The Relative Determination of the Soret Coefficients of Electrolytes. IV

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(Received October 29, 1973)

The relative values of the Soret coefficients of 0.01 M aqueous solutions of symmetric tetraalkylammonium chlorides (R_4NCl, R=Me, Et, *n*-Pr, *n*-Bu, and *n*-Am) were determined by measuring the initial thermoelectric power of "combined thermocells" made up of AgCl electrode systems, taking LiCl as a reference. The results obtained were found to be rather high, higher by about 20% than those previously found on the combined thermocells made up of calomel-electrode systems.

In a previous paper,[1)] the Soret coefficients of a series of symmetric tetraalkylammonium chlorides were determined by using a "combined thermocell" made up of calomel-electrode systems. The merit of using a combined thermocell for the determination of the Soret coefficients is that thereby the nature of the electrode system used in the cell is completely canceled out. On the other hand, the electrode potentials of calomel-electrodes have rather high temperature coefficients as much as 950 μV/deg at 0.01 M; accordingly, a considerable error may be caused in the thermoelectric power by an occasional slight shift in the temperature of an electrode system, thereby losing the merit of using combined thermocells. For this reason, in the present work, silver chloride electrodes with a relatively low temperature coefficient of about 600 μV/deg were used in place of the calomel-electrodes.

A combined thermocell of the following system was constructed:

$$\underset{T}{\text{Ag-AgCl}},\ \text{LiCl}(m),\ \underset{T+\Delta T}{\text{AgCl-Ag-AgCl}},\ \text{R}_4\text{NCl}(m),\ \underset{T}{\text{AgCl-Ag}} \tag{1}$$

where R_4NCl represents a symmetric tetraalkylammonium chloride of the same concentration, *m*, as that of lithium chloride. Lithium chloride was chosen here as a reference substance because it shows a very slight Soret effect. From the measured initial thermoelectric power, $(\mathrm{d}E/\mathrm{d}T)_0$, of the cell (1), the Soret coefficient, σ, of R_4NCl can be calculated by means of the following equation:[2)]

$$\sigma^{\text{QCl}} = \frac{t_{\text{Li}^+}^{\text{LiCl}} B^{\text{LiCl}}}{t_{\text{Q}^+}^{\text{QCl}} B^{\text{QCl}}} \sigma^{\text{LiCl}} - \frac{F(\mathrm{d}E/\mathrm{d}T)_0}{2RTt_{\text{Q}^+}^{\text{QCl}} B^{\text{QCl}}} - \frac{\bar{\bar{S}}_{\text{Cl}^-}^{\text{QCl}} - \bar{\bar{S}}_{\text{Cl}^-}^{\text{LiCl}}}{2RTt_{\text{Q}^+}^{\text{QCl}} B^{\text{QCl}}} \tag{2}$$

where Q stands for R_4N, where σ's are the Soret coefficients, where *t*'s are the ionic transport numbers for the ions indicated by the subscripts corresponding to the solution phases indicated by the superscripts, where *F* is the Faraday constant, where *T* is the absolute temperature, and where the *B*'s are defined by:

$$B^{\text{LiCl}} = (1 + \mathrm{d}\ \ln\gamma_{\pm}{}^{\text{LiCl}}/\mathrm{d}\ln m)_{T,P}$$

$$B^{\text{QCl}} = (1 + \mathrm{d}\ \ln\gamma_{\pm}{}^{\text{QCl}}/\mathrm{d}\ln m)_{T,P}$$

where the $\gamma_{\pm}$'s are the mean activity coefficients on the molality scale in an *m* molal solution and where the $\bar{\bar{S}}_{\text{Cl}^-}$'s represent the transported entropies of the chloride ions in the solution phases indicated by the superscripts. In the present work, the third term on the right-hand side of Eq. (2) was omitted in the practical calculation because this contribution is negligible in the present experimental accuracy.

Experimental

Materials. The symmetrical tetraalkylammonium chlorides, R_4NCl (R: Me=CH_3, Et=C_2H_5, *n*-Pr=*n*-C_3H_7, *n*-Bu=*n*-C_4H_9, and *n*-Am=*n*-C_5H_{11}), were of the C. P. grade, while the lithium chloride was of a Guaranteed Reagent grade obtained from Wako Pure Chemical Industry, Ltd. All the solutions were prepared to a concentration of 0.01 M ± 0.3% using conductivity water.

Silver Chloride Electrodes. Two ways of preparation were tried: (a) the chlorination of the silver electrode by electrolysis and (b) a modification of Haase's process of thermal decomposition.[3)] These two processes were found to give practically the same electrochemical stability, and so both were used conveniently. The practice of these processes was as follows: (a) the silver-plated surface of a silver electrode (10×10 mm² in area) was converted into silver chloride by anodic electrolysis in 1 N hydrochloric acid under a current of 15—20 mA for about 5 min, washed with water, and dried in the open air. After it had been heated in an electric furnace at about 500 °C for 15 min, it was left overnight in the furnace to allow for natural cooling for annealing. (b) A silver electrode, 10×10 mm² in area, the surface of which was coated with a muddy paste of a 4 : 1 mixture of silver oxide and silver chloride in weight, was heated in an electric furnace at about 500 °C for about 15 min and then cooled for a few minutes in the open air. This process of coating the surface with paste and heating was repeated several times, and then finally the electrode was subjected overnight to natural cooling from 600 °C to room temperature for annealing.

Cells and Measurements. An H-type cell was used to make single thermocells of LiCl and R_4NCl. The outside of the H-cell was painted black to keep the silver chloride electrode from the light. The temperature of the cell was controlled by thermostated water in a Dewar vessel as has been described previously;[2)] however, it was changed in a descending way from room temperature (about 25°) down to about 15° in order to minimize the vertical thermal convection of electrolytes in the legs of the H-cell. The temperature near the silver chloride electrode was measured directly by the aid of a mercury thermometer of 0.1 degree divisions which was inserted near the electrode in a leg of the H-cell. The electromotive force of the combined thermocell was measured with a Yokogawa D. C. potentiometer, Type P-7B, using a sensitive Yokogawa electronic galvanometer, Type 2700, as a zero indicator accurately to 0.1 μV.

Results and Discussion

Some typical results are represented in Fig. 1. The initial thermoelectric powers, $(\mathrm{d}E/\mathrm{d}T)_0$, of the combined thermocells were determined by the method of the least squares; they are listed in Table 1. Despite the lower temperature coefficient of the electrode potential of the silver chloride electrode used here, fairly large fluctuations were unexpectedly found in the observed values of $(\mathrm{d}E/\mathrm{d}T)_0$. This may possibiy be caused by a thermal convection occasionally occurring in the electrolyte solutions in the cell. The Soret coefficient of lithium chloride, which was used as a reference in the present work, was assigned to be $-0.01\times10^{-3}\ \mathrm{deg}^{-1}$, a value obtained by adjusting Snowdon and Turner's value[4] of $-0.02\times10^{-3}\ \mathrm{deg}^{-1}$ at 0.01 M and at 25.3 °C to the value at 25 °C. Using this value and our data on $(\mathrm{d}E/\mathrm{d}T)_0$, the relative values of the Soret coefficients, σ^{QCl}, at 25 °C and at 0.01 M were determined by the aid of Eq. (2) taking $\bar{\bar{S}}_{\mathrm{Cl}^-}^{\mathrm{QCl}}=\bar{\bar{S}}_{\mathrm{Cl}^-}^{\mathrm{LiCl}}$; the results are listed in Table 1. Here, the σ-values determined in the present work are found to be rather higher (by about 20%) than our previous results[1] and the value of tetraalkylammonium chloride found by the use of the direct method by Snowdon and Turner.[4] Though the mean temperature is not 25° but 20° in the present work, such a large difference in the σ-values cannot be explained by the difference in mean temperature, because, in many cases, the influence of the mean temperature upon the σ-values of univalent electrolytes at 0.01 M is known to be of an order of magnitude of $0.1\times10^{-3}\ \mathrm{deg}^{-2}$.[5] For the present, it is difficult to judge which of them is proper; however, the results of the present work may be nicely compared with the σ-values of symmetrical tetraalkylammonium bromides, $\mathrm{R_4NBr}$: σ in $10^{-3}\ \mathrm{deg}^{-1}$ are -5.78 for R=Me, -9.65 for R=Et, -13.4 for R=*n*-Pr, -16.3 for R=*n*-Bu, and -18.5 for R=*n*-Am, all of which were previously estimated by one of the present authors[6] from the initial thermoelectric powers[7] of single thermocells of the $\mathrm{HgBr/R_4NBr}$(0.01 M) system at 25 °C. Further, Agar and Turner[5] reported a value of $-9.20\times10^{-3}\ \mathrm{deg}^{-1}$ for $\mathrm{Et_4NCl}$ at 0.01 M and at 25 °C. Upon taking into consideration the fact that the σ-values of the bromides should, accodring to Snowdon and Turner,[4] be higher by only about $0.06\times10^{-3}\ \mathrm{deg}^{-1}$ in absolute value than those of the chlorides at 25° in 0.01 M aqueous solutions of univalent salts, the σ-values found for the symmetrical tetraalkylammonium chlorides in the present work seem likely to be more reasonable.

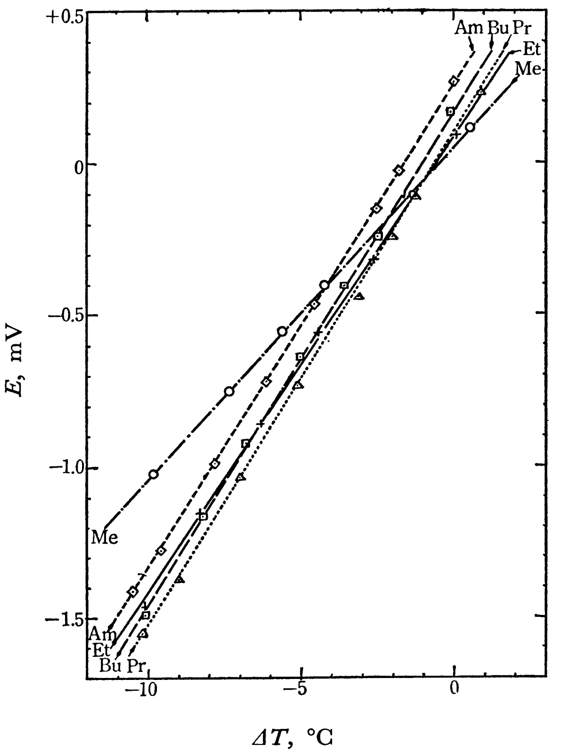

Fig. 1. Plots of emfs of the combined thermocells (1) *vs.* temperature difference, ΔT.

TABLE 1. SORET COEFFICIENTS OF SYMMETRIC TETRAALKYLAMMONIUM CHLORIDES IN WATER AT 25 °C AND AT 0.01 M

Chlorides	t_+	B	$(\mathrm{d}E/\mathrm{d}T)_0$ μV/deg	$10^3\sigma$, deg^{-1}		
				This work	Ref. 4	Ref. 1
LiCl	0.3289[a]	0.969	—	(+0.01)†	+0.01	(0.01)†
$\mathrm{Me_4NCl}$	0.3699[b]	0.941[d]	94.0±4.1	−5.25	—	−5.17
$\mathrm{Et_4NCl}$	0.2996[b]	0.943[d]	146.8±3.8	-10.0_9	−8.38	−8.61
n-$\mathrm{Pr_4NCl}$	0.2350[b]	0.945[d]	160.9±2.7	-14.0_8	—	−10.91
n-$\mathrm{Bu_4NCl}$	0.2004[b]	0.947[d]	161.5±3.7	-16.5_3	—	−13.27
n-$\mathrm{Am_4NCl}$	0.180_0[c]	0.949[c]	160.7±3.2	-18.3_0	—	—

a) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Amsterdam, (1952). b) Calculated from the data on the ionic mobilities at 25 °C, Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 6. Auflage, II. Band, 7. Teil., Elektrische Eigenschaften II, Springer-Verlag, Berlin (1960). c) An extrapolated value. d) Graphical determination from S. Lindenbaum and G. E. Boyd, *J. Phys. Chem.*, **68**, 911 (1964). Values for the concentrations below 0.1 M were estimated by extrapolation.

† A value adopted as a standard for the relative determination of σ.

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