thermostated cell compartment and 1.00-cm matched quartz cuvettes. Distilled water was used as the blank for all measurements and absorbance measurements were always made at 596 nm with a spectral band-pass of 0.3 nm. Special care was taken to assure that thermal equilibration and readings were made only after absorbances were stable for at least 3 min.

Acknowledgment

We thank Professor Lowell M. Schwartz for several helpful discussions and his assistance in the preparation of this manuscript.

Registry No. Amantadine hydrochloride, 665-66-7.

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Received for review October 19, 1982. Accepted March 7, 1983. The financial support of the National Institute of General Medical Sciences, U.S. Public Health Service (Grant No. GM 26004), is gratefully acknowledged.

Transference Number Measurements in Aqueous Solutions at 25 °C. 1. Sodium Iodide

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Cation and anion transference numbers for aqueous solutions of NaI at different ionic concentrations are determined by using the moving-boundary method. The values of the ionic transference numbers at each concentration of NaI are verified through the value of their sum. The small variation with the NaI concentration of the transference number obtained is attributed mainly to the variation of the electrophoretic effect, in accord with the Debye–Hückel picture. The limiting cation transference number, T_+°, is calculated by employing the various Fuoss–Onsager (FO) and Pitts (P) equations. Limiting ionic conductances, $\lambda_\pm^\circ$, are also reported.

Introduction

Ionic transference numbers can be used to understand the ion–solvent interactions in electrolytic solutions. Nevertheless, only a few experimental data of such parameters have been reported, even in water, it being necessary to resort to the utilization of limiting ionic conductances for their calculation.

This paper reports the transference numbers for NaI in water at 25 °C, obtained by measuring both the cation and the anion transference numbers at different concentrations of salt to contribute to a better knowledge of electrolytic aqueous solutions.

Experimental Section

Chemicals and Solutions. NaI (Merck Suprapur) was dried in vacuo at 150 °C for 72 h before use. Merck analytical-reagent-grade $NaOOCCH_3$ was recrystallized twice from a saturated aqueous solution. $(C_2H_5)_4NClO_4$, for polarography, was supplied by Carlo Erba and recrystallized once from a methanol–water mixture. All the chemicals were stored in a desiccator over P_2O_5.

Conductivity-grade water with a specific conductivity $\kappa_0 = 5 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ was used as solvent. The solutions were prepared by weighing and correcting to vacuo each of the components.

Apparatus. The apparatus to detect and follow the moving boundary has been described in a previous paper from this laboratory (*1*) as well as the falling-boundary cell employed. In the cation runs a silver electrode was used as the anode in the closed compartment whereas an electrolytic cadmium electrode was the closed anode in the anion runs. In all runs, a platinum wire was used as the cathode in the open compartment.

Results and Discussion

The transference numbers observed are presented in Table I together with the current interval employed.

The volume correction at each concentration studied was calculated from (*2*, *3*)

$$\Delta T_{vol} = C\cdot\Delta V \qquad (1)$$

where ΔV is the volume change per faraday between the closed electrode compartment and a point in the leading solution. These corrections are given in Table I and are added to the values observed in the anion runs but subtracted from those in the cation runs.

In the cation runs $(C_2H_5)_4NClO_4$ was used as following electrolyte and their volume increases per faraday were calculated from

$$\Delta V_+ \simeq \phi^0(AgClO_4) - \bar{V}(Ag) + \phi^0(Et_4NI) - \phi^0(Et_4NClO_4) - T_+(NaI)\ \phi(NaI) \qquad (2)$$

where $\phi(Et_4NI)$ and $\phi(Et_4NClO_4)$ have been replaced by their ϕ^0 values.

In the anion runs $NaOOCCH_3$ was used as the following electrolyte. The volume increase per faraday for these runs was given by

$$\Delta V_- \simeq \tfrac{1}{2}\phi^0(CdI_2) - \tfrac{1}{2}\bar{V}(Cd) - T_+(NaI)\ \phi(NaI) \qquad (3)$$

where $\phi(CdI_2)$ has been approximated to its ϕ^0 value. The values used for $\bar{V}(Ag)$ and $\bar{V}(Cd)$ were 10.3 and 13.0 $cm^3\ mol^{-1}$, respectively (*4*), and the apparent partial molar volumes, $\phi(NaI)$, were determined at each concentration from

$$\phi = 35.10 + 1.346C^{1/2} \qquad (4)$$

Table I. Transference Numbers Observed and Corrected for NaI in Water at 25 °C

C, M	current, mA	T_+	T_-	$10^4 \cdot \Delta T_{vol}$	$10^4 \cdot \Delta T_{sol}$	$(T_+)_{cor}$	$(T_-)_{cor}$	$\Sigma(T_\pm)_{cor}$
0.019 93	0.71-0.99	$0.388\,5_3$		2.4	1.2	$0.388\,4_1$		$1.000\,5_0$
	0.51-0.80		$0.611\,7_9$	1.2	1.8		$0.612\,0_9$	
0.029 88	1.01-1.20	$0.388\,0_4$		3.6	0.8	$0.387\,7_6$		$1.000\,4_0$
	0.79-1.11		$0.612\,3_4$	1.8	1.2		$0.612\,6_4$	
0.049 77	1.49-1.70	$0.387\,0_7$		6.1	0.5	$0.386\,5_1$		$1.000\,5_4$
	1.30-1.62		$0.613\,6_5$	3.0	0.8		$0.614\,0_3$	
0.074 58	1.94-2.30	$0.385\,9_4$		9.1	0.4	$0.385\,0_7$		$1.000\,0_5$
	2.07-2.42		$0.614\,4_7$	4.5	0.6		$0.614\,9_8$	
0.099 36	2.91-3.16	$0.385\,9_2$		12.1	0.3	$0.384\,7_4$		$1.000\,6_1$
	2.69-2.92		$0.615\,2_2$	6.0	0.5		$0.615\,8_7$	

Table II. Summary of "Best" and Limiting Cation Transference Numbers for NaI in Water at 25 °C

		T_+°			a, Å		
C, M	T_+	(FO)$_1$	(FO)$_2$	(P)	(FO)$_1$	(FO)$_2$	(P)
0.019 93	0.3882	0.3937	0.3945	0.3937	8.3	4.7	8.1
0.029 88	0.3876						
0.049 77	0.3863						
0.074 58	0.3850						
0.099 36	0.3845						

as has been proposed by Scott (*5*).

The solvent correction, calculated from (*4*)

$$\Delta T_{sol} = \{(T_\pm)_{obsd} \pm \Delta T_{vol}\}(\kappa_{solv}/\kappa_{solute}) \quad (5)$$

is given in Table I. Their values were determined by using κ(NaI) obtained from the equation

$$\Lambda = 126.55 - 89.2C^{1/2} + 46.44C \log C + 281.8C \quad (6)$$

proposed by Lasselle et al. (*6*) for $\kappa a \le 0.2$, κ being the Debye parameter. When $\kappa a > 0.2$ the linear term in C was not considered.

The T_{cor} for both ions, with the volume and solvent correction applied, are also presented in Table I. Since cation and anion transference numbers were measured, the unit value of their sum was verified as a validity criterion, the "best" T value being calculated from this sum. An inspection of these optimum values shows that they are influenced by the concentration of the electrolyte, diminishing as this concentration increases. This small variation (less than 1% between 0.02 and 0.1 equiv dm^{-3}) should be mainly understood, in accord with the Debye-Hückel theory, as the result of the variation, due to the change of the ionic atmosphere size, of the electrophoretic term modifying the ion motion, and to a lesser degree as the result of changes in the structure-breaking character of the ions as the concentration varies.

The electrophoretic term was determined by applying the 1957 Fuoss-Onsager (FO)$_1$ equation, the 1963 Fuoss-Onsager (FO)$_2$ equation, and the Pitts (P) equation to these best values (*7*). The T_+° values obtained are summarized in Table II together with the values of the parameter a from which they are calculated.

The T_+° value obtained from (FO)$_1$ is equal to that obtained from (P) and both differ from that of (FO)$_2$ in about 0.2 unit percent. The values of parameter a are very high in (FO)$_1$ and (P), but in (FO)$_2$ it agrees well with the values obtained for other sodium halides (approximately 5 Å). We have, therefore, concluded that the (FO)$_2$ theory fits adequately the experimental data in terms of both the T_+° value and physical reasonableness of the a value.

The ionic conductances $\lambda^\circ(Na^+) = 49.92\ \Omega^{-1}$ cm^2 equiv^{-1} and $\lambda^\circ(I^-) = 76.63\ \Omega^{-1}$ cm^2 equiv^{-1} were obtained from $T_+^\circ = 0.3945$ and $\Lambda^\circ(NaI) = 126.55\ \Omega^{-1}$ cm^2 equiv^{-1} (*6*).

Registry No. NaI, 7681-82-5; Na$^+$, 17341-25-2; I$^-$, 20461-54-5.

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Received for review September 7, 1982. Accepted March 23, 1983.