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Soret Coefficients and Heat of Transport of Polyvalent Electrolytes in an Aqueous Solution

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The Soret coefficients of aqueous electrolytes were measured by the conductometric method for salts of K_2SO_4, Na_2SO_4, $ZnSO_4$, and $CdSO_4$ in the concentration range from 0.001 to 0.01 M at 25 °C and 35 °C. The heats of transport were calculated from the Soret coefficients. The concentration dependence of the heat of transport was ascertained to be proportional to the square root of the ionic strength, and the slopes for Na_2SO_4 and K_2SO_4 salts at 25 °C were found to be larger than those reported by Snowdon and Turner. The temperature dependence of the heat of transport was examined based on the data at 25 °C and 35 °C. The heat capacities concerning the transported entropy were found to be negative for the four salts examined.

In the basic construction of irreversible thermodynamics, Onsager's reciprocal relation plays an important role. Its validity has been checked experimentally by several investigators[1)] by studying a diffusion phenomenon of a ternary system. In this phenomenon, a cross effect is due to coupling between diffusion fluxes. The another cross effect was observed in coupling of a heat flux and a diffusion flux. In this case, the concept of the heat of transport was introduced by using Onsager's reciprocal relation. There are several molecular interpretations of the heat of transport concerning the thermal diffusion of an electrolytic aqueous solution. Eastman[2)] interpreted the heat of transport in terms of the interaction between ion and solvent; to his mind, the positive and negative values of the heat of transport were related to structure-forming and structure-breaking ions respectively. On the other hand, Helfand and Kirkwood[3)] interpreted the heat of transport as being due to the interaction between ions; they based their consideration on the non-equilibrium statistical mechanics. They could derive the concentration dependence of the heat of transport as proportional to the square root of the ionic strength. Agar[4)] studied the interaction of the ion-solvent in a hydrodynamical approximation and also derived a similar concentration dependence. In order to unify these molecular interpretations, the data in the heat of transport of an ion in several different solvents may be very useful. The temperature dependence of the heat of transport may also be expected to give important information, because the change in temperature necessarily gives rise to a change in the thermal motion of the solvent. The purposes of the present work are, first, to construct a thermal diffusion cell which can be used for the aqueous and non-aqueous electrolytes; second, to measure the temperature dependence of the heats of transport of several aqueous electrolytes, and finally, to discover some thermodynamical properties useful for the theoretical development of the molecular interpretation of the heat of transport.

Experimental

Apparatus. The arrangement of the cell is shown in Fig. 1. The solution was placed in a central cylindrical hole, 20 mm in inside diameter and 10 mm in height, drilled vertically in a polycarbonate plate. The ends of the hole are tightly covered by caps of platinized copper, which act as electrodes, secured with a small amount of epoxy resin adhesive. These platinized caps were faced to the copper blocks which were used as thermal baths, the temperature of each being maintained constant by circulating water from an external thermostat tank equipped with a mercury regulator. The temperature of each electrode was measured by means of a copper-constantan thermocouple embedded in the central part of the copper electrode. The cell was then filled, emptied, and washed out through a lateral hole, which had been closed by a polycarbonate rod during the measurement. The polycarbonate plate and the copper blocks were joined with four polycarbonate bolts. The total arrangement was especially designed to assure an uniform temperature distribution in the radial direction of a solution. This cell was set in an air thermostat and incorporated into an audio-frequency bridge with a Wagner earth operated between 900–1000 Hz/s. Thereading precision of the bridge was one part in 10^5.

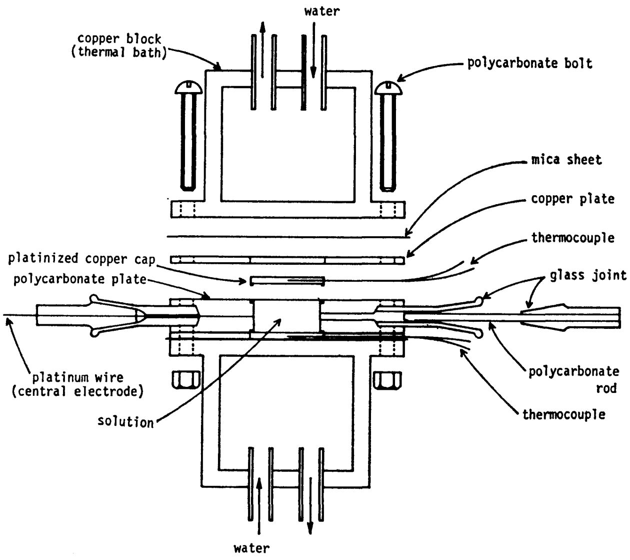

Fig. 1. Description of the cell.

Solution. Commercial extra pure salts were dried and weighed. The solution was prepared using conductivity water(specific resistance> 10^6 Ω cm) purified by means of an ion-exchange resin column. The Na_2SO_4, $CdSO_4$, and $ZnSO_4$ were carefully dried in order to remove the water of crystallization completely.

Measurements. The concentration gradient in a solution induced by a thermal gradient was measured as a resistivity gradient of the solution. When the resistance of the upper part of a solution is R'' and that of the lower part, R', the quantity, Y, was defined by this relation; $Y=(R'-R'')/(R'+R'')$. According to Agar and Turner[5], the Soret coefficient was calculated by means of the following relation;

$$Y_t - Y_0 = (bS\Delta T/4)[1-(32/\pi^3)\exp(-t/\theta)],$$
$$b = -[1+(\partial \ln \Lambda/\partial \ln C)].$$

Here, Y_0 and Y_t represent the initial value of Y and that at time t respectively and S the Soret coefficient; θ is called the relaxation time and is related to the interdiffusion coefficient by this equation; $\theta=a^2/(\pi^2 D)$. a is the height of the cell; D, the interdiffusion coefficient of a solution; Λ, the equivalent conductivity; C, the concentration of the solution, and ΔT, the temperature difference between the upper and lower ends of the solution. The measurements were performed as follows. First, the total cell was inversely set (*i.e.*, the lower-temperature side was upward, and the upper, downward), and the temperature gradient was applied in the solution by circulating water, the temperature of which was kept constant withinin ±0.02 °C, into each thermal bath from the external thermostat tank. This state was held for about 1 hr to insure the stational temperature distribution in the cell. During this inverse setting the concentration gradient induced by ΔT was almost completely destroyed by the strong convective stream in the solution; the concentration of the solution was kept uniform in spite of the application of the temperature gradient. When the measurement was started, the direction of the cell was set normal by turning the cell (*i.e.*, the hot side was now up, and the cold, down); this instance was defined as time zero, t_0, and during the run of the thermal diffusion, Y_t was followed by means of the resistance bridge for a long time. The measurements were performed for the solutions of Na_2SO_4, K_2SO_4, $ZnSO_4$, and $CdSO_4$ in the concentration range from 0.001 to 0.01 M and at mean temperatures of 25 °C and 35 °C; the temperature difference, ΔT, applied across the solution was about 5 °C, which was determined within 0.01 °C for each thermal-diffusion run.

Results

Soret Coefficient. The Soret coefficient was determined from the slope of the curve of Y_t against exp$(-t/\theta)$, which is shown in the case of a 0.005 M solution of K_2SO_4 in Fig. 2. The interdiffusion coefficients, D, necessary for the calculation of the relaxation times, θ, are available in the literature at 25 °C and 35 °C for K_2SO_4[6] and at only 25 °C for Na_2SO_4.[7] Therefore for the analysis for Na_2SO_4 at 35 °C it was assumed that the D_{35}/D_{25} ratio is the same as the ratio for K_2SO_4. For the calculation of θ for $ZnSO_4$ and $CdSO_4$, the integrated interdiffusion coefficients were used; they were measured by the diaphragm-cell method for 0.01 M salt diffusing into water.[8]

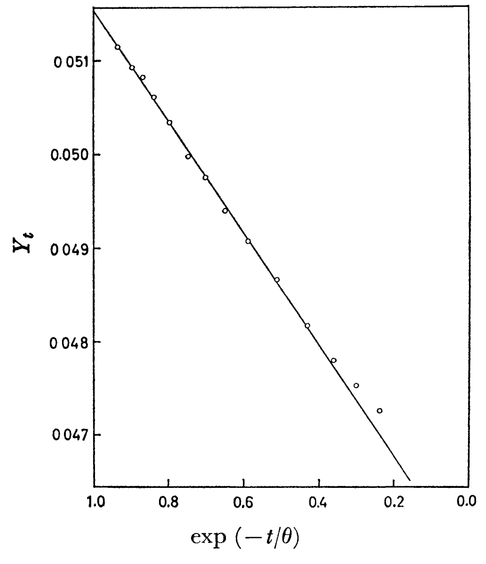

Fig. 2. The experimental plot of Y_t against exp $(-t/\theta)$ for the 0.005 M K_2SO_4 solution at 25 °C.

Table 1. Soret coefficients and heats of transport at 25 °C and 35 °C

Salt	Molality	25 °C $S\times10^3$ (deg^{-1})	 $\hat{Q}$ (kcal/mol)	35 °C $S\times10^3$ (deg^{-1})	 $\hat{Q}$ (kcal/mol)
Na_2SO_4	0.002	6.80	3.32	7.92	4.13
	0.005	6.07	2.87	6.83	3.45
	0.010	5.40	2.44	5.93	2.86
K_2SO_4	0.002	6.29	3.07	6.98	3.64
	0.005	5.33	2.52	6.50	3.28
	0.010	5.04	2.28	5.65	2.73
$ZnSO_4$	0.001	8.54	2.70	10.4	3.69
	0.010	8.30	1.98	9.39	2.40
$CdSO_4$	0.001	10.22	2.98	11.4	3.58
	0.010	8.22	2.12	8.90	2.46

Table 2. Some parameters used for the calculation of Soret coefficients

Salt	Molality	$-b$	$\left(1+\frac{\partial \ln \gamma}{\partial \ln m}\right)$	$D\times10^5$ (cm²/s) 25 °C	 35 °C
Na_2SO_4	0.002	0.951	0.921	1.159	1.508
	0.005	0.936	0.892	1.124	1.462
	0.010	0.926	0.853	1.093	1.422
K_2SO_4	0.002	0.959	0.921	1.406	1.829
	0.005	0.937	0.892	1.398	1.819
	0.010	0.923	0.853	1.369	1.781
$ZnSO_4$	0.001	0.897	0.895	0.789	1.27
	0.010	0.793	0.675	0.789	1.27
$CdSO_4$	0.001	0.875	0.830	0.701	1.26
	0.010	0.805	0.730	0.701	1.26

In some experiments the plot of Y_t against exp$(-t/\theta)$ showed a deviation from linearity at high values of exp$(-t/\theta)$. Since such lack of a linearity resulted from convective mixing,[5] the determination of the Soret coefficient was performed by using the linear relation at lower values of exp$(-t/\theta)$. The Soret coefficients thus obtained are summarized in Table 1, while the data which were necessary for the calculation summarized in Table 2.

Heat of Transport. The heat of transport is defined by irreversible thermodynamics[1] as:

$$\hat{Q} = RT^2(\nu_1+\nu_2)\left(1+\frac{\partial \ln \gamma}{\partial \ln m}\right)S.$$

Here, $\hat{Q}$ stands for the heat of transport; ν_1, and ν_2 the stoichiometric numbers of ions of Species 1 and 2 when the salt is dissociated in a solution; γ, the activity coefficients, and m, the molality. For the calcultaion it is necessary to have the values of $(1+\partial \ln \gamma/\partial \ln m)$, which are available in the literature for all solutions at 25 °C.[9] The data at 25 °C cited in Table 2 were also used for the analysis at 35 °C, because the experimental results show that the temperature dependence of $(\partial \ln \gamma/\partial \ln m)$ is not very large. The obtained heats of transport are summarized in Table 1.

Disscussion

Calculation of the Soret Coefficient. In the present experiment a deviation from linearity was often observed in the plot of Y_t against exp $(-t/\theta)$ in the latter half of the thermal-diffusion run when θ was calculated by using the interdiffusion coefficient data. If θ was adjusted so that the linearity of the plot of Y_t against exp $(-t/\theta)$ held, its value tended to become smaller than that calculated from the isothermal interdiffusion data. Agar and Turner[5] and Sagert and Breck[10] observed similar situations and interpreted them as being due to the convective mixing. Since such convective interference could be considered to be very small in the earlier stage of the thermal diffusion run, where the concentration gradient induced by the temperature gradient has not yet become very large, the initial linear part of the plot of Y_t against exp $(-t/\theta)$ was adopted to calculate the Soret coefficients in Table 1.

The Soret coefficients and the heats of transport of the present three salts of K_2SO_4, Na_2SO_4, and $CdSO_4$ were measured at 25 °C by Snowdon and Turner[11]; their values agree with those of the present work in the range of concentrations near 0.002 M for K_2SO_4 and 0.01 M for Na_2SO_4, but the concentration dependences do not agree with each other (see Figs. 3 and 4). These discrepancies in the concentration dependence of $\hat{Q}$ may result from the unreliable estimation of the convective interference, since we could not determine unambiguously the instant from which the convective mixing began to have appreciable influence on the construction of the concentration gradient. In fact, the Soret coefficient varied in a range of about 5 per cent depending upon the method used to estimate the linearity of the plot of Y_t against exp $(-t/\theta)$. It should be noted, however, that the precision of the reproducibility of the measurement is within 1 per cent. Therefore, the values of the Soret coefficient and the heat of transport summarized in Table 1 may involve an ambiguity of only a few per cent. In the case of the $CdSO_4$ solution, the two sets of data agree with each other, as is shown in Fig. 5. This agreement is significant because the Soret coefficient of the dilute $CdSO_4$ solution obtained by the conductivity method has been ascertained to be smoothly related to that of a higher concentration measured by a optical method.[11)]

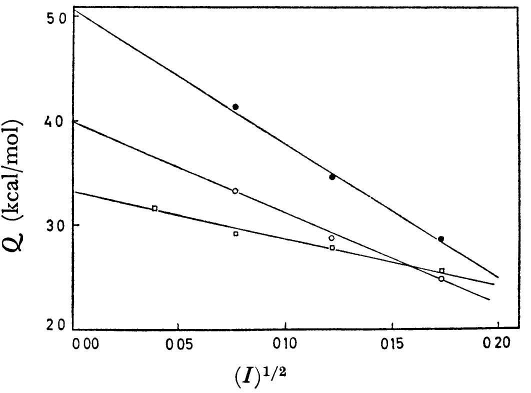

Fig. 3. The concentration dependence of the heat of transport of Na_2SO_4 solution at 25 °C and 35 °C. The open and filled circles represent the present work at 25 °C and 35 °C, respectively. The rectangles stand for the data of Snowdon and Turner at 25 °C.

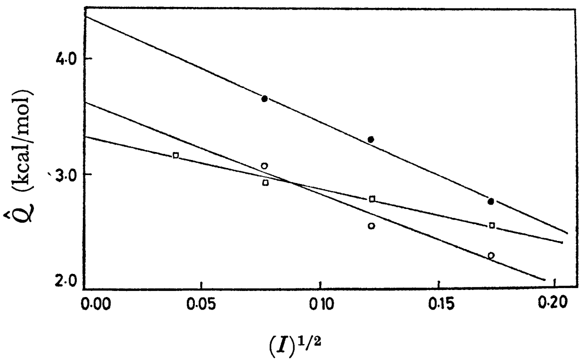

Fig. 4. The concentration dependence of the heat of transport of K_2SO_4 solution at 25 °C and 35 °C. The open and filled circles represent the present work at 25 °C and 35 °C, respectively. The rectangles stand for the data of Snowdon and Turner at 25 °C.

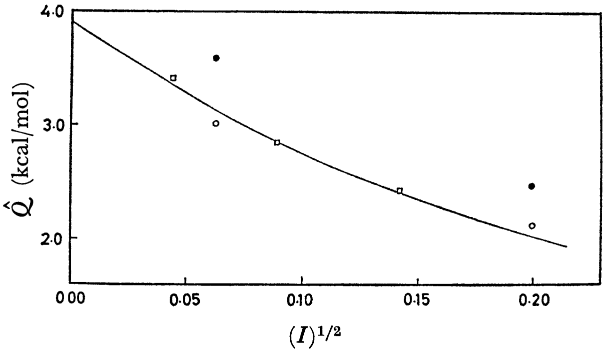

Fig. 5. The concentration dependence of the heat of transport of $CdSO_4$ solution at 25 °C and 35 °C. The open and filled circles represent the present work at 25 °C and 35 °C, respectively. The rectangles stand for the data of Snowdon and Turner at 25 °C.

Concentration Dependence of $\hat{Q}$. Agar[4] developed Eastman's idea of the molecular interpretation of $\hat{Q}$ and derived the concentration dependence of $\hat{Q}$ as proportional to the square root of the ionic strength. He could calculate the slope of the concentration dependence of $\hat{Q}$ at 25 °C in the dilute range for the 1 : 2 electrolyte as;

$$\hat{Q}_0 - \hat{Q} \approx 7500\sqrt{I}.$$

where $\hat{Q}_0$ is the value of $\hat{Q}$ at an infinite dilution, and I, the ionic strength.[4] The present results for the two alkali sulfates indicate that the $\hat{Q}_0 - \hat{Q}$ varies from about $800\sqrt{I}$ for K_2SO_4 to about $900\sqrt{I}$ for Na_2SO_4. The slopes of the present results are larger than those reported by Snowdon and Turner[11] and are rather nearer to the above theoretical results. This agreement, however, must not be overestimated because of the crude approximation of the theory.

Temperature Dependence of $\hat{Q}$. The temperature dependence of $\hat{Q}$ has been studied by Alexander[12] and Agar[4] and some thermodynamical quantities has been defined. The transported entropy, $\bar{\bar{S}}$, was defined as;

$$\bar{\bar{S}} = \hat{S} + s.$$

where $\hat{S}$ stands for the entropy of transport, and s, partial molar entropy. $\hat{S}$ can be related to the heat of transport, $\hat{Q}$, by $\hat{S} = \hat{Q}/T$. The "heat capacities", $\hat{C}$ and $\bar{\bar{C}}$ were also defined as;

$$\hat{C} \equiv T(\partial\hat{S}/\partial T) = (\partial\hat{Q}/\partial T) - (\hat{Q}/T)$$

$$\bar{\bar{C}} \equiv T(\partial\bar{\bar{S}}/\partial T) = C + C_p.$$

where C_p represents the ordinary partial molar heat capacity at a constant pressure. $\bar{\bar{C}}$ can be calculated from the experimental results of the heat of transport at 25 °C and 35 °C. The C_p values for Na_2SO_4 and K_2SO_4 solutions are available in the literature.[13] The C_p values for $ZnSO_4$ and $CdSO_4$ solutions were calculated from the previously reported data of the heat capacity of the solution at 19 °C.[14,15] As the temperature dependence of the C_p of solution is not usually so large, using the data at 19 °C for the present analysis may not produce any significant error. The results are shown for the 0.01 M solution in Table 3, which shows that the values of $\bar{\bar{C}}$ are negative for all the present four salts. This result forms a striking contrast to the cases of many 1 : 1 salts summarized by Agar[4], in which the values of $\bar{\bar{C}}$ are all positive. The fact that the values of $\bar{\bar{C}}$ are positive in the cases of such alkali halides as NaCl and KCl suggests that the negative values of $\bar{\bar{C}}$ for Na_2SO_4 and K_2SO_4 may be attributed to the SO_4^{2-} ion. By summarizing many data, Tyrrell[16] showed that the contribution of the entropy of transport, $\hat{S}$, to the transported entropy, $\bar{\bar{S}}$, is relatively small as compared with the partial molar entropy, s, and that there is a good correlation between the transported entropies and the conventional partial molar standard ionic entropy except for the cases of H^+, OH^-, and SO_4^{2-}, which have larger transported entropies in spite of their small values of s relative to other cations and anions.

TABLE 3. "HEAT CAPACITIES", $\hat{C}$, C_p AND $\bar{\bar{C}}$ (cal/mol·K) FOR 0.01 M SOLUTION AT 25 °C

Salt	$\hat{C}$	C_p	$\bar{\bar{C}}$
Na_2SO_4	34.8	−42.2	−7.4
K_2SO_4	37.0	−54.7	−17.7
$ZnSO_4$	33.3	−55	−22
$CdSO_4$	36.8	−61	−24

These two exceptional aspects of the behavior of SO_4^{2-} ion may be explained in terms of the interaction between ion and solvent. The theory by Helfand and Kirkwood based on the non-equilibrium statistical mechanics may be so rigorous that it is difficult to include such a solvation effect of an ion in the theory. On the other hand, the interpretation originated by Eastman and developed by Agar, while it is phenomenological and less rigorous from the viewpoint of non-equilibrium statistical mechanics, yet has the merit of giving a simple insight into the physical significance of the approximation involved in the theory. Consequently, it would be better to examine the ion-ion contribution to the heat of transport as rigorously as possible by the theory of Helfand and Kirkwood, and to discuss the interaction between ion and solvent by the theory based on Eastman's idea: the heat of transport must be considered as a sum of those contributions.

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