis, no dispersion of the data was observed in all the vapor pressure curve. Therefore only two measurements made at essentially the same temperature measured at two different frequencies, where the signal on the oscilloscope was clear, are reported.

Temperature was measured by using a platinum resistance thermometer calibrated on the IPTS-68. This thermometer was located in a thermowell inside the sample cell in contact with the liquid. The temperature could be maintained within ±0.005 K during the measurements. The fluid sample was obtained by successively degassing and freezing commercially available

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