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The Concentration Dependence of the Apparent Molal Adiabatic Compressibility of Electrolytes in Water

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The apparent molal adiabatic compressibilities of NaCl, KCl, NaBr, and KBr in water have been measured in the concentration range from 0.01 to 1 mol kg^{-1} at 5, 25, and 45 °C. The results have been fitted to a Redlich-type equation: $\phi_{Ks}=\phi^\circ_{Ks}+S_{Ks}c^{1/2}+B_{Ks}c$. The limiting slope, S_{Ks}, was found experimentally as 5.6×10^{-4} at an ordinary temperature. Convenient equations for the conversion of adiabatic to isothermal compressibilities have been derived; the limiting slope for isothermal compressibility, S_{KT}, should be larger than S_{Ks} at all the temperatures studied. The value of S_{Ks} determined experimentally has been compared with that predicted from the S_{KT} values calculated by Mathieson and Conway, by Millero, and by Bradley and Pitzer.

In earlier papers,[1] we have shown that the effects of polar groups on the hydrophobic hydration play an important role in the volumetric behavior of aqueous organic electrolyte solutions. Compressibility study is of great use in obtaining further information concerning the structural effects. For dilute nonelectrolyte solutions, the limiting partial molal adiabatic compressibility, $\bar{K}^\circ_s(=\phi^\circ_{Ks})$, can readily be determined from a linear plot of the apparent molal adiabatic compressibility, ϕ_{Ks}, against the molal concentration;[2] on the contrary, the reliable estimation of $\bar{K}^\circ_s$ of electrolytes may be difficult for reasons to be described below.

In dilute solutions, the apparent molal quantities of electrolytes are usually fitted to a Redlich-type equation in terms of molarity, c:

$$\phi_X = \phi^\circ_X + S_X c^{1/2} + B_X c, \tag{1}$$

where ϕ°_X is the limiting apparent (partial) molal quantity, S_X is the theoretical slope given by the limiting Debye-Hückel law, and B_X is a deviation constant. The values of ϕ°_X and B_X can be determined from a linear plot of $(\phi_X - S_X c^{1/2})$ against c. For the apparent molal adiabatic compressibility, unfortunately such a linear plot cannot be obtained because the limiting slope, S_{Ks}, has not yet been calculated. Mathieson and Conway[3] measured the ϕ_{Ks} values of various electrolytes in a very low concentration range and represented its concentration dependence by this simple limiting-law equation:

$$\phi_{Ks} = \phi^\circ_{Ks} + S_{Ks} m^{1/2}. \tag{2}$$

This extrapolation procedure, however, may be disadvantageous, since Eq. 2 holds only in highly dilute solutions (where the $B_{Ks}c$ term in Eq. 1 should be negligible) and the error in ϕ_{Ks} is progressively increased with a decrease in the concentration.

In our opinion, a more reliable evaluation of ϕ°_{Ks} would be based on Eq. 1; therefore, it is necessary to estimate the limiting slope, S_{Ks}. In a preliminary study,[4] we derived a simple relation for the conversion of the limiting slope for isothermal compressibility, S_{KT}, to S_{Ks} and showed that S_{KT} is larger by about 10% than S_{Ks} at 25 °C. In the present paper, we wish to report on our measurements of the adiabatic compressibility of NaCl, KCl, NaBr, and KBr solutions at 5, 25, and 45 °C and compare the experimental with the theoretical S_{Ks} values in order to obtain a reasonable value of the limiting slope.

Experimental

All the salts used were of a "Merck Ultra Pure" grade and were dried at 50 °C *in vacuo*. All the solutions were prepared in molalities with doubly distilled water.

The ultrasonic velocities, v cm s^{-1}, in solutions were measured at 5, 25, and 45 °C using a "sing-around" velocimeter which is capable of a precision of 1 cm s^{-1}. The details of the apparatus and procedure have been reported elsewhere.[2] The densities, d g ml^{-1}, of the solutions were determined at 5 and 45 °C with a float densimeter described previously.[5,6]

The adiabatic compressibility, β_s bar^{-1}, and the apparent molal adiabatic compressibility, ϕ_{Ks} ml mol^{-1} bar^{-1}, are given by:

$$\beta_s = 10^6/v^2 d, \tag{3}$$

$$\phi_{Ks} = 10^3(\beta_s - \beta_{s0})/c + \beta_{s0}\phi_V, \tag{4}$$

where ϕ_V ml mol^{-1} is the apparent molal volume related to the solution density and the solute molecular weight, M_2, by

$$\phi_V = 10^3(d_0 - d)/d_0 c + M_2/d_0. \tag{5}$$

Here, the subscript zero refers to pure water. The density and sound-velocity data for water were taken from Kell[7] and from Del Grosso and Mader[8] respectively.

Results and Discussion

The sound velocities in aqueous NaCl, KCl, NaBr, and KBr solutions were measured relative to pure water at 5, 25, and 45 °C from 0.01 to 1 mol kg^{-1}. The results are given in Table 1,[9] along with the calculated ϕ_{Ks} values.

In dilute solutions, the concentration dependence of ϕ_V is represented by the Redlich-type equation 1:[10]

$$\phi_V = \phi^\circ_V + S_V c^{1/2} + B_V c. \tag{6}$$

The values of ϕ°_V and B_V obtained at 5 and 45 °C are summarized in Table 2, along with the values derived by Desnoyers *et al.*[11] at 25 °C. The ϕ°_V values obtained here were in good agreement with the literature values, and the accuracy of the data was confirmed by the additivity principle.[10] The additivity was within ±0.05 ml mol^{-1} units. On the other hand, the agreement between the B_V values obtained here and the literature values was less satisfactory, especially at 45 °C.

Table 2. Limiting apparent molal volumes and deviation constants of alkali halides in water at 5, 25, and 45 °C

	ϕ°_V/ml mol^{-1}			B_V/l ml mol^{-2}		
	5 °C	25 °C[a)]	45 °C	5 °C	25 °C[a)]	45 °C
NaCl	14.09	16.62	17.64	0.76	−0.03	−0.74
KCl	24.67	26.87	27.59	0.82	0.10	−0.61
NaBr	20.58	23.48	24.83	0.64	−0.26	−1.64
KBr	31.07	33.73	34.72	0.74	−0.16	−1.34

a) Ref. 11.

Error in ϕ_{Ks}. The accuracy of ϕ_{Ks} depends on the precision of the determination of the density, the sound velocity, and the concentration. In this study, the apparent molal volume, and hence the density, of each solution used for the sound-velocity measurement were evaluated from Eqs. 5 and 6, where a succesive approximation method was applied to the conversion of the molality to molarity. In view of the accuracies of the ϕ°_V and B_V data mentioned above, it seems that the uncertainty in d or ϕ_V may be small, but it *increases* as the concentration is *increased.*

Now, neglecting the density errors and differentiating Eqs. 3 and 4, the uncertainty in ϕ_{Ks} caused by uncertainties in the sound velocity and concentration, δv and δc, is given by:

$$\delta\phi_{Ks} = \frac{2\times 10^3\beta_s}{c}\left(\frac{\delta v}{v}\right) + \frac{10^3(\beta_{s0}-\beta_s)}{c}\left(\frac{\delta c}{c}\right). \quad (7)$$

The absolute error in determining the sound velocity is $\delta v = \pm 1$ cm s^{-1}; hence, the relative error is $(\delta v/v) = \pm 6.6\times 10^{-6}$. The uncertainty due to the sound-velocity error rapidly decreases with an increase in the concentration, whereas the uncertainty due to the concentration error is approximately constant. The scatter of ϕ_{Ks} values at higher concentrations observed in Fig. 1 is, therefore, mainly due to the concentration error. We estimated the uncertainty in the concentration determination to be within 0.1%, *i.e.*, $(\delta c/c) = 10^{-3}$. Thus, the total error in ϕ_{Ks} is:

$$\delta\phi_{Ks} = \frac{1}{c}\{1.33\times 10^{-2}\beta_s + (\beta_{s0}-\beta_s)\}. \quad (8)$$

Experimental Estimation of S_{Ks}. A typical example of the plot of ϕ_{Ks} against $c^{1/2}$ is shown in Fig. 1, from which it is apparent that the simple limiting-law equation 2 does not hold in the concentration range studied. Alternatively, our ϕ_{Ks} data should be represented by Eq. 1. Thus,

$$\phi_{Ks} = \phi^\circ_{Ks} + S_{Ks}c^{1/2} + B_{Ks}c. \quad (9)$$

Taking into account the large error in ϕ_{Ks} at lower concentrations, the estimation of three parameters was based on the relationship between β_s and c instead of on the ϕ_{Ks} *vs.* $c^{1/2}$ plot. The combination of Eqs. 4, 6, and 9 leads to an expression with this form:

$$10^3(\beta_s-\beta_{s0}) = (\phi^\circ_{Ks}-\beta_{s0}\phi^\circ_V)c + (S_{Ks}-\beta_{s0}S_V)c^{3/2} + (B_{Ks}-\beta_{s0}B_V)c^2. \quad (10)$$

The parameters, ϕ°_{Ks}, S_{Ks}, and B_{Ks}, were calculated by the least-squares method and are given in Table 3.

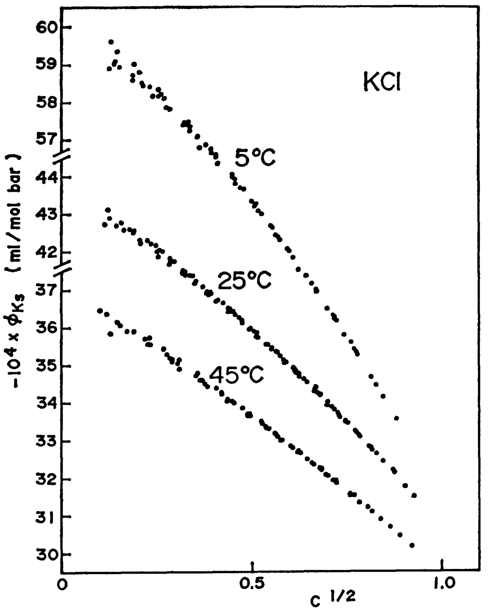


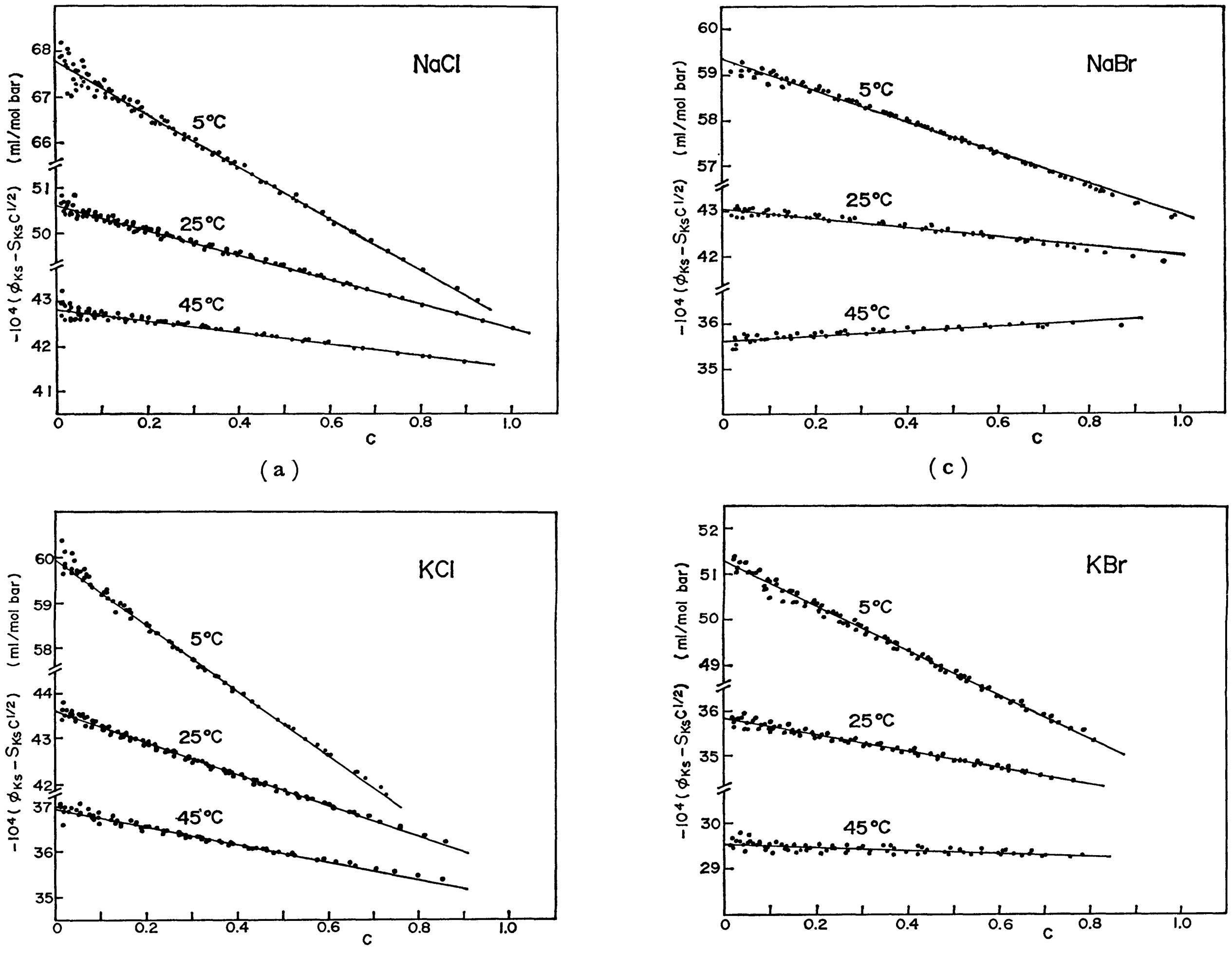
Fig. 1. ϕ_{Ks} as a function of $c^{1/2}$ for KCl in water at 5, 25, and 45 °C.

Table 3. Parameters of Eq. 9 determined by using Eq. 10 for salt concentrations less than 0.5 mol dm^{-3}

	$-10^4\phi^\circ_{Ks}$	10^4S_{Ks}	10^4B_{Ks}
		5 °C	
NaCl	67.67(67.91)[a)]	5.12(6.10)[a)]	6.28(5.33)[a)]
KCl	60.25(60.45)	6.72(7.66)	6.34(5.34)
NaBr	59.00(59.24)	4.15(5.05)	4.78(3.99)
KBr	51.30(51.36)	5.75(6.01)	4.73(4.49)
av.		5.43(6.20)	
		25 °C	
NaCl	50.63(50.59)	5.75(5.53)	2.50(2.77)
KCl	43.74(43.82)	6.16(6.50)	3.00(2.64)
NaBr	42.91(42.81)	4.96(4.54)	1.65(2.06)
KBr	35.87(35.79)	5.85(5.53)	1.52(1.85)
av.		5.68(5.52)	
		45 °C	
NaCl	42.71(42.74)	5.16(5.29)	1.67(1.54)
KCl	37.10(37.14)	6.30(6.50)	1.31(1.11)
NaBr	35.53(35.46)	5.08(4.78)	0.01(0.29)
KBr	29.63(29.52)	6.11(5.61)	−0.20(0.28)
av.		5.66(5.54)	

a) The values in parentheses are those calculated by using Eq. 10 over the entire concentration range.

3. Since S_{Ks} corresponds to the limiting Debye-Hückel slope for adiabatic compressibility, it depends only on the temperature and solvent properties for electrolytes of a fixed valency. As is shown in Table 3, however, we could not obtain a constant S_{Ks} value for four alkali halides; furthermore, we found no simple relationship between S_{Ks} and the temperature. These empirical S_{Ks} values for various salts and temperatures ranged between 4.2×10^{-4} and 6.7×10^{-4}, with the mean value being $(5.6\pm 0.7)\times 10^{-4}$ ml mol$^{-3/2}$ l$^{1/2}$ bar^{-1}. This mean value is in fair agreement with that



(a) (c)

(b) (d)

Fig. 2. $\phi_{KS}-S_{KS}c^{1/2}$ as a function of c for NaCl, KCl, NaBr, and KBr in water at 5, 25, and 45 °C, where S_{KS} was taken as 5.6×10^{-4} ml mol$^{-3/2}$ l$^{1/2}$ bar^{-1}.

estimated by Mathieson and Conway³⁾ using Eq. 2 at very low concentrations for most 1:1 electrolytes at 25 °C.

Gucker and his co-workers¹²⁾ studied the concentration dependence of ϕ_{KS} for some alkali halides at 25 °C. They also calculated the empirical S_{KS} value by using Eq. 10; their mean S_{KS} value is $(10.5\pm1.6)\times10^{-4}$, which is considerably higher than that estimated in this study. This disagreement seems to be ascribable to the fact that their work was performed at higher concentrations (up to 2—6 mol kg^{-1}) than those used here. Millero and his coworkers¹³⁾ have recently reported on their sound-velocity measurements of 28 electrolyte solutions at 25 °C and fitted the ϕ_{KS} data to Eq. 9. The S_{KS} values thus determined ranged between 1.74×10^{-4} and 7.79×10^{-4}. They have regarded S_{KS} as an adjustable parameter for the purpose of the estimation of the ϕ°_{KS} values. However, we believe that the S_{KS} should be the limiting slope, which is independent of the electrolyte species except for the valency.

Table 4. Limiting apparent molal adiabatic compressibilities and deviation constants of alkali halides determined using $S_{KS}=5.6\times10^{-4}$ ml mol$^{-3/2}$ l$^{1/2}$ bar^{-1}

	$-10^4\phi^\circ_{KS}$ ml mol^{-1} bar^{-1}			10^4B_{KS} ml mol^{-2} l bar^{-1}		
	5 °C	25 °C	45 °C	5 °C	25 °C	45 °C
NaCl	67.8	50.6	42.8	5.9	2.7	1.3
KCl	59.9	43.6	36.9	7.2	3.5	1.9
NaBr	59.3	43.0	35.6	3.4	1.0	−0.6
KBr	51.3	35.8	29.6	4.9	1.8	0.3

Literature values of $-10^4\phi^\circ_{KS}$ at 25 °C: NaCl 50.5,³⁾ 52.88,¹²⁾ 50.5,¹³⁾ 52.79,²¹⁾ 50.8²²⁾; KCl 43.5,³⁾ 46.34,¹²⁾ 44.1,¹³⁾ 45.58,²¹⁾ 42.6²²⁾; NaBr 42.8,³⁾ 46.47,¹²⁾ 41.8¹³⁾; KBr 36.0,³⁾ 35.0.¹³⁾

Figure 2 shows the plot of $(\phi_{KS}-S_{KS}c^{1/2})$ *vs.* c, where S_{KS} was taken as 5.6×10^{-4}, irrespective of the temperature. As may be anticipated from Table 3, good linearities were obtained over the concentration range studied, except for KCl and NaBr solutions at higher concentrations. The values of ϕ°_{KS} and B_{KS}, estimated graphically from Fig. 2, are given in Table 4. The ϕ°_{KS} values at 25 °C agree very well with those obtained from Eq. 2 by Mathieson and Conway.³⁾ This means that the absolute values of B_{KS} are small for alkali halides at 25 °C (see Table 4) and that the

TABLE 5. LIMITING APPARENT MOLAL ADIABATIC COMPRESSIBILITIES OF ELECTROLYTES OBTAINED FROM THE ORIGINAL SOUND VELOCITY AND DENSITY DATA OF MILLERO *et al.*[13] USING $S_{Ks}=5.6\times10^{-4}$ at 25 °C

	$-10^4\ \phi^\circ_{Ks}$/ml mol^{-1} bar^{-1}					
	F	Cl	Δ	Br	I	NO_3
Na	74.8 (75.4)[a]	50.5 (50.5)	7.7	42.8 (41.8)	32.5 (31.9)	40.4 (39.9)
Δ	10.9	7.1		7.2	7.2	7.4
K	63.9 (64.5)	43.4 (44.1)	7.8	35.6 (35.0)	25.3 (23.9)	33.0 (33.0)
NH_4		20.6 (21.2)	7.6	13.0 (13.7)		

a) The values in parentheses are the results of Millero *et al.*[13]

accuracy of their ϕ_{Ks} determination is very excellent in spite of the measurements having been done at very low concentrations. The self-consistency of our data can be confirmed by the additivity principle; the differences in ϕ°_{Ks} between chlorides and bromides, or between sodium and potassium salts, show that the ϕ°_{Ks} values are additive to a precision of 0.2 ml mol^{-1} bar^{-1} at all the temperatures studied.

It is evident from Fig. 1 and Table 4 that the deviation constant, B_{Ks}, is increased with a decrease in the temperature and varies with the electrolytes. Particularly large deviations are anticipated for organic salts or polyvalent electrolytes considering that the ϕ_V data show large deviations from the limiting law for these salts.[10] These facts suggest that the extrapolation procedure based on Eq. 2 is, even in a very low concentration range, not convincingly applicable to solutions of any electolyte or at any temperature. Furthermore, as has been described in the previous section, the error in the measurement of ϕ_{Ks} becomes significantly larger as the concentration is decreased. Therefore, despite the limitations in the experimental determination of S_{Ks}, the linear extrapolation method based on Eq. 9, as shown in Fig. 2, appears to be more reliable than that based on Eq. 2 for the evaluation of ϕ°_{Ks}. Based on our linear extrapolation method, we recalculated the ϕ°_{Ks} values of several 1:1 electrolytes from the sound velocity and density data recently reported by Millero and his co-workers.[13] The results are summarized in Table 5, which gives the differences in the ϕ°_{Ks} of the cations (K^+–Na^+) and anions (Br^-–Cl^-). Compared with the results of Millero and his co-workers,[13] given in parentheses, the recalculated ϕ°_{Ks} values agree more closely with our results and the results reported by Mathieson and Conway.[3] Furthermore, it may be pointed out that the accuracy of the recalculated values was checked from the additivity of the ϕ°_{Ks}, except in the case of fluorides: $\phi^\circ_{Ks}(K^+)-\phi^\circ_{Ks}(Na^+)=(7.2\pm0.1)\times10^{-4}$ and $\phi^\circ_{Ks}(Br^-)-\phi^\circ_{Ks}(Cl^-)=(7.7\pm0.1)\times10^{-4}$. These results are in fair agreement with our results (Table 4).

Relation between S_{Ks} and S_{KT}. The difference between ϕ_{Ks} and the apparent molal isothermal compressibility, ϕ_{KT}, is also given by Eq. 1 as a function of the concentration. Thus,

$$\phi_{KT}-\phi_{Ks} = (\phi^\circ_{KT}-\phi^\circ_{Ks}) + (S_{KT}-S_{Ks})c^{1/2} + (B_{KT}-B_{Ks})c. \tag{11}$$

The difference, $\phi_{KT}-\phi_{Ks}$, is related to the volume, the expansivity, and the heat capacity by:

$$\phi_{KT} - \phi_{Ks} = 10^3(\delta-\delta_0)/c + \delta_0\phi_V, \tag{12}$$

$$\delta = \beta_T-\beta_S = \alpha^2T/10\sigma, \tag{13}$$

where α is the thermal expansivity and σ is the volumetric specific heat.[14] Here, α and σ can be converted to the apparent molal expansibility, ϕ_E, and heat capacity, ϕ_C, using these relations:

$$\phi_E = 10^3(\alpha-\alpha_0)/c + \alpha_0\phi_V, \tag{14}$$

$$\phi_C = 10^3(\sigma-\sigma_0)/c + \sigma_0\phi_V. \tag{15}$$

The combination of these equations with Eqs. 12 and 13 leads to:

$$\phi_{KT}-\phi_{Ks} = \frac{10^3\delta_0\sigma_0\{10^{-3}(\phi_E-\alpha_0\phi_V)c+\alpha_0\}^2}{\alpha_0{}^2c\{10^{-3}(\phi_C-\sigma_0\phi_V)c+\sigma_0\}} + \delta_0\left(\phi_V-\frac{10^3}{c}\right). \tag{16}$$

Since, as in the case of ϕ_V, the concentration dependence of ϕ_E or ϕ_C is also given by Eq. 1, Eq. 16 can be expressed in terms of ϕ°_X, S_X, and B_X (X=V, E, and C). Now, expanding this equation with respect to $c^{1/2}$, and neglecting the terms higher than $c^{3/2}$, we may rewrite it in the same form as in Eq. 11. Thus, we obtain the following simple relations:[4]

$$\phi^\circ_{KT} - \phi^\circ_{Ks} = \delta_0(2\phi^\circ_E/\alpha_0-\phi^\circ_C/\sigma_0), \tag{17}$$

$$S_{KT} - S_{Ks} = \delta_0(2S_E/\alpha_0-S_C/\sigma_0), \tag{18}$$

$$B_{KT}-B_{Ks} = \delta_0\{2B_E/\alpha_0-B_C/\sigma_0+10^{-3}(\phi^\circ_E/\alpha_0-\phi^\circ_C/\sigma_0)^2\}. \tag{19}$$

Equation 17 is the same as that derived by Desnoyers and Philip.[15] We note that, for the conversion of ϕ_{Ks} to ϕ_{KT}, Harned and Owen[14] have derived alternative formulas, which can be reduced to much simpler expressions, 17 and 18.

Since the expansivity[7] and heat capacity[16] of pure water are known, and since the limiting slopes, S_E,[17] S_C,[18] and S_{KT},[3,19,20] have been calculated, we can estimate the value of S_{Ks} from Eq. 18. The results at 5, 25, and 45 °C are given in Table 6. Unfortunately, the S_{KT} values reported in the references are inconsistent with one another; nevertheless, the calculated S_{Ks} (even S_{KT}) values are, in any event, smaller than the experimental S_{Ks} value obtained in the previous section. Mathieson and Conway[3] have stated that S_{Ks} appears experimentally to be about twice the isothermal S_{KT} value at 25 °C. The difference ($S_{KT}-S_{Ks}$) in Table 6, however, clearly shows

Table 6. Theoretical estimation of S_{Ks} from S_{KT} for 1:1 electrolytes in water at 5, 25, and 45 °C[a)]

	5 °C		25 °C			45 °C	
$10^2 S_E$[b)]	1.674		1.717			1.892	
S_C[c)]	22.52		28.99			35.74	
$10^4 \alpha_0$[d)]	0.1598		2.5705			4.2260	
σ_0[e)]	4.2017		4.1669			4.1383	
$10^7 \delta_0$	0.0169		4.728			13.73	
$10^4(S_{KT}-S_{Ks})$	0.035		0.599			1.142	
$10^4 S_{KT}$	0.776[f)]	1.9[g)]	2.550[f)]	3.8[g)]	3.25[h)]	3.913[f)]	5.3[g)]
$10^4 S_{Ks}$	0.741	1.9	1.951	3.2	2.65	2.771	4.2

a) Units: S_E, ml mol$^{-3/2}$ l$^{1/2}$ deg^{-1}; S_C, J mol$^{-3/2}$ l$^{1/2}$ deg^{-1}; S_{KT} and S_{Ks}, ml mol$^{-3/2}$ l$^{1/2}$ bar^{-1}; α_0, deg^{-1}; σ_0, J deg^{-1} cm^{-3}; δ_0, bar^{-1}. b) Ref. 17; c) Ref. 18; d) Ref. 7; e) Ref. 16; f) Ref. 3; g) Ref. 19; h) Ref. 20.

that the isothermal S_{KT} value should be *larger* than the adiabatic S_{Ks} value at all the temperatures studied. It seems to us that the S_{KT} values in Table 6 are too small; this may originate from difficulties in the estimation of the second derivatives of the dielectric constant and the density of water with respect to the pressure *at one atmosphere* used for the calculation of S_{KT}. It appears that a reliable S_{KT} or S_{Ks} value cannot yet be definitely determined theoretically, although S_{KT} values over a wide range of temperatures and pressures have very recently been tabulated by Bradley and Pitzer.[20)] Attempts to linearize the plot of $\phi_{Ks}-S_{Ks}c^{1/2}$ against c by using $S_{Ks}=2.65\times10^{-4}$ at 25 °C were unsuccessful, even in a very low concentration range.

In conclusion, it seems to us at present that the concentration dependence of ϕ_{Ks} of the 1:1 electrolytes in dilute aqueous solutions is reasonably represented by Eq. 9, with $S_{Ks}=5.6\times10^{-4}$ ml mol$^{-3/2}$ l$^{1/2}$ bar^{-1} at an ordinary temperature, although there still remains some uncertainty as to the absolute accuracy of the S_{Ks} value.

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