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The Soret Effect in Dilute Aqueous Alkaline Earth and Nickel Chloride Solutions at 25°C[1]

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The Soret effect in dilute aqueous solutions of alkaline earth and nickel chlorides at 25°C has been investigated by the potentiometric method. The molar entropies of transport have been obtained from the measurements of the initial (homoheneous) and final (Soret steady-state) thermoelectric powers. The Soret coefficients at 0.005 *M* (molarity) have been calculated. The variation of the conventional ionic entropies of transport with the ionic radii is investigated and its possible implications for ionic hydration phenomena are discussed.

KEY WORDS: aqueous solutions; alkaline earth chlorides; heat of transport and ion hydration; nickel chloride; Soret effect; thermal diffusion.

1. INTRODUCTION

The Soret effect, which is due to the coupling of heat and material transports, is commonly observed as thermal diffusion. The existence of a temperature gradient in a solution gives rise to the process of thermal diffusion, whereby the concentration, initially homogeneous, becomes nonuniform with the concentration of the solute, usually increasing in the colder regions. As this separation proceeds, however, an opposing process of ordinary diffusion develops, which eventually exactly balances the thermal diffusion process, and the system reaches a steady state referred to as the Soret steady state.

In an electrolyte solution, the condition of zero current during diffusion imposes a restriction on the velocities of ions, which in general will be satisfied only if the effect of the temperature gradient is supplemented by

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an electrical potential gradient. Thus, for an electrochemical cell at nonuniform temperatures (a thermocell), this coupling of the thermal and diffusion forces contributes to the e.m.f. of the cell, known as the thermal e.m.f. Consequently, measurement of the thermal e.m.f. (or the thermoelectric power) constitutes an effective method to investigate the Soret effect in electrolyte solutions.

The magnitude of the Soret effect may be expressed by the Soret coefficient, defined by

$$\sigma = -[\text{grad} \ln (m)/\text{grad}\, T]_{\text{st}} \tag{1}$$

where m is the molality of the solute and the subscript (st) means that the gradient of $\ln(m)$ refers to the Soret steady state. Eastman [1], based on a thermodynamic analysis, has shown that σ is related to the heat of transport Q^*. For 1 mol of an electrolyte which dissociates into v_+ and v_- moles of cation and anion, respectively, the molar heat of transport Q^*_{+-} is related to the Soret coefficient by the equation

$$\begin{aligned} Q^*_{+-} &= (v_+ + v_-)\, RT^2[1 + (d \ln \gamma_\pm)/(d \ln m)]_{T,P}\, \sigma \\ &= v_+ Q^*_+ + v_- Q^*_- \end{aligned} \tag{2}$$

where $\gamma_\pm$ is the mean activity coefficient and Q^*_i is the ionic heat of transport.

The result obtained in Eq. (2) may be derived from Onsager nonequilibrium thermodynamics [2]. Although a temperature gradient must be applied in a thermal diffusion experiment, the heat of transport is an isothermal quantity (as a consequence of the Onsager reciprocal relation), so that the entropy of transport $S^*(=Q^*/T)$ may be derived from thermocell studies. A comprehensive discussion of thermocells based on nonequilibrium thermodynamics has been given by Agar [3].

It is the purpose of this paper to report the results for the molar entropies of transport of $MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$, and $NiCl_2$ obtained from the measurements of the thermoelectric powers of the silver, silver-chloride thermocell. Our results have been compared with data which exist in the literature. The concentration dependence of the molar entropy of transport has been investigated. Finally, we have exploited the concept that the entropy of transport is an "extra" entropy due to diffusion and discuss our results in terms of ion hydration phenomena.

2. EXPERIMENTAL

With the exception of $MgCl_2$, all chlorides were Aldrich gold-label ultrapure-grade chemicals. $MgCl_2$ was Baker analyzed reagent grade. They were used without further purification. Stock solutions were prepared from conductivity water and by weighing. The concentrations of the solution was further checked by precipitation as AgCl. Solutions for measurements were prepared by successive dilutions.

The silver, silver-chloride thermocell may be represented schematically as

$$\begin{array}{c}\text{Terminal—Ag/AgCl/electrolytes } (M)\text{/AgCl/Ag—terminal}\\ T \qquad\qquad\qquad\qquad T+\Delta T\end{array}$$

The cell we used is of the sandwich type, where the solutions are confined between the two silver, silver-chloride disks with a cell length (the distance between the electrodes) of approximately 0.35 cm. A typical run begins with a measurement of the residual e.m.f. (0–50 μV) for background correction by setting $\Delta T = 0$. When this is done, the temperature gradient is switched on at time $t = 0$ and the thermal e.m.f. is measured as a function of time using an HP-3456A digital voltmeter and an HP-3497A data acquisition unit interfaced to an HP-85 computer. Each measurement requires less than 0.01 s and the thermal e.m.f. is measured to 0.1 μV. Experimental details may be found in the papers by Lin *et al.* [4] and Yow and Lin [5].

The phenomenology of the approach to the steady state may be expressed as [6]

$$(E_{\mathrm{st}} - E_{\mathrm{t}}) = (E_{\mathrm{st}} - E_0)(8/\pi^2) \sum (1/n^2) \exp[-n^2(t - t^*)/\phi] \tag{3}$$

where the summation is over $n = 1, 3, \ldots$, E_{t} is the thermal e.m.f. at time t, t^* is the warming up correction [7], and ϕ is the thermal diffusion characteristic time. ϕ is given by $a^2/(\pi^2 D)$, where a is the cell length and D is the diffusion coefficient. Denoting K as the thermal diffusivity of the liquid and τ as the warming-up characteristic time, $t^* = \tau - (a^2/12K)$. E_{t} measured may be fitted to Eq. (3) to obtain E_0 and E_{st}. This is also discussed by Lin *et al.* [4].

The molar entropies of transport may be derived from the thermoelectric powers ($\varepsilon = dE/dT$). According to Agar, for a 1:2 electrolyte

$$\begin{aligned} F\varepsilon_{\mathrm{st}} &= \bar{\bar{S}}_{\mathrm{Cl}^-} - S_{\mathrm{AgCl}} + S_{\mathrm{Ag}} - \bar{\bar{S}}_{\mathrm{e}} \\ F(\varepsilon_{\mathrm{st}} - \varepsilon_0) &= t_+(S^*_- + S^*_+/2) = t_+ S^*_{+-}/2 \end{aligned} \tag{4}$$

where F is the Faraday constant and t_+ is the cation transport number. $\bar{\bar{S}}_i$ is the transported entropy. It is also known as the entropy of the moving ion. This is because as a result of the Onsager reciprocity relation, the entropy flux J_s in the system may be expressed in terms of the diffusion fluxes J_i as

$$J_s = \sum_i J_i \bar{\bar{S}}_i \tag{5}$$

at the limiting isothermal state ($\Delta T = 0$). Since

$$S^*_i = \bar{\bar{S}}_i - S_i \tag{6}$$

where S_i is the partial molar entropy of i, the ionic entropy of transport S^*_i clearly is an extra entropy due to diffusion. In Eq. (4), $\bar{\bar{S}}_e$ is the transported entropy of the electron in the metal leads which connect the thermocell to the digital voltmeter. For metals such as Cu and Ag, values of $\bar{\bar{S}}_e$ are available.

3. RESULTS

An example of the observed and calculated E_t are shown in Fig. 1. For $t > \phi/3$, the series in Eq. (3) may be truncated by retaining only the first term without introducing a serious error. Under this approximation, $\ln(E_{st} - E_t)$ varies linearly with t. Values of E_0 and E_{st} may be determined to within $\pm 10\,\mu V$ by fitting E_t to Eq. (3).

Cation transport numbers, which are needed for the calculations of the molar entropies of transport, were taken from Stokes *et al.* [8] for $NiCl_2$,

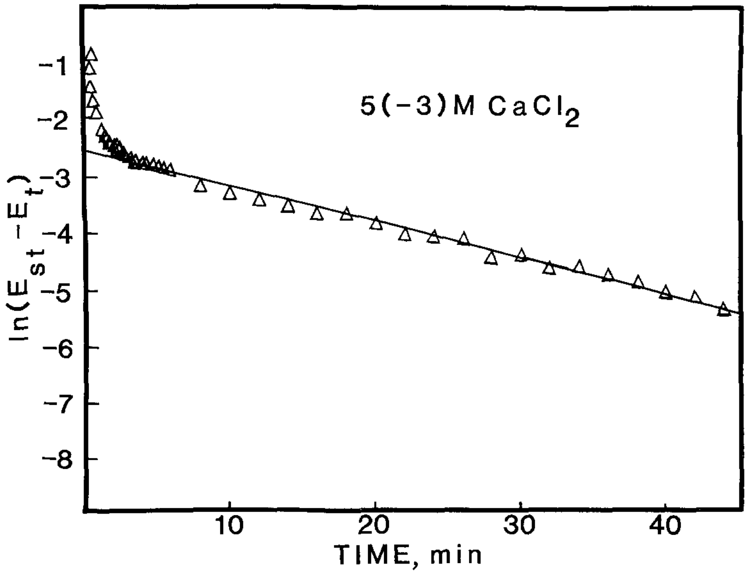

Fig. 1. $\ln(E_{st} - E_t)$ vs time. △, Observed; ——, calculated according to Eq. (3), retaining only the term with $n = 1$.

Miller *et al.* [9] and Lee and Kay [10] for $MgCl_2$, Kennan *et al.* [11] and Longsworth [12] for $CaCl_2$, Lucasse [13] for $SrCl_2$, and Jones and Dole [14] for $BaCl_2$. Results of our measurements along with cation transport numbers are listed in Tables IA and IB. They are plotted against the square root of the ionic strength, $I^{1/2}$, in Figs. 2 and 3. Our results on S^*_{+-} carry an experimental uncertainty of approximately $\pm 5\%$, except for the most dilute solution (5×10^{-4} *M*), where the uncertainty is $\pm 10\%$. The Soret coefficient may be evaluated from Eq. (2) recognizing that $Q^*_{+-} = TS^*_{+-}$. Data are available in the literature for the Soret coefficients at 0.005 *M*. The term related to the activity coefficients has been

Table IA. The Molar Entropies of Transport at 25°C[a]

	Concentration (*M*)					
	5.0×10^{-4}	1.0×10^{-3}	2.0×10^{-3}	2.5×10^{-3}	3.0×10^{-3}	5.0×10^{-3}[b]
$NiCl_2$						
t_+	0.4097	0.4080	0.4059		0.4048	0.4016
ε_0	0.766	0.747	0.691		0.644	0.608
ε_{st}	0.839	0.812	0.750		0.698	0.657
S^*	33.93	30.67	28.03		26.15	23.68
$MgCl_2$						
t_+	0.4115	0.4080		0.3993		0.3955
ε_0	0.825	0.751		0.672		0.617
ε_{st}	0.897	0.810		0.721		0.659
S^*	34.35	28.37		23.64		20.50
$CaCl_2$						
t_+	0.4354	0.4349	0.4335		0.4324	0.4307
ε_0	0.774	0.732	0.679		0.652	0.604
ε_{st}	0.852	0.802	0.746		0.711	0.656
S^*	34.94	30.84	29.92		26.95	23.30
$SrCl_2$						
t^+	0.4323	0.4312		0.4288		0.4262
ε_0	0.759	0.720		0.643		0.594
ε_{st}	0.846	0.802		0.713		0.659
S^*	38.83	36.74		31.67		29.66
$BaCl_2$						
t_+	0.4453	0.4444	0.4431		0.4421	0.4405
ε_0	0.782	0.699	0.643		0.616	0.570
ε_{st}	0.884	0.792	0.730		0.701	0.643
S^*	44.31	40.46	37.70		37.11	32.05

[a] ε's are in $mV \cdot K^{-1}$, and S^*'s are in $J \cdot K^{-1} \cdot mol^{-1}$.

[b] Preliminary results at 0.005 *M* have been reported at the Colston Research Symposium, The University at Bristol, April, 1985.

estimated by Payton and Turner [15] and Ikeda *et al.* [16, 17]. Results obtained in this work are compared with the literature values in Table II. In Table II, results obtained by Payton and Turner [15] and Ikeda and Mita [18] were based on conductimetric measurements. Results due to Ikeda *et al.* were from the combined thermocell method and calculated relative to the Soret effect of 0.01 M LiCl based on the measurements of E_0. It seems clear that Ikeda and Mita's results are generally too low compared with all the other measurements. The agreement between the present results and others seem satisfactory, although in general, our results seem systematically higher.

The ionic entropy of transport may not be measured directly. However, a set of "conventional" ionic entropies of transport may be computed based on the convention that $S^*_{\mathrm{Cl}^-}(0.01\ M) = 0$. Conventional ionic entropies of transport have been plotted versus the ionic radii r_i in Fig. 4.

Table IB. The Molar Entropies of Transport at 25°C

	Concentration (M)						
	7.5×10^{-3}	1.0×10^{-2}	2.0×10^{-2}	2.5×10^{-2}	3.0×10^{-2}	5.0×10^{-2}	7.5×10^{-2}
$NiCl_2$							
t_+		0.3962	0.3897		0.3843	0.3762	
ε_0		0.552	0.503		0.474	0.434	
$\varepsilon_{\mathrm{st}}$		0.593	0.539		0.505	0.459	
S^*		20.04	17.74		16.15	13.22	
$MgCl_2$							
t_+	0.3927	0.3915		0.3812		0.3775	0.3657
ε_0	0.594	0.562		0.489		0.437	0.407
$\varepsilon_{\mathrm{st}}$	0.633	0.600		0.517		0.460	0.426
S^*	20.38	19.08		14.02		11.80	10.13
$CaCl_2$							
t_+		0.4277	0.4225		0.4191	0.4143	
ε_0		0.552	0.492		0.460	0.427	
$\varepsilon_{\mathrm{st}}$		0.598	0.532		0.497	0.457	
S^*		20.92	18.37		16.99	13.68	
$SrCl_2$							
t_+	0.4242	0.4224		0.4148		0.4061	
ε_0	0.564	0.536		0.467		0.414	
$\varepsilon_{\mathrm{st}}$	0.628	0.591		0.517		0.457	
S^*	28.95	28.16		23.01		20.21	
$BaCl_2$							
t_+		0.4375	0.4338		0.4302	0.4253	
ε_0		0.525	0.474		0.451	0.405	
$\varepsilon_{\mathrm{st}}$		0.595	0.533		0.502	0.457	
S^*		31.13	26.53		22.89	23.51	

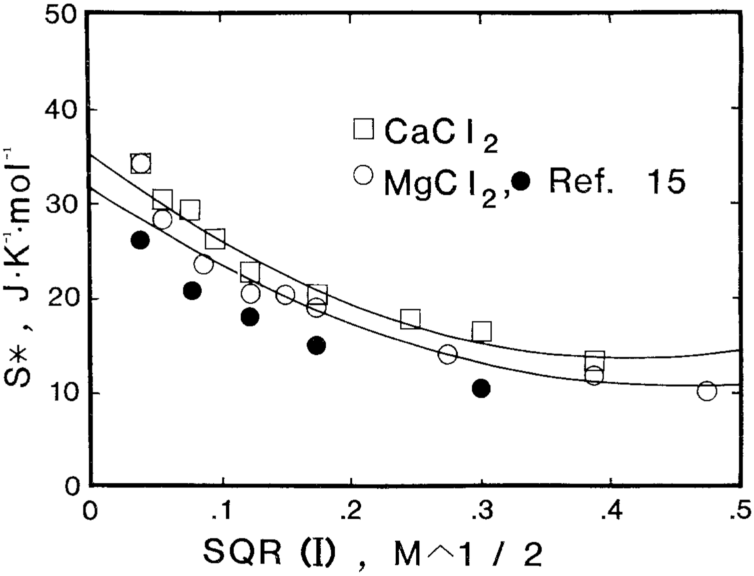

Fig. 2. The molar entropy of transport vs the square root of the ionic strength. $MgCl_2$ (○, present work; ●, Payton and Turner [15]) and $CaCl_2$ (□).

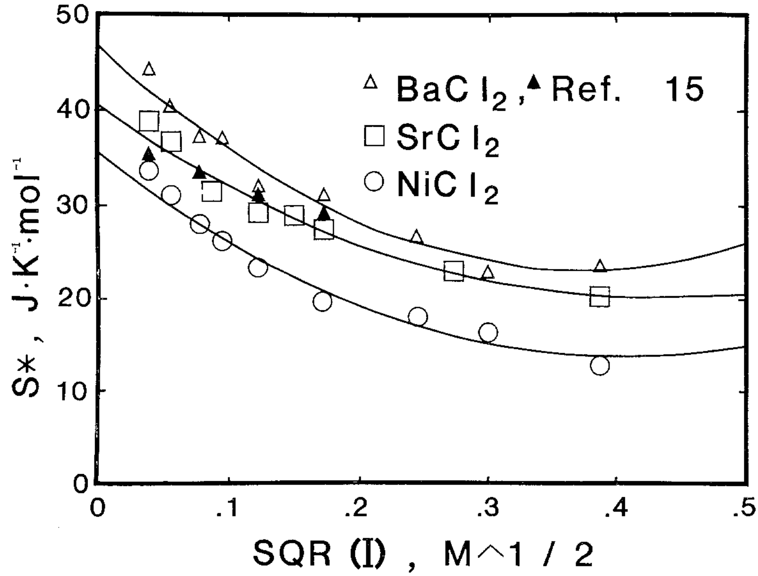

Fig. 3. The molar entropy of transport vs the square root of the ionic strength. $NiCl_2$ (○), $SrCl_2$ (□), and $BaCl_2$ (△, present work; ▲, Payton and Turner [15]).

Table II. The Molar Entropy of Transport and Soret Coefficient at 0.005 M and 25°C[a]

	S^*_{+-} ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)					$\sigma \times 10^3$ ($\mathrm{K^{-1}}$)				
	A	B	C	D	E	A	B	C	D	E
$MgCl_2$	19.6	18.79	18.79		13.01	2.86	2.80	2.79		1.90
$CaCl_2$	23.30	21.30	23.18		16.07	3.45	3.14	3.43		2.38
$SrCl_2$	29.66	26.78	27.91		22.76	4.35	3.99	4.09		3.34
$BaCl_2$	32.05	31.17	31.55		28.12	4.81	4.65	4.73		4.22
$NiCl_2$	21.59			19.79		3.20			2.67	

[a] (A) This work; (B) Ref. 15; (C) Ref. 16; (D) Ref. 17; (E) Ref. 18.

4. DISCUSSION

The molar entropies of transport have been extrapolated to infinite dilution to obtain the standard molar entropies of transport S^{*0}_{+-}. The limiting concentration dependence of the molar entropy of transport of electrolyte solutions has been discussed by several authors [19]. The limiting slope consists of two terms: a direct ion–ion electrostatic term and an electrophoretic term. There is agreement that the limiting slope for the

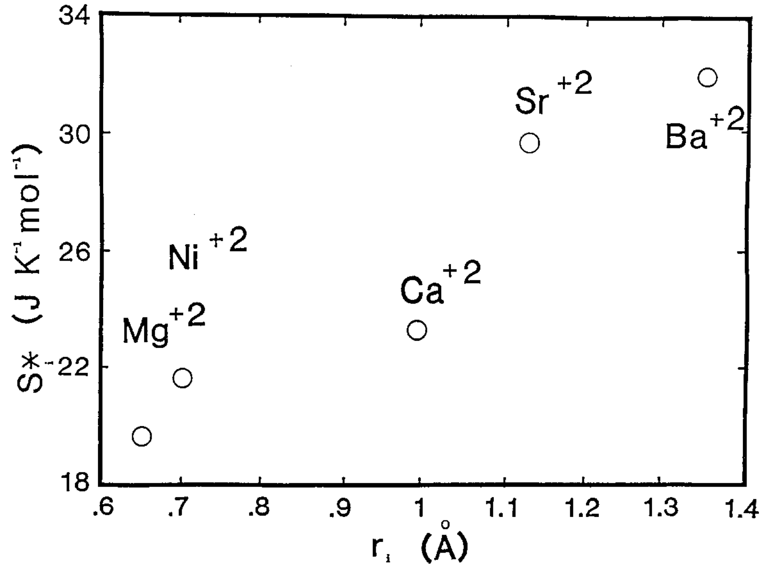

Fig. 4. The conventional ionic entropies of transport vs the ionic radii.

ion–ion term is $-18.0Z_i^2$, where Z_i is the ionic valence. The electrophoretic limiting slope depends on the difference of the Stokes law radii of the cation and anion and must be estimated. Following Agar [3], the limiting law expression for 1:2 electrolytes may be written as

$$\begin{aligned} S^*_{+-} &= S^{*0}_{+-} + AI^{\frac{1}{2}} \\ &= S^{*0}_{+-} + (-108.0 + B)\, I^{\frac{1}{2}} \end{aligned} \tag{7}$$

where B is the electrophoretic limiting slope and is given by

$$B = 0.329(v_+ v_- / v_+ + v_-)(r^S_+ - r^S_-)(S^{*0}_+ - S^{*0}_-) \tag{8}$$

In Eq. (8) r^S_i is the Stokes law radius and S^{*0}_i is the standard ionic entropy of transport. To calculate B, we estimate S^{*0}_+ assuming $S^{*0}_{Cl^-} = 0.84\ J \cdot K^{-1} \cdot mol^{-1}$ [20]. Table III lists the values of A and B based on S^{*0}_{+-} obtained in Figs. 2 and 3. In extrapolating the molar entropies of transport, we have assumed that S^*_{+-} may be expressed as $S^*_{+-} = S^{*0}_{+-} + \alpha I^{\frac{1}{2}} + \beta I$ and fitted our experimental results (excluding the results of the most dilute solution, since they carry an unusually large uncertainty) accordingly (smooth curves in the figures). The slope α obtained is also listed in Table III. With the exception of $BaCl_2$, the agreement between α and A is quite satisfactory overall. Values of $S^*_{MgCl_2}$ and $S^*_{BaCl_2}$ obtained by Payton and Turner [15] have also been plotted in Figs. 2 and 3, respectively, for comparison. It is interesting to note that the concentration dependence of $S^*_{MgCl_2}$ observed by Payton and Turner agrees quite well with our results, although such is not the case for $BaCl_2$.

Since the ionic entropy of transport may be regarded as an "extra" entropy due to diffusion, values of S^*_i may be expected to reveal

Table III. The Limiting Slope[a]

	r^s_i	$\Delta r^s_i{}^b$	$S^{*0}_{MCl_2}$	$\Delta S^{*0}_i{}^c$	B^d	A^e	α
$MgCl_2$	3.46	2.26	33.9	31.4	15.5	−92.5	−93.3
$NiCl_2$	3.46	2.26	35.1	32.6	16.3	−91.6	−105.9
$CaCl_2$	3.09	1.89	36.8	34.3	14.2	−94.1	−106.3
$SrCl_2$	3.09	1.89	41.0	38.5	15.9	−92.0	−93.3
$BaCl_2$	2.88	1.68	45.6	43.1	15.9	−92.0	−126.8

[a] Units for S^{*0}'s are $J \cdot K^{-1} \cdot mol^{-1}$, and r^s_i's are Å.

[b] $\Delta r^s_i = r^s_{M^{2+}} - r^s_{Cl^-}$, $r^s_{Cl^-} = 1.2$ Å.

[c] $\Delta S^{*0}_i = S^{*0}_{M^{2+}} - S^{*0}_{Cl^-}$.

[d] $B = 0.219(r^s_{M^{2+}} - r^s_{Cl^-})(S^{*0}_{M^{2+}} - S^{*0}_{Cl^-})$; see Eq. (8).

[e] $A = -108.0 + B$; see Eq. (7).

order–disorder experienced by the ions during diffusions. In this connection it is interesting to note that Yow and Lin [5] and Chakraborty and Lin [21] have considered the size and structure effects of the entropy of transport and concluded that the Soret data may be useful in the discussion of ionic hydration phenomena. An interesting example is the Li^+ ion. The conventional ionic entropy of transport of Li^+ is $-0.04\ J \cdot K^{-1} \cdot mol^{-1}$ at 0.01 *M*, the least among the alkali metal ions. Because the structure-breaking effect and disorder contribute negatively to the entropy of transport, the Soret data indicate that Li^+ ion is the least structure maker among all the alkali metal cations. This is interesting and may be explained in terms of the results of recent neutron scattering experiments. Based on high-resolution quasi-elastic neutron scattering experiments, Hewish *et al.* [22] have demonstrated unambiguously the existence of a second zone of water molecules weakly interacting around ions such as Ni^{2+} and Mg^{2+}. The water molecules in the second zone exchange with water molecules in the bulk slowly and the system is a "slow-exchange" system as compared to ions such as Ca^{2+} and Li^+, which are in the "fast-exchange" limit. For the Li^+ ion, therefore, fast exchange of water molecules creates disorder. Consequently, the conventional ionic entropy of transport of Li^+ is small compared to that of the other alkali metal ions.

For the bivalent metal ions studied in this work, the variation of the conventional ionic entropies of transport with ionic radii is shown in Fig. 4. It is interesting to note that the value of $S^*_{Ni^{2+}}$ is slightly larger than that of $S^*_{Mg^{2+}}$. Both ions are slow-exchange systems so that the difference in the values of the conventional ionic entropies of transport may reflect a slight increase in the ionic radii going from Mg^{2+} to Ni^{2+}. The situation is quite different between Ni^{2+} and Ca^{2+}, where $S^*_{Ni^{2+}} \approx S^*_{Ca^{2+}}$ in spite of the fact that the value of r_i for Ca^{2+} is approximately 50% larger than that of Ni^{2+}. This may appear somewhat exceptional in view of the general trend observed in Fig. 4. However, Ca^{2+} is in the fast-exchange limit and the disorder due to the fast exchange of water molecules may possibly have a large negative contribution to the ionic entropy of transport of Ca^{2+}.

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