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# Thermodynamic Properties of Aqueous Electrolyte Solutions. Volumetric and Compressibility Studies in 0.1 mol·kg$^{-1}$, 0.5 mol·kg$^{-1}$, and 1.0 mol·kg$^{-1}$ Sodium Carbonate and Sodium Sulfate Solutions at Temperatures from 278.15 K to 323.15 K[†]

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Densities and sound velocities in 0.1 mol·kg$^{-1}$, 0.5 mol·kg$^{-1}$, and 1.0 mol·kg$^{-1}$ sodium carbonate and sodium sulfate solutions were determined at 1 K temperature intervals in the 278.15 K to 323.15 K range. Measured quantities were expressed as polynomials of temperature, and these polynomials were used to evaluate the apparent molar volumes $V_{2,\phi}(T,m)$, the isobaric thermal expansibilities $\alpha(T,m)$, the product of temperature and the second-order derivatives of volume with respect to temperature $T(\partial^2V/\partial T^2)_{P,m}$ (changes in isobaric heat capacities with respect to pressure $-(\partial C_P/\partial P)_{T,m}$), the isentropic compressibilities $\kappa_S(T,m)$, the isothermal compressibilities $\kappa_T(T,m)$, the apparent molar compressibilities $K_{2,\phi}(T,m)$, the isochoric thermal pressure coefficients $(\partial P/\partial T)_{V,m}$, the change of cubic expansion coefficients with pressure at constant temperature $(\partial\alpha/\partial P)_{T,m}$, and the second-order derivatives of pressure with respect to temperature $T(\partial^2P/\partial T^2)_{V,m}$ (changes in isochoric heat capacities with respect to volume $(\partial C_V/\partial V)_{T,m}$).

## Introduction

Thermodynamic properties of aqueous solutions of inorganic salts were widely determined taking into account their importance in natural and industrial processes. They were mostly determined as a function of concentration at one or a few fixed temperatures. Contrary to this practice, in a series of our papers,[1−6] the volumetric properties of 0.1 mol·kg$^{-1}$, 0.5 mol·kg$^{-1}$, and 1.0 mol·kg$^{-1}$ aqueous solutions of electrolytes were determined at closely spaced 1 K temperature intervals. Even when velocities of sound were determined as a function of temperature, they were usually linked with the influence of concentration on the temperature of maximum sound velocity rather then with the thermodynamic properties of solutions.[7,8] Measurements performed with small changes in variables permits an accurate differentiation of experimental quantities with respect to temperature $T$ at constant molality $m$.

Determined in such a way, volumetric properties of solutions included densities $\rho(T,m)$, the cubic expansion coefficients $\alpha(T,m)$, the apparent molar volumes $V_{2,\phi}(T,m)$, and the second derivatives of volume with respect to temperature $(\partial^2V/\partial T^2)_{P,m}$. The last quantity is related to the change of molar heat capacity with pressure $P$, $(\partial C_P/\partial P)_{T,m}$. In this work, these volumetric and thermal properties of solutions are interrelated with the compressibility properties, which are derived from systematic determinations of sound velocities $u(T,m)$ also in 1 K temperature intervals. From sound velocities were derived the isentropic compressibilities $\kappa_S(T,m)$, the isothermal compressibilities $\kappa_T(T,m)$, the apparent molar compressibilities $K_{2,\phi}(T,m)$, the isochoric thermal pressure coefficients $(\partial P/\partial T)_{V,m}$, the change of cubic expansion coefficients with pressure at constant temperature $(\partial\alpha/\partial P)_{T,m}$, and the changes of heat capacities $C_V$ with volume $(\partial C_V/\partial V)_{T,m}$. Determined quantities are correlated and discussed in terms of changes in the water structure and hydration of ions in aqueous solutions.

The densities of sodium carbonate aqueous solutions (for $m \leq 1.0$ mol·kg$^{-1}$) were determined by Hershey et al.[9] from 273.15 K to 318.15 K in 5 K intervals and at 298.15 K by Millero et al.[10] (for more concentrated solutions, see, for example, the Lobo tabulation[11]). In the case of sodium sulfate aqueous solutions, densities were measured many times, considering their importance in geological and desalination processes. A number of wide-ranging with regard to temperature investigations are only mentioned here. Millero and Knox[12] determined densities at 273.15 K and 323.15 K, Chen et al.[13] from 273.15 K to 308.15 K, Isono[14] from 288.15 K to 328.15 K, Fabuss et al.[15] from 298.15 K to 448.15 K, Korosi and Fabuss[16] from 298.15 K to 423.15 K, Phutela and Pitzer[17] from 273.15 K to 473.15 K, Sharygin and Wood[18] from 298.15 K to 623.15 K, and Lo Surdo et al.[19] from 273.15 K to 323.15 K (for other investigations, see Lobo[11]). Compressibilities of aqueous sodium carbonate solutions based on the sound velocities were determined by Hershey et al.[9] from 273.15 K to 318.15 K and at 298.15 K by Millero at al.[10] In the case of sodium sulfate solutions, similar measurements were performed in the 273.15 K to 373.15 K temperature range by the Millero group[10,20−23] (for an application of the piezometric technique, see ref 23). Yasunaga et al.[24] determined sound velocities from 303.15 K to 307.15 K and Marks[25] from 273.15 K to 353.15 K. Compressibilities of solutions are also available from a number of determinations of densities at higher pressures.[17−19] Specific heat capacities (required in calculation of isothermal compressibilities) are, as a rule, better documented in the literature[26−40] for sodium sulfate solutions than for sodium carbonate solutions, and in many cases, their values are only reported at 298.15 K.

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## Experimental Section

Analytical-grade quality sodium carbonate (mass fraction > 0.995) and sodium sulfate (mass fraction > 0.99) from Fluka were dissolved in double distilled and degassed water (solutions were prepared by mass). Density determinations were performed using a Metler-Toledo DA-310 M densimeter. Detailed description of the applied procedure and estimated accuracy of $\rho(T;m)$ is reported in our previous investigations.[1,4] Used in calculations, the densities of pure water $\rho_1(T)$ were taken from the following equation[4]

$$\rho_1(T)/\mathrm{g{\cdot}cm^{-3}} = 0.999883 + 5.509202{\cdot}10^{-5}(t/°\mathrm{C}) - 7.867989{\cdot}10^{-6}(t/°\mathrm{C})^2 + 5.026034{\cdot}10^{-8}(t/°\mathrm{C})^3 - 1.933126{\cdot}10^{-10}(t/°\mathrm{C})^4 \qquad t/°\mathrm{C} = T/\mathrm{K} - 273.15 \quad (1)$$

Ultrasound measurements were performed in the 278.15 K to 323.15 K temperature range using a Sing-Around Meter constructed in the Silesian University (Katowice, Poland). The sample cell was immersed in a thermostat (± 0.05 K) to reach thermal equilibrium, and temperatures were changed in 1 K intervals. The ultrasonic velocimeter was calibrated with pure water over the entire temperature range. The mean value of deviation from the Marczak equation[41]

$$u_1(T)/\mathrm{m{\cdot}s^{-1}} = 1.402385{\cdot}10^3 + 5.038813{\cdot}10^0(t/°\mathrm{C}) - 5.799136{\cdot}10^{-2}(t/°\mathrm{C})^2 + 3.287156{\cdot}10^{-4}(t/°\mathrm{C})^3 - 1.398845{\cdot}10^{-6}(t/°\mathrm{C})^4 + 2.78786{\cdot}10^{-9}(t/°\mathrm{C})^5 \quad (2)$$

which is based on critical analysis of existing equations in the literature for sound velocities of pure water, was $\pm\, 0.42\ \mathrm{m{\cdot}s^{-1}}$. The estimated uncertainties of determined quantities derived from the sound velocity measurements are discussed in ref 6.

## Results and Discussion

***Volumetric and Compressibility Properties in Terms of Thermodynamic Relations.*** From determined densities $\rho(T,m)$, the apparent molar volumes $V_{2,\phi}(T,m)$ were calculated using

$$V_{2,\phi}(T,m) = \frac{M_2}{\rho(T,m)} + \frac{1000}{m}\left(\frac{1}{\rho(T,m)} - \frac{1}{\rho_1(T)}\right) \quad (3)$$

where $M_2$ is the molar mass of sodium carbonate or sodium sulfate. The temperature dependence of densities permits evaluatation of the cubic expansion coefficients, $\alpha(T,m)$, (isobaric thermal expansibilities)

$$\alpha(T,m) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\mathrm{P,m}} = -\left(\frac{\partial \ln \rho(T,m)}{\partial T}\right)_{\mathrm{P,m}} \quad (4)$$

Applying the Maxwell relation to the differential of enthalpy

$$\mathrm{d}H = C_\mathrm{P}\mathrm{d}T + \left[V - T\left(\frac{\partial V}{\partial T}\right)_\mathrm{P}\right]\mathrm{d}P \quad (5)$$

volumetric and thermal properties of solutions can be interrelated by

$$\left(\frac{\partial C_\mathrm{P}}{\partial P}\right)_\mathrm{T} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_\mathrm{P} \quad (6)$$

or in terms of the cubic expansion coefficients

$$T\left(\frac{\partial^2 V}{\partial T^2}\right)_{\mathrm{P,m}} = TV\left[\alpha^2(T,m) + \left(\frac{\partial \alpha(T,m)}{\partial T}\right)_{\mathrm{P,m}}\right] \quad (7)$$

The second-order derivatives of volume with respect to temperature can be directly expressed in terms of the derivatives of density

$$T\left(\frac{\partial^2 V}{\partial T^2}\right)_{\mathrm{P,m}} = \frac{T(1000 + mM_2)}{\rho^2(T,m)}\left\{\frac{2}{\rho(T,m)}\left[\left(\frac{\partial \rho(T,m)}{\partial T}\right)_{\mathrm{P,m}}\right]^2 - \left(\frac{\partial^2 \rho(T,m)}{\partial T^2}\right)_{\mathrm{P,m}}\right\} \quad (8)$$

where $V(T,m) = (1000 + mM_2)/\rho(T,m)$ is the volume of solution which is used in eq 8.

The isothermal compressibility coefficient at molality $m$ is defined as the change of volume $V$ with pressure $P$ at constant temperature $T$

$$\kappa_\mathrm{T}(T,m) = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T,m}} \quad (9)$$

and from the thermodynamic relation

$$\left(\frac{\partial P}{\partial T}\right)_\mathrm{V}\left(\frac{\partial T}{\partial V}\right)_\mathrm{P}\left(\frac{\partial V}{\partial P}\right)_\mathrm{T} = -1 \quad (10)$$

the isochoric thermal pressure coefficient is

$$\gamma_\mathrm{V}(T,m) = \left(\frac{\partial P}{\partial T}\right)_\mathrm{V} = \frac{\alpha(T,m)}{\kappa_\mathrm{T}(T,m)} \quad (11)$$

Since $(\partial V/\partial T)_\mathrm{V} = (\partial S/\partial V)_\mathrm{T}$ and $(\partial V/\partial T)_\mathrm{P} = -(\partial S/\partial P)_\mathrm{T}$, the volume and pressure dependence of the entropy is available from the experimentally determined quantities $\alpha(T,m)$ and $\gamma_\mathrm{V}(T,m)$.

Considering that

$$\frac{\partial}{\partial P}\left[\left(\frac{\partial V}{\partial T}\right)_\mathrm{P}\right]_\mathrm{T} = \frac{\partial}{\partial T}\left[\left(\frac{\partial V}{\partial P}\right)_\mathrm{T}\right]_\mathrm{P} \quad (12)$$

the change of expansion coefficient $\alpha$ with pressure is the complement of the change of the isothermal compressibility coefficient $\kappa_\mathrm{T}$ with temperature

$$\left(\frac{\partial \alpha}{\partial P}\right)_\mathrm{T} = -\left(\frac{\partial \kappa_\mathrm{T}}{\partial T}\right)_\mathrm{P} \quad (13)$$

and using

$$\left(\frac{\partial \alpha}{\partial T}\right)_\mathrm{V} = \left(\frac{\partial \alpha}{\partial T}\right)_\mathrm{P} + \left(\frac{\partial \alpha}{\partial P}\right)_\mathrm{T}\left(\frac{\partial P}{\partial T}\right)_\mathrm{V} \quad (14)$$

it follows from eqs 4 and 6 that

$$\left(\frac{\partial \alpha}{\partial T}\right)_\mathrm{V} = \left(\frac{\partial \alpha}{\partial T}\right)_\mathrm{P} - \gamma_\mathrm{V}\left(\frac{\partial \kappa_\mathrm{T}}{\partial T}\right)_\mathrm{P} = \left(\frac{\partial \alpha}{\partial T}\right)_\mathrm{P} - \alpha\left(\frac{\partial \ln \kappa_\mathrm{T}}{\partial T}\right)_\mathrm{P} \quad (15)$$

The isentropic (adiabatic) compressibility coefficient is defined by

$$\kappa_\mathrm{S}(T,m) = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\mathrm{S,m}} \quad (16)$$

and the isothermal and isentropic compressibility coefficients are interrelated by

$$\kappa_\mathrm{T}(T,m) = \kappa_\mathrm{S}(T,m) + \frac{T\alpha^2(T,m)}{C_\mathrm{P}(T,m)} \quad (17)$$

where $C_\mathrm{P}(T,m)$ is the isobaric heat capacity of solution per unit volume given by $C_\mathrm{P}(T,m) = \rho(T,m){\cdot}c_\mathrm{P}(T,m)$, where $c_\mathrm{P}(T,m)$ denotes the isobaric specific heat capacity. It is worthwhile to note that the ratio of compressibility coefficients is equal to the ratio of heat capacities $\kappa_\mathrm{S}/\kappa_\mathrm{T} = C_\mathrm{V}/C_\mathrm{P}$.

From the Newton−Laplace equation, $\kappa_\mathrm{S}(T,m)$ is related to measurable quantities, to the sound velocities $u(T,m)$ and densities $\rho(T,m)$ of solutions

$$\kappa_S(T,m) = \frac{1}{u^2(T,m)\rho(T,m)} \tag{18}$$

With the analogy to the apparent molar volume $V_{2,\phi}(T,m)$, the apparent molar isothermal or isentropic compressibilities are defined by

$$K_{2,\phi(j)}(T,m) = \frac{M_2\kappa_{(j)}(T,m)}{\rho(T,m)} + \frac{1000}{m}\left(\frac{\kappa_{(j)}(T,m)}{\rho(T,m)} - \frac{\kappa_{0(j)}(T)}{\rho_0(T)}\right) \qquad j = \mathrm{T\ or\ S} \tag{19}$$

In similar way as in eq 5, from the differential of internal energy

$$\mathrm{d}U = C_V\mathrm{d}T + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\mathrm{d}V \tag{20}$$

the change of heat capacity with volume at constant temperature is

$$\left(\frac{\partial C_V}{\partial V}\right)_{T,m} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V,m} = T\left(\frac{\partial \gamma_V(T,m)}{\partial T}\right)_{V,m} \tag{21}$$

From eqs 11 and 21, it follows that

$$\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_{T,m} = \left[\frac{\partial}{\partial T}\left(\frac{\alpha(T,m)}{\kappa_T(T,m)}\right)\right]_{V,m} = \left[\frac{1}{\kappa_T(T,m)}\left(\frac{\partial\alpha(T,m)}{\partial T}\right)_{V,m} - \frac{\alpha(T,m)}{\kappa_T^2(T,m)}\left(\frac{\partial\kappa_T(T,m)}{\partial T}\right)_{V,m}\right] \tag{22}$$

Considering that $\alpha(T,P)$ and $\kappa_T(T,P)$ are functions of $P$ and $T$

$$\mathrm{d}\alpha\left(\frac{\partial\alpha}{\partial T}\right)_P = \mathrm{d}T + \left(\frac{\partial\alpha}{\partial P}\right)_T\mathrm{d}P \tag{23}$$

and

$$\mathrm{d}\kappa_T\left(\frac{\partial\kappa_T}{\partial T}\right)_P = \mathrm{d}T + \left(\frac{\partial\kappa_T}{\partial P}\right)_T\mathrm{d}P \tag{24}$$

it follows using eq 13 that

$$\left(\frac{\partial\alpha}{\partial T}\right)_V = \left(\frac{\partial\alpha}{\partial T}\right)_P + \left(\frac{\partial\alpha}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial\alpha}{\partial T}\right)_P - \frac{\alpha}{\kappa_T}\left(\frac{\partial\kappa_T}{\partial P}\right)_T \tag{25}$$

and

$$\left(\frac{\partial\kappa_T}{\partial T}\right)_V = \left(\frac{\partial\kappa_T}{\partial T}\right)_P + \left(\frac{\partial\kappa_T}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial\kappa_T}{\partial T}\right)_P + \frac{\alpha}{\kappa_T}\left(\frac{\partial\kappa_T}{\partial P}\right)_T \tag{26}$$

which gives the change of heat capacity with volume at constant temperature[42]

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{T}{\kappa_T}\left[\left(\frac{\partial\alpha}{\partial T}\right)_P - 2\frac{\alpha}{\kappa_T}\left(\frac{\partial\kappa_T}{\partial T}\right)_P - \left(\frac{\alpha}{\kappa_T}\right)^2\left(\frac{\partial\kappa_T}{\partial P}\right)_T\right] \tag{27}$$

In principle, since $(\partial C_V/\partial V)_T$ and the temperature dependence of $\alpha$ and $\kappa_T$ are available, it is possible to obtain the pressure dependence of the isothermal compressibility coefficients with pressure $(\partial\kappa_T/\partial P)_T$. However, as pointed out by Kohler,[42] for liquids, the first and third terms in the brackets of eq 27 are nearly equal, and the second term is small as compared to them; therefore, the final result is usually not sufficiently accurate to be correct. Therefore, the pressure dependence of the isothermal compressibility coefficients with pressure is usually evaluated from the Tait-type equations (for details, see ref 6 and the Kohler book[37]).

***Data Reduction, Results, and Discussion.*** With an exception of the apparent molar volumes $V_{2,\phi}(T,m)$ and the isentropic compressibilities $\kappa_S(T,m)$, which are directly calculated using the experimental values of densities $\rho(T,m)$ and sound velocities $u(T,m)$, all other reported properties of solutions as a function of temperature are based on the smoothed densities and sound velocities. For the purpose of mathematical operations (differentiation with respect to temperature), the calculated quantities were arbitrarily fitted to polynomials of third, fourth, or fifth order

$$Y(t)/[\mathrm{unit}] = A + B(t/°\mathrm{C}) + C(t/°\mathrm{C})^2 + D(t/°\mathrm{C})^3 + E(t/°\mathrm{C})^4 + F(t/°\mathrm{C})^5 \tag{28}$$

where $t/°\mathrm{C} = T/\mathrm{K} - 273.15$ and the dimensionless coefficients $A$, $B$, $C$, $D$, and $E$ were determined by an unweighted least-squares method.

In Table 1 are presented experimental values of densities $\rho(T,m)$, and the corresponding apparent molar volumes $V_{2,\phi}(T,m)$ are given in Table 3. Measured velocities of sound $u(T,m)$, $\kappa_S(T,m)$, and $K_{2,\phi}(T,m)$ are reported in Tables 2, 4, and 5. In Figures 1 and 2, our $V_{2,\phi}(T,m)$ values are compared with those in the literature.[7,8,10−12,17,25,28,35] As can be observed, an excellent agreement is reached for both salts. The same situation exists (Figures 3, 4, and 5) when differences between the sound velocities of solutions and those of pure water, $\Delta u(T,m) = u(T,m) - u_1(T)$, are compared with the literature values[9,10,17,20,22] (differences between sound velocities give a more sensitive test than velocities themselves). Since the literature values of $V_{2,\phi}(T,m)$ or $\kappa_S(T,m)$ are rarely known for exact 0.1 $\mathrm{mol\cdot kg^{-1}}$, 0.5 $\mathrm{mol\cdot kg^{-1}}$, and 1.0 $\mathrm{mol\cdot kg^{-1}}$ solutions, the linearly interpolated values were used. Thus, there is no doubt about the consistency of the volumetric and compressibility properties presented here as expressed in terms of the coefficients in eq 28 (Tables 6 and 7) with those reported in the literature for sodium carbonate and sodium sulfate solutions.

As pointed out earlier, specific heat capacities $c_p(T,m)$ necessary for converting the isentropic compressibilities $\kappa_S(T,m)$ to the isothermal compressibilities $\kappa_T(T,m)$ were determined many times. However, they are less known as a function of temperature, and therefore, Hershey et al.[9] estimated them in the case of sodium carbonate using corresponding NaCl and $Na_2SO_4$ values. Since recently Magalhães et al.[40] reported very accurate values of $c_p(298.15\ \mathrm{K};m)$ for both salts, the Hershey et al.[9] specific heat capacities were shifted to match exactly these values at 298.15 K. In a similar way, the Millero et al.[21] $c_p(T,m)$ values were shifted in the case of sodium sulfate. Evidently, when more reliable $c_p(T,m)$ are available, the results of calculations reported here can be corrected (coefficients of eq 28 used for $c_p(T,m)$ values are given in Table 7).

An analysis of volumetric properties of solutions shows that $V_{2,\phi}(T,m;Na_2SO_4) \gg V_{2,\phi}(T,m;Na_2CO_3)$, and the apparent molar volumes have maxima at about 327 K for sodium carbonate and nearly 333 K for sodium sulfate (Figures 1 and 2). Similar to the behavior of isobaric thermal expansibilities, before the maxima, we have $\Delta\alpha(T,m) = [\alpha(T,m) - \alpha_1(T)] > 0$, and after the maxima, we have $\Delta\alpha(T,m) = [\alpha(T,m) - \alpha_1(T)] < 0$, where $\alpha_1(T)$ denotes corresponding values of pure water.[43] In the considered temperature interval, cubic expansion coefficients of both salts and water always increase with temperature, that is, $\partial\alpha(T,m)/\partial T > 0$, but after the maximum for 0.5 $\mathrm{mol\cdot kg^{-1}}$ solutions of sodium carbonate, it is observed that $\partial\alpha(T,m)/\partial T < 0$ (Figure 6). However, if both salts are compared, more

**Table 1. Experimental Densities $\rho(T,m)$ of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate As a Function of Temperature $t$/°C = $T$/K − 273.15**

| | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m$/mol·kg$^{-1}$ | | | | | |
| $t$/°C | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $\rho(T,m)$/g·cm$^{-3}$ | | | | | |
| 5 | 1.01153 | 1.05519 | 1.10454 | 1.01324 | 1.06310 | 1.11995 |
| 6 | 1.01146 | 1.05490 | 1.10424 | 1.01318 | 1.06289 | 1.11965 |
| 7 | 1.01140 | 1.05459 | 1.10392 | 1.01313 | 1.06283 | 1.11936 |
| 8 | 1.01130 | 1.05431 | 1.10357 | 1.01303 | 1.06261 | 1.11906 |
| 9 | 1.01120 | 1.05402 | 1.10323 | 1.01293 | 1.06238 | 1.11874 |
| 10 | 1.01107 | 1.05375 | 1.10291 | 1.01281 | 1.06214 | 1.11840 |
| 11 | 1.01092 | 1.05344 | 1.10255 | 1.01267 | 1.06178 | 1.11806 |
| 12 | 1.01080 | 1.05315 | 1.10219 | 1.01254 | 1.06162 | 1.11771 |
| 13 | 1.01065 | 1.05286 | 1.10183 | 1.01239 | 1.06136 | 1.11736 |
| 14 | 1.01048 | 1.05257 | 1.10147 | 1.01223 | 1.06110 | 1.11700 |
| 15 | 1.01030 | 1.05227 | 1.10112 | 1.01203 | 1.06069 | 1.11663 |
| 16 | 1.01010 | 1.05198 | 1.10074 | 1.01183 | 1.06038 | 1.11627 |
| 17 | 1.00992 | 1.05168 | 1.10035 | 1.01166 | 1.06027 | 1.11590 |
| 18 | 1.00973 | 1.05139 | 1.09996 | 1.01146 | 1.05999 | 1.11551 |
| 19 | 1.00949 | 1.05107 | 1.09956 | 1.01122 | 1.05962 | 1.11511 |
| 20 | 1.00926 | 1.05075 | 1.09918 | 1.01099 | 1.05930 | 1.11472 |
| 21 | 1.00901 | 1.05043 | 1.09878 | 1.01074 | 1.05897 | 1.11431 |
| 22 | 1.00876 | 1.05011 | 1.09836 | 1.01050 | 1.05865 | 1.11391 |
| 23 | 1.00850 | 1.04976 | 1.09795 | 1.01024 | 1.05831 | 1.11349 |
| 24 | 1.00824 | 1.04942 | 1.09755 | 1.00997 | 1.05796 | 1.11308 |
| 25 | 1.00796 | 1.04909 | 1.09713 | 1.00970 | 1.05761 | 1.11266 |
| 26 | 1.00768 | 1.04873 | 1.09670 | 1.00943 | 1.05725 | 1.11224 |
| 27 | 1.00740 | 1.04836 | 1.09627 | 1.00913 | 1.05689 | 1.11182 |
| 28 | 1.00710 | 1.04800 | 1.09583 | 1.00883 | 1.05653 | 1.11139 |
| 29 | 1.00678 | 1.04763 | 1.09539 | 1.00851 | 1.05614 | 1.11093 |
| 30 | 1.00646 | 1.04723 | 1.09494 | 1.00820 | 1.05576 | 1.11050 |
| 31 | 1.00613 | 1.04686 | 1.09450 | 1.00787 | 1.05536 | 1.11004 |
| 32 | 1.00579 | 1.04647 | 1.09405 | 1.00754 | 1.05497 | 1.10959 |
| 33 | 1.00546 | 1.04607 | 1.09356 | 1.00721 | 1.05458 | 1.10914 |
| 34 | 1.00512 | 1.04567 | 1.09313 | 1.00686 | 1.05417 | 1.10868 |
| 35 | 1.00475 | 1.04526 | 1.09266 | 1.00650 | 1.05375 | 1.10820 |
| 36 | 1.00439 | 1.04484 | 1.09219 | 1.00613 | 1.05334 | 1.10774 |
| 37 | 1.00401 | 1.04443 | 1.09170 | 1.00576 | 1.05289 | 1.10725 |
| 38 | 1.00364 | 1.04400 | 1.09124 | 1.00538 | 1.05249 | 1.10678 |
| 39 | 1.00324 | 1.04357 | 1.09074 | 1.00498 | 1.05203 | 1.10629 |
| 40 | 1.00285 | 1.04313 | 1.09025 | 1.00458 | 1.05159 | 1.10580 |
| 41 | 1.00244 | 1.04269 | 1.08975 | 1.00417 | 1.05114 | 1.10530 |
| 42 | 1.00203 | 1.04224 | 1.08927 | 1.00377 | 1.05069 | 1.10481 |
| 43 | 1.00163 | 1.04181 | 1.08877 | 1.00336 | 1.05023 | 1.10431 |
| 44 | 1.00121 | 1.04135 | 1.08826 | 1.00293 | 1.04976 | 1.10380 |
| 45 | 1.00078 | 1.04089 | 1.08777 | 1.00252 | 1.04930 | 1.10330 |
| 46 | 1.00034 | 1.04042 | 1.08726 | 1.00210 | 1.04882 | 1.10278 |
| 47 | 0.99990 | 1.03996 | 1.08676 | 1.00163 | 1.04835 | 1.10227 |
| 48 | 0.99945 | 1.03949 | 1.08625 | 1.00120 | 1.04786 | 1.10175 |
| 49 | 0.99898 | 1.03899 | 1.08573 | 1.00073 | 1.04736 | 1.10125 |
| 50 | 0.99853 | 1.03852 | 1.08521 | 1.00029 | 1.04688 | 1.10073 |
| 51 | 0.99807 | 1.03804 | 1.08469 | 0.99983 | 1.04638 | 1.10020 |
| 52 | 0.99761 | 1.03759 | 1.08417 | 0.99935 | 1.04587 | 1.09967 |
| 53 | 0.99711 | 1.03711 | 1.08364 | 0.99888 | 1.04536 | 1.09913 |
| 54 | 0.99663 | 1.03664 | 1.08314 | 0.99839 | 1.04486 | 1.09858 |
| 55 | 0.99615 | 1.03617 | 1.08261 | 0.99789 | 1.04428 | 1.09802 |
| 56 | 0.99566 | 1.03567 | 1.08207 | 0.99739 | 1.04375 | 1.09747 |
| 57 | 0.99516 | 1.03519 | 1.08154 | 0.99689 | 1.04338 | 1.09693 |
| 58 | 0.99467 | 1.03475 | 1.08101 | 0.99638 | 1.04287 | 1.09637 |
| 59 | 0.99416 | 1.03429 | 1.08047 | 0.99587 | 1.04233 | 1.09579 |
| 60 | 0.99366 | 1.03380 | 1.07991 | 0.99537 | 1.04176 | 1.09522 |
| 61 | 0.99317 | 1.03338 | 1.07939 | | | |
| 62 | 0.99265 | 1.03292 | 1.07885 | | | |
| 63 | 0.99212 | 1.03246 | 1.07830 | | | |
| 64 | 0.99159 | 1.03203 | 1.07774 | | | |
| 65 | 0.99105 | 1.03160 | 1.07719 | | | |
| 66 | 0.99053 | 1.03118 | 1.07666 | | | |
| 67 | 0.99000 | 1.03079 | 1.07610 | | | |
| 68 | 0.98945 | 1.03039 | 1.07557 | | | |
| 69 | 0.98891 | 1.03001 | 1.07502 | | | |
| 70 | 0.98835 | 1.02967 | 1.07447 | | | |

**Table 2. Experimental Velocity of Sound $u(T,m)$ of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate As a Function of Temperature $t$/°C = $T$/K − 273.15**

| | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m$/mol·kg$^{-1}$ | | | | | |
| $t$/°C | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $u(T,m)$/m·s$^{-1}$ | | | | | |
| 5 | 1446.08 | 1518.10 | 1605.78 | 1445.58 | 1513.29 | 1596.28 |
| 6 | 1449.87 | 1521.22 | 1608.90 | 1449.63 | 1516.42 | 1599.23 |
| 7 | 1454.19 | 1524.93 | 1612.00 | 1453.56 | 1520.40 | 1602.40 |
| 8 | 1458.33 | 1528.90 | 1615.00 | 1457.92 | 1523.65 | 1605.35 |
| 9 | 1462.45 | 1532.02 | 1617.90 | 1461.58 | 1527.03 | 1608.16 |
| 10 | 1466.55 | 1535.23 | 1620.70 | 1465.33 | 1530.51 | 1610.94 |
| 11 | 1469.99 | 1538.98 | 1623.14 | 1469.25 | 1534.00 | 1613.49 |
| 12 | 1473.71 | 1542.14 | 1626.10 | 1472.73 | 1537.29 | 1616.12 |
| 13 | 1477.27 | 1545.32 | 1628.80 | 1476.39 | 1540.11 | 1618.76 |
| 14 | 1480.88 | 1548.45 | 1631.43 | 1479.89 | 1543.10 | 1621.10 |
| 15 | 1483.91 | 1551.60 | 1633.57 | 1483.37 | 1546.23 | 1623.43 |
| 16 | 1487.54 | 1554.31 | 1636.13 | 1486.45 | 1548.91 | 1625.82 |
| 17 | 1490.65 | 1557.08 | 1637.91 | 1489.57 | 1551.65 | 1627.93 |
| 18 | 1493.85 | 1559.72 | 1640.43 | 1492.64 | 1554.52 | 1630.26 |
| 19 | 1497.23 | 1562.18 | 1642.59 | 1495.74 | 1557.13 | 1632.15 |
| 20 | 1500.22 | 1565.16 | 1644.58 | 1498.98 | 1559.69 | 1634.13 |
| 21 | 1503.06 | 1567.49 | 1646.77 | 1501.72 | 1562.25 | 1636.10 |
| 22 | 1505.64 | 1569.87 | 1648.72 | 1504.66 | 1564.42 | 1637.88 |
| 23 | 1508.61 | 1572.27 | 1650.54 | 1507.23 | 1566.81 | 1639.71 |
| 24 | 1511.20 | 1574.73 | 1652.45 | 1509.90 | 1569.04 | 1641.42 |
| 25 | 1513.71 | 1576.74 | 1654.05 | 1512.41 | 1571.23 | 1642.99 |
| 26 | 1516.08 | 1579.09 | 1655.61 | 1515.02 | 1573.16 | 1644.55 |
| 27 | 1518.66 | 1581.25 | 1657.47 | 1517.33 | 1575.13 | 1646.22 |
| 28 | 1520.96 | 1583.15 | 1658.99 | 1519.94 | 1577.33 | 1647.77 |
| 29 | 1523.01 | 1585.14 | 1660.48 | 1522.05 | 1579.17 | 1649.24 |
| 30 | 1525.56 | 1587.04 | 1661.78 | 1524.20 | 1581.06 | 1650.68 |
| 31 | 1527.66 | 1588.92 | 1663.24 | 1526.61 | 1582.82 | 1651.96 |
| 32 | 1529.87 | 1590.57 | 1664.60 | 1528.67 | 1584.70 | 1653.33 |
| 33 | 1532.03 | 1592.18 | 1665.68 | 1530.65 | 1586.22 | 1654.48 |
| 34 | 1533.61 | 1593.91 | 1667.04 | 1532.49 | 1587.85 | 1655.63 |
| 35 | 1535.62 | 1595.44 | 1668.08 | 1534.40 | 1589.34 | 1656.74 |
| 36 | 1537.61 | 1596.97 | 1669.28 | 1536.22 | 1590.72 | 1657.80 |
| 37 | 1539.07 | 1598.39 | 1670.32 | 1537.89 | 1592.16 | 1658.84 |
| 38 | 1541.04 | 1599.75 | 1671.45 | 1539.70 | 1593.57 | 1659.82 |
| 39 | 1542.77 | 1601.00 | 1672.24 | 1541.35 | 1594.93 | 1660.75 |
| 40 | 1544.19 | 1602.58 | 1673.11 | 1542.95 | 1596.25 | 1661.55 |
| 41 | 1545.62 | 1603.74 | 1674.00 | 1544.46 | 1597.50 | 1662.31 |
| 42 | 1547.05 | 1604.99 | 1674.73 | 1545.94 | 1598.71 | 1663.15 |
| 43 | 1548.37 | 1606.08 | 1675.68 | 1547.29 | 1599.82 | 1663.90 |
| 44 | 1549.93 | 1607.18 | 1676.20 | 1548.68 | 1600.87 | 1664.60 |
| 45 | 1551.23 | 1608.19 | 1676.91 | 1549.98 | 1601.95 | 1665.84 |
| 46 | 1552.47 | 1609.17 | 1677.57 | 1551.19 | 1602.73 | 1666.44 |
| 47 | 1553.69 | 1610.20 | 1678.11 | 1552.41 | 1603.75 | 1667.00 |
| 48 | 1554.87 | 1610.97 | 1678.65 | 1553.49 | 1604.68 | 1667.44 |
| 49 | 1556.01 | 1611.68 | 1679.16 | 1554.73 | 1605.38 | 1667.47 |
| 50 | 1557.07 | 1612.70 | 1679.75 | 1555.82 | 1606.17 | 1667.94 |

important differences are evident when $T(\partial^2 V/\partial T^2)_{P,m}$ or $T(\partial^2(V - V_1)/\partial T^2)_{P,m}$ are considered (Figures 7 and 8). From the thermodynamic eq 6, it follows that the volume−temperature relations are associated with the thermal properties of solutions. The product of temperature $T$ and the second derivative of volume with respect to $T$ are equal to the changes in the isobaric heat capacities $f(T,m) = T(\partial^2 V/\partial T^2)_{P,m} = -(\partial C_P/\partial P)_{T,m}$. The "abnormal" high heat capacity of water is usually attributed to a highly ordered cooperative hydrogen-bonded structure. This structure, at least partially, will be destroyed when pressure increases, and therefore, it is expected that $(\partial C_{P,1}/\partial P)_T$ will be negative and the product for water $f(T,m{=}0)$ will be positive. Temperature has a similar effect as pressure on the isobaric heat capacity; $f(T,m{=}0)$ is positive and decreases with $T$. However, at higher temperatures (or pressures), the product $f(T,m{=}0)$ increases only slightly due to the fact that water starts to behave like a "normal" liquid.[44] The change in the structure of water starts to be rather complex when the combined effect of increasing temperature (or pressure) and adding electrolyte is considered. In order to minimize the effect of ion−ion interactions, Hepler[44] suggested in interpretation of volume−temperature relations to replace the second derivatives of the total volume $V(T,m)$ with the second derivatives of the partial molar volume of solute at infinite dilution, $\bar{V}_2^{\infty}(T) = \bar{V}_2(T,m\rightarrow 0)$. Thus,

**Table 3. Apparent Molar Volumes of $V_{2,\phi}(T,m)$ of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate As a Function of Temperature $t$/°C = $T$/K − 273.15**

| $t$/°C | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m$/mol·kg$^{-1}$ | | | | | |
| | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $V_{2,\phi}(T,m)$/cm$^3$·mol$^{-1}$ | | | | | |
| 5 | −9.62 | −4.24 | 1.28 | 9.23 | 14.81 | 19.69 |
| 6 | −9.13 | −3.73 | 1.53 | 9.62 | 15.17 | 19.94 |
| 7 | −8.94 | −3.22 | 1.78 | 9.72 | 15.20 | 20.17 |
| 8 | −8.45 | −2.79 | 2.05 | 10.20 | 15.52 | 20.39 |
| 9 | −8.16 | −2.38 | 2.29 | 10.49 | 15.82 | 20.61 |
| 10 | −7.68 | −2.03 | 2.50 | 10.88 | 16.11 | 20.84 |
| 11 | −7.09 | −1.62 | 2.74 | 11.36 | 16.61 | 21.06 |
| 12 | −7.01 | −1.29 | 2.95 | 11.55 | 16.70 | 21.27 |
| 13 | −6.72 | −0.98 | 3.16 | 11.83 | 16.95 | 21.47 |
| 14 | −6.34 | −0.69 | 3.36 | 12.11 | 17.19 | 21.67 |
| 15 | −6.06 | −0.42 | 3.53 | 12.59 | 17.67 | 21.86 |
| 16 | −5.69 | −0.19 | 3.71 | 12.97 | 17.94 | 22.03 |
| 17 | −5.51 | 0.06 | 3.91 | 13.05 | 17.83 | 22.21 |
| 18 | −5.43 | 0.25 | 4.09 | 13.22 | 18.00 | 22.38 |
| 19 | −4.96 | 0.48 | 4.26 | 13.70 | 18.32 | 22.56 |
| 20 | −4.68 | 0.69 | 4.41 | 13.97 | 18.53 | 22.72 |
| 21 | −4.41 | 0.86 | 4.55 | 14.24 | 18.72 | 22.88 |
| 22 | −4.14 | 1.03 | 4.72 | 14.42 | 18.89 | 23.02 |
| 23 | −3.86 | 1.23 | 4.86 | 14.69 | 19.08 | 23.18 |
| 24 | −3.69 | 1.40 | 4.99 | 14.96 | 19.27 | 23.31 |
| 25 | −3.42 | 1.53 | 5.12 | 15.13 | 19.43 | 23.45 |
| 26 | −3.25 | 1.70 | 5.26 | 15.20 | 19.60 | 23.58 |
| 27 | −3.18 | 1.86 | 5.38 | 15.47 | 19.75 | 23.69 |
| 28 | −3.01 | 1.99 | 5.50 | 15.64 | 19.87 | 23.81 |
| 29 | −2.75 | 2.11 | 5.62 | 15.91 | 20.04 | 23.94 |
| 30 | −2.58 | 2.27 | 5.73 | 15.97 | 20.16 | 24.04 |
| 31 | −2.42 | 2.36 | 5.82 | 16.14 | 20.30 | 24.15 |
| 32 | −2.15 | 2.48 | 5.92 | 16.30 | 20.43 | 24.25 |
| 33 | −2.09 | 2.61 | 6.05 | 16.37 | 20.53 | 24.35 |
| 34 | −2.02 | 2.71 | 6.12 | 16.53 | 20.66 | 24.44 |
| 35 | −1.76 | 2.81 | 6.21 | 16.70 | 20.78 | 24.54 |
| 36 | −1.70 | 2.91 | 6.29 | 16.86 | 20.86 | 24.62 |
| 37 | −1.54 | 2.97 | 6.38 | 16.92 | 21.00 | 24.71 |
| 38 | −1.48 | 3.07 | 6.44 | 17.08 | 21.04 | 24.78 |
| 39 | −1.21 | 3.15 | 6.53 | 17.34 | 21.18 | 24.86 |
| 40 | −1.16 | 3.23 | 6.60 | 17.50 | 21.26 | 24.94 |
| 41 | −1.00 | 3.29 | 6.67 | 17.66 | 21.34 | 25.01 |
| 42 | −0.84 | 3.37 | 6.72 | 17.72 | 21.42 | 25.07 |
| 43 | −0.88 | 3.39 | 6.78 | 17.78 | 21.50 | 25.13 |
| 44 | −0.83 | 3.45 | 6.84 | 17.94 | 21.58 | 25.19 |
| 45 | −0.67 | 3.51 | 6.88 | 17.89 | 21.64 | 25.24 |
| 46 | −0.51 | 3.56 | 6.93 | 17.85 | 21.71 | 25.30 |
| 47 | −0.46 | 3.58 | 6.96 | 18.20 | 21.75 | 25.34 |
| 48 | −0.30 | 3.62 | 6.99 | 18.16 | 21.83 | 25.39 |
| 49 | −0.15 | 3.67 | 7.02 | 18.31 | 21.88 | 25.40 |
| 50 | −0.09 | 3.69 | 7.06 | 18.27 | 21.92 | 25.44 |
| 51 | −0.04 | 3.70 | 7.09 | 18.32 | 21.98 | 25.48 |
| 52 | −0.09 | 3.64 | 7.10 | 18.47 | 22.03 | 25.51 |
| 53 | 0.16 | 3.62 | 7.12 | 18.42 | 22.06 | 25.53 |
| 54 | 0.11 | 3.55 | 7.10 | 18.47 | 22.06 | 25.56 |
| 55 | −0.04 | 3.46 | 7.09 | 18.52 | 22.19 | 25.59 |
| 56 | −0.09 | 3.43 | 7.10 | 18.57 | 22.22 | 25.60 |
| 57 | −0.05 | 3.37 | 7.10 | 18.62 | 21.94 | 25.61 |
| 58 | −0.20 | 3.20 | 7.08 | 18.67 | 21.91 | 25.63 |
| 59 | −0.15 | 3.07 | 7.08 | 18.72 | 21.94 | 25.66 |
| 60 | −0.31 | 2.98 | 7.08 | 18.56 | 22.01 | 25.68 |
| 61 | −0.68 | 2.74 | 7.03 | | | |
| 62 | −0.73 | 2.57 | 7.01 | | | |
| 63 | −0.79 | 2.37 | 6.98 | | | |
| 64 | −0.85 | 2.12 | 6.96 | | | |
| 65 | −0.91 | 1.85 | 6.93 | | | |
| 66 | −1.15 | 1.56 | 6.87 | | | |
| 67 | −1.41 | 1.19 | 6.83 | | | |
| 68 | −1.61 | 0.81 | 6.75 | | | |
| 69 | −1.88 | 0.40 | 6.70 | | | |
| 70 | −2.05 | −0.12 | 6.63 | | | |

**Table 4. Isentropic Compressibility Coefficients $\kappa_S(T,m)$ of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate As a Function of Temperature $t$/°C = $T$/K − 273.15**

| $t$/°C | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m$/mol·kg$^{-1}$ | | | | | |
| | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $\kappa_S(T,m)\cdot 10^6$/MPa$^{-1}$ | | | | | |
| 5 | 4.728 | 4.112 | 3.511 | 4.723 | 4.108 | 3.504 |
| 6 | 4.703 | 4.096 | 3.498 | 4.697 | 4.092 | 3.492 |
| 7 | 4.676 | 4.078 | 3.486 | 4.672 | 4.071 | 3.479 |
| 8 | 4.650 | 4.058 | 3.474 | 4.644 | 4.055 | 3.467 |
| 9 | 4.624 | 4.042 | 3.463 | 4.621 | 4.038 | 3.456 |
| 10 | 4.599 | 4.026 | 3.452 | 4.598 | 4.020 | 3.445 |
| 11 | 4.578 | 4.008 | 3.443 | 4.574 | 4.003 | 3.436 |
| 12 | 4.555 | 3.993 | 3.431 | 4.553 | 3.987 | 3.425 |
| 13 | 4.534 | 3.977 | 3.421 | 4.532 | 3.973 | 3.415 |
| 14 | 4.513 | 3.962 | 3.411 | 4.511 | 3.959 | 3.407 |
| 15 | 4.495 | 3.947 | 3.403 | 4.491 | 3.944 | 3.398 |
| 16 | 4.474 | 3.935 | 3.394 | 4.473 | 3.931 | 3.389 |
| 17 | 4.456 | 3.922 | 3.388 | 4.455 | 3.918 | 3.381 |
| 18 | 4.438 | 3.910 | 3.378 | 4.438 | 3.905 | 3.373 |
| 19 | 4.419 | 3.899 | 3.371 | 4.420 | 3.893 | 3.366 |
| 20 | 4.402 | 3.885 | 3.364 | 4.402 | 3.881 | 3.359 |
| 21 | 4.387 | 3.875 | 3.356 | 4.387 | 3.870 | 3.353 |
| 22 | 4.373 | 3.864 | 3.349 | 4.371 | 3.860 | 3.346 |
| 23 | 4.357 | 3.854 | 3.343 | 4.357 | 3.850 | 3.340 |
| 24 | 4.343 | 3.843 | 3.337 | 4.343 | 3.840 | 3.335 |
| 25 | 4.330 | 3.834 | 3.332 | 4.330 | 3.831 | 3.329 |
| 26 | 4.318 | 3.824 | 3.327 | 4.316 | 3.823 | 3.324 |
| 27 | 4.304 | 3.815 | 3.320 | 4.304 | 3.814 | 3.319 |
| 28 | 4.292 | 3.807 | 3.316 | 4.291 | 3.805 | 3.314 |
| 29 | 4.282 | 3.799 | 3.311 | 4.280 | 3.798 | 3.309 |
| 30 | 4.269 | 3.791 | 3.307 | 4.269 | 3.790 | 3.305 |
| 31 | 4.259 | 3.784 | 3.303 | 4.257 | 3.783 | 3.301 |
| 32 | 4.248 | 3.777 | 3.299 | 4.247 | 3.775 | 3.297 |
| 33 | 4.237 | 3.771 | 3.296 | 4.238 | 3.770 | 3.294 |
| 34 | 4.230 | 3.764 | 3.292 | 4.229 | 3.763 | 3.291 |
| 35 | 4.221 | 3.759 | 3.289 | 4.220 | 3.758 | 3.288 |
| 36 | 4.211 | 3.753 | 3.286 | 4.212 | 3.753 | 3.285 |
| 37 | 4.205 | 3.748 | 3.283 | 4.204 | 3.747 | 3.282 |
| 38 | 4.196 | 3.743 | 3.280 | 4.196 | 3.742 | 3.280 |
| 39 | 4.188 | 3.738 | 3.279 | 4.188 | 3.737 | 3.277 |
| 40 | 4.182 | 3.733 | 3.277 | 4.181 | 3.733 | 3.276 |
| 41 | 4.176 | 3.729 | 3.275 | 4.175 | 3.729 | 3.274 |
| 42 | 4.170 | 3.725 | 3.273 | 4.169 | 3.725 | 3.272 |
| 43 | 4.164 | 3.721 | 3.271 | 4.163 | 3.721 | 3.271 |
| 44 | 4.158 | 3.718 | 3.271 | 4.157 | 3.717 | 3.270 |
| 45 | 4.152 | 3.715 | 3.269 | 4.152 | 3.714 | 3.266 |
| 46 | 4.148 | 3.712 | 3.268 | 4.147 | 3.712 | 3.265 |
| 47 | 4.143 | 3.709 | 3.268 | 4.143 | 3.709 | 3.265 |
| 48 | 4.139 | 3.707 | 3.267 | 4.139 | 3.706 | 3.264 |
| 49 | 4.134 | 3.705 | 3.267 | 4.134 | 3.705 | 3.266 |
| 50 | 4.131 | 3.702 | 3.266 | 4.130 | 3.703 | 3.266 |

according to Hepler, the product $T(\partial^2\bar{V}_2^{\infty}/\partial T^2)_P$ should be negative for the structure-breaking solutes, and usually, this product increases with $T$, and the curve is concave downward. For the structure-making solutes, the product is positive and increases with $T$, and the curve is concave upward. However, the partial molar volumes of solutes at infinite dilution $\bar{V}_2^{\infty}(T)$ are not especially accurate because they are derived at each temperature by an extrapolation of the partial molar volume for $m \rightarrow 0$. Evidently, it should be expected that their second derivatives will be even less accurate. Thus, it was difficult to apply directly these indicative criteria, and they were replaced by[5]

$$T\left(\frac{\partial^2\bar{V}_2^{\infty}}{\partial T^2}\right)_P \approx \Delta f(T,m) = f(T,m) - f(T,m=0) \quad (29)$$

where $f(T,m{=}0)$ is given in ref 1. In an alternative approach, changes in isobaric heat capacities are associated with changes in the hydration of ions (see, for example, Ackermann[45]), but this subject will considered later in the context of compressibility measurements.

In Figures 7 and 8 are plotted the $\Delta f(T,m)$ = [$f(T,m)$ − $f(T,m{=}0)$] functions of sodium carbonate and sodium sulfate. As can be observed in both cases, they are negative, $\Delta f(T,m) < 0$, but the curvature of the curves is dissimilar. Thus, according

**Table 5. Apparent Molar Compressibilities $K_{2,\phi}(T,m)$ of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate As a Function of Temperature $t/°C = T/K - 273.15$**

| | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m/mol \cdot kg^{-1}$ | | | | | |
| $t/°C$ | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $-K_{2,\phi}(T,m) \cdot 10^5/cm^3 \cdot mol^{-1} \cdot MPa^{-1}$ | | | | | |
| 5 | 192.2 | 162.3 | 140.1 | 188.9 | 155.3 | 134.4 |
| 6 | 189.2 | 159.8 | 138.3 | 185.4 | 153.0 | 132.5 |
| 7 | 186.6 | 157.4 | 136.5 | 182.3 | 150.7 | 130.8 |
| 8 | 183.8 | 155.2 | 134.8 | 179.0 | 148.6 | 129.1 |
| 9 | 181.2 | 153.1 | 133.1 | 176.0 | 146.5 | 127.4 |
| 10 | 178.6 | 151.0 | 131.5 | 173.1 | 144.6 | 125.9 |
| 11 | 176.0 | 149.0 | 130.0 | 170.2 | 142.6 | 124.3 |
| 12 | 173.8 | 147.2 | 128.5 | 167.6 | 140.8 | 122.8 |
| 13 | 171.6 | 145.4 | 127.1 | 165.1 | 139.1 | 121.4 |
| 14 | 169.3 | 143.7 | 125.7 | 162.7 | 137.4 | 120.0 |
| 15 | 167.2 | 142.0 | 124.4 | 160.2 | 135.7 | 118.7 |
| 16 | 165.0 | 140.4 | 123.1 | 157.9 | 134.1 | 117.4 |
| 17 | 163.2 | 138.9 | 121.8 | 156.0 | 132.6 | 116.1 |
| 18 | 161.4 | 137.5 | 120.6 | 154.0 | 131.2 | 114.9 |
| 19 | 159.4 | 136.0 | 119.4 | 151.9 | 129.7 | 113.7 |
| 20 | 157.6 | 134.7 | 118.3 | 150.0 | 128.3 | 112.6 |
| 21 | 155.7 | 133.4 | 117.2 | 148.1 | 127.0 | 111.4 |
| 22 | 154.0 | 132.1 | 116.2 | 146.5 | 125.7 | 110.4 |
| 23 | 152.4 | 130.9 | 115.1 | 144.8 | 124.4 | 109.3 |
| 24 | 150.8 | 129.7 | 114.2 | 143.2 | 123.2 | 108.3 |
| 25 | 149.2 | 128.5 | 113.2 | 141.7 | 122.0 | 107.4 |
| 26 | 147.8 | 127.4 | 112.3 | 140.4 | 120.9 | 106.4 |
| 27 | 146.4 | 126.3 | 111.4 | 138.9 | 119.8 | 105.5 |
| 28 | 145.0 | 125.3 | 110.5 | 137.5 | 118.7 | 104.6 |
| 29 | 143.6 | 124.3 | 109.7 | 136.1 | 117.7 | 103.8 |
| 30 | 142.2 | 123.3 | 108.9 | 134.9 | 116.7 | 103.0 |
| 31 | 140.9 | 122.4 | 108.1 | 133.6 | 115.7 | 102.2 |
| 32 | 139.6 | 121.5 | 107.4 | 132.4 | 114.8 | 101.4 |
| 33 | 138.5 | 120.6 | 106.6 | 131.4 | 113.9 | 100.7 |
| 34 | 137.4 | 119.8 | 105.9 | 130.2 | 113.0 | 100.0 |
| 35 | 136.2 | 119.0 | 105.2 | 129.1 | 112.2 | 99.3 |
| 36 | 135.1 | 118.2 | 104.6 | 128.0 | 111.4 | 98.7 |
| 37 | 134.0 | 117.5 | 103.9 | 126.9 | 110.6 | 98.0 |
| 38 | 133.0 | 116.8 | 103.3 | 125.9 | 109.9 | 97.4 |
| 39 | 131.9 | 116.1 | 102.7 | 124.8 | 109.2 | 96.9 |
| 40 | 131.0 | 115.4 | 102.2 | 123.8 | 108.6 | 96.3 |
| 41 | 130.0 | 114.8 | 101.6 | 122.9 | 107.9 | 95.8 |
| 42 | 129.2 | 114.2 | 101.1 | 122.1 | 107.3 | 95.2 |
| 43 | 128.5 | 113.6 | 100.6 | 121.3 | 106.7 | 94.8 |
| 44 | 127.7 | 113.0 | 100.1 | 120.4 | 106.4 | 94.3 |
| 45 | 127.0 | 112.5 | 99.6 | 119.8 | 105.9 | 93.8 |
| 46 | 126.3 | 112.0 | 99.2 | 119.3 | 105.4 | 93.4 |
| 47 | 125.7 | 111.5 | 98.8 | 118.4 | 104.9 | 92.9 |
| 48 | 125.2 | 111.0 | 98.4 | 118.0 | 104.3 | 92.5 |
| 49 | 124.6 | 110.5 | 98.0 | 117.4 | 103.8 | 92.1 |
| 50 | 124.2 | 110.1 | 97.6 | 117.2 | 103.3 | 91.7 |
| 51 | −0.04 | 3.70 | 7.09 | 18.32 | 21.98 | 25.48 |
| 52 | −0.09 | 3.64 | 7.10 | 18.47 | 22.03 | 25.51 |
| 53 | 0.16 | 3.62 | 7.12 | 18.42 | 22.06 | 25.53 |
| 54 | 0.11 | 3.55 | 7.10 | 18.47 | 22.06 | 25.56 |
| 55 | −0.04 | 3.46 | 7.09 | 18.52 | 22.19 | 25.59 |
| 56 | −0.09 | 3.43 | 7.10 | 18.57 | 22.22 | 25.60 |
| 57 | −0.05 | 3.37 | 7.10 | 18.62 | 21.94 | 25.61 |
| 58 | −0.20 | 3.20 | 7.08 | 18.67 | 21.91 | 25.63 |
| 59 | −0.15 | 3.07 | 7.08 | 18.72 | 21.94 | 25.66 |
| 60 | −0.31 | 2.98 | 7.08 | 18.56 | 22.01 | 25.68 |
| 61 | −0.68 | 2.74 | 7.03 | | | |
| 62 | −0.73 | 2.57 | 7.01 | | | |
| 63 | −0.79 | 2.37 | 6.98 | | | |
| 64 | −0.85 | 2.12 | 6.96 | | | |
| 65 | −0.91 | 1.85 | 6.93 | | | |
| 66 | −1.15 | 1.56 | 6.87 | | | |
| 67 | −1.41 | 1.19 | 6.83 | | | |
| 68 | −1.61 | 0.81 | 6.75 | | | |
| 69 | −1.88 | 0.40 | 6.70 | | | |
| 70 | −2.05 | −0.12 | 6.63 | | | |

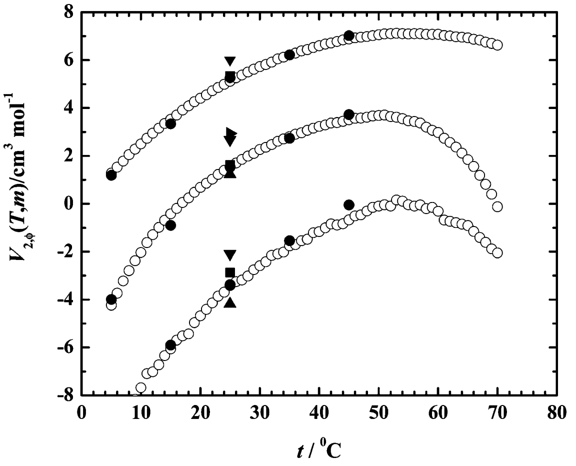

**Figure 1.** Apparent molar volumes $V_{2,\phi}(T,m)$ of 0.1 mol·kg$^{-1}$, 0.5 mol·kg$^{-1}$, and 1.0 mol·kg$^{-1}$ sodium carbonate solutions as a function of temperature $t/°C = T/K - 273.15$. ●, ref 9; ▲, ref 29; ▼, ref 32; ■, ref 39; ○, this work.

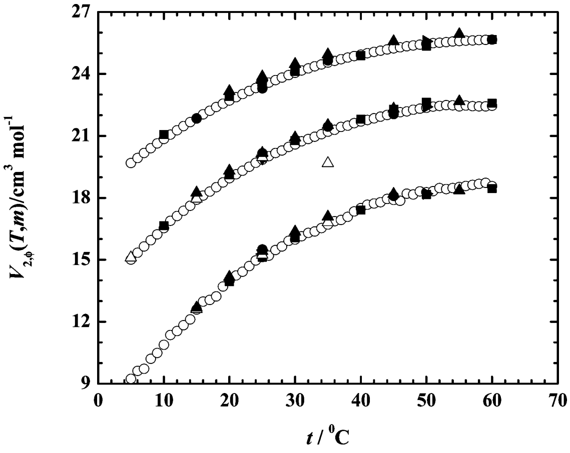

**Figure 2.** Apparent molar volumes $V_{2,\phi}(T,m)$ of 0.1 mol·kg$^{-1}$, 0.5 mol·kg$^{-1}$, and 1.0 mol·kg$^{-1}$ sodium sulfate solutions as a function of temperature $t/°C = T/K - 273.15$. ▼, ref 10; right-pointing shaded triangle, ref 12; △, ref 13; ▲, ref 14; ■, ref 17; ●, ref 19; left-pointing shaded triangle, ref 39; ○, this work.

to the modified Hepler indicative criteria (eq 29), the overall effect is that sodium carbonate and sodium sulfate behave in water as the structure-breaking solutes. The curvature of $\Delta f(T,m)$ in sodium carbonate solutions is concave downward, that is, the second derivative of $\Delta f(T,m=\text{const.})$ with respect to $T$ is negative (Figure 7) and increases with $T$ (maxima are in the 308 K to 313 K region), which supports the above conclusion about the structure-breaking solute. It is worthwhile to note that in moderately concentrated solutions, $m = 0.5$ mol·kg$^{-1}$, sodium carbonate behaves differently than in more dilute or in more concentrated solutions, and this is observed for both salts. In case of sodium sulfate, $\Delta f(T,m)$ also increases with $T$, but the curvature is concave upward, that is, the second derivative of $\Delta f(T,m=\text{const.})$ with respect to $T$ is positive (Figure 8). Once again, the curve of $m = 0.5$ mol·kg$^{-1}$ solutions has the concave-upward curvature and increases with $T$ up to 308 K. Thus, conclusions coming from using eq 29 can be summarized as an addition of sodium carbonate or sodium sulfate to water producing a less structured structure of water, the magnitude of the effect being different ($\Delta f(T,m;Na_2SO_4)$ < ($\Delta f(T,m;Na_2CO_3)$), and it depending on the amount of dissolved salt.

As in cases of other aqueous solutions of electrolytes, sound velocities, $u = u(T,m=\text{const.})$, of sodium carbonate and sodium sulfate as a function of temperature have the parabolic form, and always, $[u(T,m) - u_1(T)] > 0$ is observed (Figures 3, 4, and 5). The positions of the maxima of sound velocities are known only for $Na_2SO_4$ solutions, and according to Marks,[25] they lie

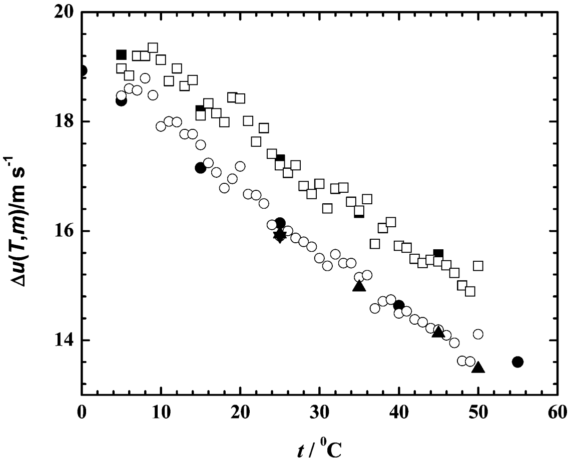

**Figure 3.** Differences between the sound velocity of 0.1 $\text{mol}\cdot\text{kg}^{-1}$ sodium carbonate and sodium sulfate solutions and that of pure water, $\Delta u(T,m)$, as a function of temperature $t/°\text{C} = T/\text{K} - 273.15$. $Na_2CO_3$: ■, ref 17; □, this work. $Na_2SO_4$: ▼, ref 10; ●, ref 20; ▲, ref 22; ○, this work.

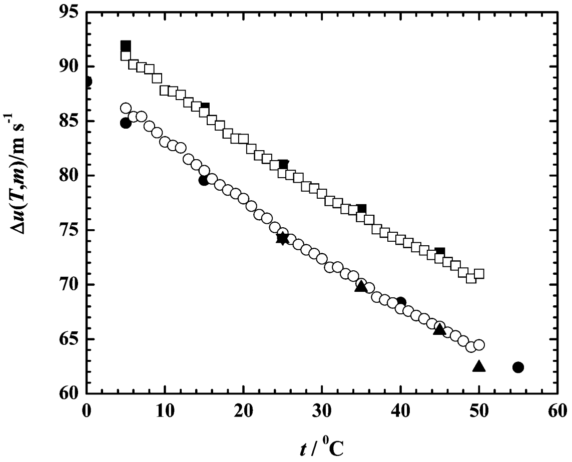

**Figure 4.** Differences between the sound velocity of 0.5 $\text{mol}\cdot\text{kg}^{-1}$ sodium carbonate and sodium sulfate solutions and that of pure water, $\Delta u(T,m)$, as a function of temperature $t/°\text{C} = T/\text{K} - 273.15$. $Na_2CO_3$: ■, ref 9; ▼, ref 10; □, this work. $Na_2SO_4$: ▼, ref 10; ●, ref 20; ▲, ref 22; ○, this work.

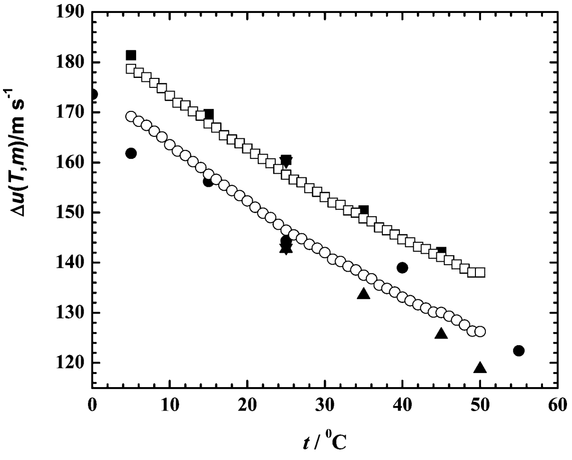

**Figure 5.** Differences between the sound velocity of 1.0 $\text{mol}\cdot\text{kg}^{-1}$ sodium carbonate and sodium sulfate solutions and that of pure water, $\Delta u(T,m)$, as a function of temperature $t/°\text{C} = T/\text{K} - 273.15$. $Na_2CO_3$: ■, ref 9; ▼, ref 10; □, this work. $Na_2SO_4$: ▼, ref 10; ●, ref 20; ▲, ref 22; ○, this work.

in the 333 K to 343 K temperature interval, and they depend linearly on concentration.

**Table 6. Adjustable Coefficients *A*, *B*, *C*, *D*, and *E* of Equations of Type *28* for the Volumetric Properties of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate**

| | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m/\text{mol}\cdot\text{kg}^{-1}$ | | | | | |
| | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $\rho(T,m)/\text{g}\cdot\text{cm}^{-3}$ | | | | | |
| $A$ | 1.01172 | 1.05665 | 1.10603 | 1.01337 | 1.06403 | 1.12132 |
| $B\cdot 10^4$ | −0.0223 | −3.0614 | −2.8201 | 0.1394 | −1.5001 | −2.4785 |
| $C\cdot 10^6$ | −6.6370 | 2.7170 | −3.2218 | −7.6359 | −4.5708 | −4.8866 |
| $D\cdot 10^7$ | 0.3054 | −1.3133 | 0.0864 | 0.5478 | 0.1109 | 0.4490 |
| $E\cdot 10^{10}$ | −0.0484 | 1.0893 | 0.0416 | −2.4698 | 0.6147 | −2.5648 |
| | $\alpha(T,m)/\text{K}^{-1}$ | | | | | |
| $A\cdot 10^4$ | 0.0226 | 2.8951 | 2.5498 | −0.1366 | 1.4097 | 2.2108 |
| $B\cdot 10^5$ | 1.3106 | −0.5006 | 0.5891 | 1.5045 | 0.8613 | 0.8753 |
| $C\cdot 10^7$ | −0.8941 | 3.6692 | −0.2125 | −1.6010 | −0.2956 | −1.1613 |
| $D\cdot 10^9$ | 0.2379 | −3.8827 | −0.1385 | 0.9926 | −0.1944 | 0.8721 |
| $E.10^{12}$ | −0.3280 | −2.2442 | −0.2026 | −0.0392 | −0.3666 | 0.3619 |
| | $V_{2,\phi}(T,m)/\text{cm}^3\cdot\text{mol}^{-1}$ | | | | | |
| $A$ | −12.200 | −7.166 | −0.149 | 6.947 | 12.853 | 18.351 |
| $B$ | 0.5627 | 0.6919 | 0.3098 | 0.4608 | 0.4043 | 0.2843 |
| $C\cdot 10^2$ | −1.2746 | −2.1063 | −0.4867 | −0.6554 | −0.7739 | −0.3648 |
| $D\cdot 10^4$ | 1.9926 | 3.5782 | 0.4323 | 0.4780 | 0.9929 | 0.1775 |
| $E\cdot 10^6$ | −1.4685 | −2.5350 | −0.2456 | −0.2056 | −0.6722 | −0.0348 |
| | $T(\partial^2 V/\partial T^2)_{P,m} = -(\partial C_P/\partial P)_{T,m}/\text{cm}^3\cdot\text{K}^{-1}$ | | | | | |
| $A$ | 3.580 | −1.350 | 1.627 | 4.119 | 2.373 | 2.452 |
| $B\cdot 10^2$ | −3.6235 | 19.5201 | −0.4431 | −7.1595 | −0.6534 | −5.4539 |
| $C\cdot 10^3$ | 0.1133 | −2.4196 | −0.1416 | 0.5164 | −0.1913 | 0.5278 |
| $D\cdot 10^5$ | −0.0953 | −1.2640 | −0.0799 | 0.2939 | −0.1135 | 0.1918 |
| $E\cdot 10^8$ | 0.4748 | −3.8477 | −0.1836 | | −0.4065 | 1.4065 |

The isentropic compressibility coefficients $\kappa_S(T,m)$ are nearly the same for both salts (the same is observed for the isothermal compressibility coefficients $\kappa_T(T;m)$). Sodium carbonate and sodium sulfate solutions have lower compressibility coefficients than those of pure water, that is, $[\kappa_S(T;H_2O) - \kappa_S(T,m)] > 0$ (for $Na_2CO_3$, see Figure 9) and $[\kappa_T(T;H_2O) - \kappa_T(T,m)] > 0$. The coefficients $\kappa_S(T,m)$ and $\kappa_T(T,m)$ decrease with increasing $T$, but their minima lie outside of the temperature range considered here (Figure 9). For both salts, differences between the compressibility coefficients $\Delta\kappa(T,m) = [\kappa_T(T,m) - \kappa_S(T,m)]$ depend on concentration and temperature, and they increase with $m$ and $T$, but always, $[\Delta\kappa(T,m) - \Delta\kappa(T;H_2O)] > 0$.

Rao[45] suggested correlating $u(T,m)$ and $\kappa_S(T,m)$ by the empirical relation

$$R_1(m) = M_{12}u^{1/3}(T,m)/\rho(T,m) \qquad (30)$$

or in an alternative form by

$$R_2(m) = \kappa_S^{1/7}(T,m)\cdot\rho(T,m) \qquad (31)$$

because $R_1(m)$ and $R_2(m)$ quantities are weakly dependent on temperature ($M_{12} = x_1M_1 + x_2M_2$ is the average molecular mass, and $R_2(m) = (M_{12}/R_1(m))^{6/7}$). In the case of sodium carbonate solutions in the 278.15 K to 323.15 K temperature range, we have $R_1(0.1\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 207.3 \pm 2.2$, $R_1(0.5\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 208.8 \pm 2.2$, and $R_1(1.0\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 211.2 \pm 2.0$. Together with the value for water, $R_1\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 207.0 \pm 2.3$, they can be linearly correlated with the dimensionless concentration $m^* = m/m^0$, where $m^0 = 1\ \text{mol}\cdot\text{kg}^{-1}$, by $R_1(m^*)\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 207.0 + 4.096m^*$ and $R^2 = 0.9940$. The corresponding values for sodium sulfate are $R_1(0.1\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 207.6 \pm 2.3$, $R_1(0.5\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 210.5 \pm 2.2$, and $R_1(1.0\ \text{mol}\cdot\text{kg}^{-1})\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 214.6 \pm 2.0$, and $R_1(m^*)\cdot 10^6/\text{m}^{4/3}\cdot\text{s}^{-1/3}\cdot\text{mol}^{-1} = 207.0 + 7.456m^*$ and $R^2 = 0.9978$.

**Table 7. Adjustable Coefficients *A*, *B*, *C*, *D*, *E*, and *F* of Equations of Type *28* for the Compressibility Properties of Aqueous Solutions of Sodium Carbonate and Sodium Sulfate**

| | $Na_2CO_3$ | | | $Na_2SO_4$ | | |
|---|---|---|---|---|---|---|
| | $m$/mol·kg$^{-1}$ | | | | | |
| | 0.10 | 0.50 | 1.00 | 0.10 | 0.50 | 1.00 |
| | $u(T,m)$/m·s$^{-1}$ | | | | | |
| $A$ | 1422.88 | 1498.19 | 1588.67 | 1423.11 | 1493.95 | 1579.63 |
| $B$ | 4.8701 | 4.0877 | 3.6543 | 4.7313 | 3.9415 | 3.5187 |
| $C\cdot10^2$ | −5.6473 | −3.0971 | −4.8581 | −5.2856 | −1.9084 | −3.6811 |
| $D\cdot10^4$ | 3.2766 | −5.5159 | 3.6885 | 3.4889 | −11.477 | −3.8281 |
| $E\cdot10^5$ | −0.2300 | 1.3990 | −0.4336 | −0.4244 | 2.6937 | 1.4688 |
| $F\cdot10^8$ | 1.6894 | −9.9298 | 3.4399 | 3.5713 | −19.865 | −12.603 |
| | $\kappa_S(T,m)\cdot10^6$/MPa$^{-1}$ | | | | | |
| $A$ | 4.8821 | 4.2157 | 3.5822 | 4.8728 | 4.2112 | 3.5747 |
| $B\cdot10^2$ | −3.3369 | −2.1618 | −1.5533 | −3.2528 | −2.1604 | −1.5330 |
| $C\cdot10^4$ | 5.8051 | 2.3988 | 2.7835 | 5.6143 | 2.1874 | 2.5435 |
| $D\cdot10^6$ | −6.4284 | 2.0128 | −3.0450 | −6.7942 | 3.9923 | −0.9208 |
| $E\cdot10^8$ | 5.6802 | −7.3549 | 3.4226 | 7.4805 | −12.583 | −2.6103 |
| $F\cdot10^{10}$ | −2.7396 | 5.6456 | −2.1957 | −4.4168 | 9.9934 | 3.1727 |
| | $\kappa_T(T,m)\cdot10^6$/MPa$^{-1}$ | | | | | |
| $A$ | 4.8822 | 4.2701 | 3.6251 | 4.8728 | 4.2112 | 3.5747 |
| $B\cdot10^2$ | −3.3386 | −2.2984 | −1.3403 | −3.2528 | −2.1604 | −1.5330 |
| $C\cdot10^4$ | 6.9818 | 3.4356 | 3.0037 | 5.6143 | 2.1874 | 2.5435 |
| $D\cdot10^6$ | −7.7791 | 1.4820 | −3.2321 | −6.7942 | 3.9923 | −0.9208 |
| $E\cdot10^8$ | 6.5656 | −5.7801 | 3.4050 | 7.4805 | −12.583 | −2.6103 |
| $F\cdot10^{10}$ | −3.1646 | 1.9804 | −2.2999 | −4.4168 | 9.9934 | 3.1727 |
| | $K_{2,\phi}(T,m)\cdot10^5$/cm$^3$·mol$^{-1}$·MPa$^{-1}$ | | | | | |
| $A$ | −208.32 | −177.01 | −150.35 | −207.93 | −169.31 | −144.44 |
| $B$ | 3.5077 | 3.3642 | 2.2341 | 4.1241 | 3.1957 | 2.2052 |
| $C\cdot10^2$ | −5.9056 | −9.5436 | −3.9520 | −6.1875 | −9.2460 | −3.9962 |
| $D\cdot10^4$ | 5.1751 | 22.119 | 4.5138 | −4.9928 | 24.645 | 6.1214 |
| $E\cdot10^6$ | 0.2120 | −3.1661 | −0.2721 | 3.2602 | −4.0936 | −0.8000 |
| $F\cdot10^{10}$ | −6.9045 | 18.7829 | 0.1265 | −32.678 | 27.225 | 5.0649 |
| | $(\partial P)_{T,m}\cdot10^9$/K$^{-1}$·MPa$^{-1}$ | | | | | |
| $A$ | 33.386 | 22.984 | 13.403 | 32.528 | 21.604 | 15.331 |
| $B$ | −1.3964 | −0.6871 | −0.6007 | −1.1229 | −0.4375 | −0.5087 |
| $C\cdot10^2$ | 2.3337 | −0.4446 | 0.9696 | 2.0383 | −1.1977 | 0.2762 |
| $D\cdot10^4$ | −2.6262 | 2.3121 | −1.3620 | −2.9922 | 5.0332 | 1.0441 |
| $E\cdot10^6$ | 1.5823 | −0.9902 | 1.1499 | 2.2084 | −4.9967 | −1.5863 |
| | $\gamma_V(T,m)\cdot10^{-1}$/MPa·K$^{-1}$ | | | | | |
| $A$ | 0.0453 | 6.7913 | 7.0331 | −0.2828 | 3.3482 | 6.1252 |
| $B$ | 0.2689 | −0.0839 | 0.1887 | 0.3079 | 0.2156 | 0.2656 |
| $C\cdot10^3$ | −0.0002 | 7.8877 | −0.4985 | −1.3011 | 0.6272 | −2.8837 |
| $D\cdot10^5$ | −3.4861 | −5.3509 | −1.3201 | −2.6754 | −4.9881 | −0.0014 |
| $E\cdot10^7$ | 2.9196 | −9.2063 | 0.2628 | 4.3661 | 6.0607 | 4.1137 |
| $F\cdot10^9$ | −0.6855 | 6.2502 | 0.4567 | −1.5624 | −3.5359 | −2.7369 |
| | $(\partial C_V/\partial V)_{T,m}\cdot10^{-1}$/MPa·K$^{-1}$ | | | | | |
| $A$ | 73.459 | −22.923 | 51.547 | 84.090 | 58.902 | 72.552 |
| $B$ | 0.2688 | 4.2251 | −0.0836 | −0.4029 | 0.5583 | −1.3097 |
| $C\cdot10^2$ | −2.8567 | −2.8073 | −1.1814 | −2.4526 | −3.9621 | −0.5779 |
| $D\cdot10^4$ | 2.1442 | −11.664 | −0.1089 | 3.9677 | 5.1255 | 4.4942 |
| $E\cdot10^7$ | 2.3166 | 48.538 | 7.2891 | −3.8743 | −24.049 | −20.924 |
| $F\cdot10^8$ | −0.3427 | 3.1251 | 0.2284 | −0.7812 | −1.7679 | −1.3684 |
| | $c_P(T,m)$/J·g$^{-1}$·K$^{-1}$ | | | | | |
| $A$ | 4.1516 | 3.9148 | 3.7396 | 4.1515 | 3.9258 | 3.7693 |
| $B\cdot10^3$ | −3.0476 | 0.0404 | 1.7889 | −3.8579 | −3.5327 | −4.9316 |
| $C\cdot10^4$ | 1.3148 | 1.0370 | 0.7857 | 1.4181 | 1.3385 | 1.3401 |
| $D\cdot10^6$ | −2.4504 | −2.5205 | −2.3933 | −2.6188 | −2.4737 | −2.2938 |
| $E\cdot10^8$ | 1.7238 | 2.0244 | 1.9916 | 2.0652 | 1.9507 | 1.8089 |
| $F\cdot10^{11}$ | 2.5147 | −0.3626 | −1.2182 | | | |

The apparent molar isentropic compressibilities $K_{2,\phi}(T,m)$ are presented in Figure 10. The temperature dependence of $K_{2,\phi}(T,m)$ shows maxima which are at temperatures close to those of the apparent molar volumes $V_{2,\phi}(T,m)$. In all cases, it is observed that $K_{2,\phi}(T,m;Na_2SO_4) > K_{2,\phi}(T,m;Na_2CO_3)$ (Figure 10).

The isochoric thermal pressure coefficients of sodium sulfate solutions $\gamma_V(T,m) = (\partial P/\partial T)_{V,m}$ as a function of $T$ are plotted in Figure 11 ($\gamma_V(T,m;Na_2SO_4) \approx (\gamma_V(T,m;Na_2CO_3)$). They monotonically increase with $T$, and the isochoric thermal pressure coefficients of pure water are always smaller than those of both salts, that is, $[\gamma_V(T,m) - \gamma_V(H_2O)] > 0$.

From eq 13, it follows that changes of the isobaric compressibility coefficients $\kappa_T(T,m)$ with temperature $T$ are related to changes of the cubic expansion coefficients $\alpha(T, m)$ with pressure $P$. Values of $\Delta_P\alpha(T,m) = (\partial\alpha/\partial P)_{T,m}$ for pure water and for sodium carbonate and sodium sulfate solutions as a function of temperature $T$ are presented in Figures 12 and 13. $(\partial\alpha/\partial P)_{T,m}$ monotonically decreases with $T$, contrary to $(\partial\alpha/\partial T)_P$, which usually increases with $T$ (Figure 6). The changes of the cubic expansion coefficients with pressure of sodium carbonate solutions are smaller than those in pure water (Figure 12), but this not the case of sodium sulfate solutions (Figure 13).

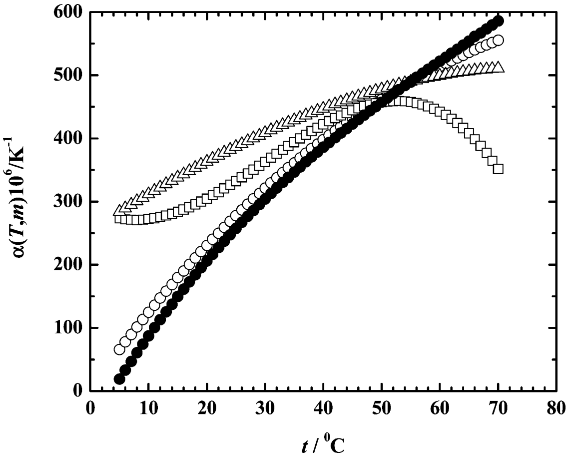

**Figure 6.** Cubic expansion coefficients $\alpha(T,m)$ of water and sodium carbonate solutions as a function of temperature $t$/°C = $T$/K − 273.15. ●, water; ○, $m = 0.1$ mol·kg$^{-1}$; □, $m = 0.5$ mol·kg$^{-1}$; △, $m = 1.0$ mol·kg$^{-1}$.

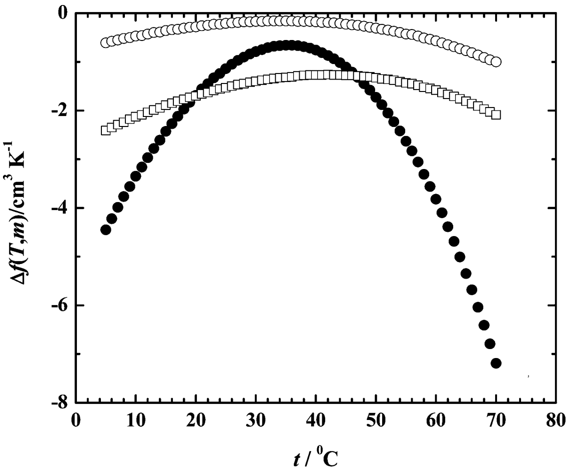

**Figure 7.** Differences in the change of molar heat capacities with pressure of sodium carbonate solutions and pure water $\Delta f(T,m) = [\partial(C_P - C_{P,1})/\partial P]_{T,m}$ as a function of temperature $t$/°C = $T$/K − 273.15. ○, 0.1 mol·kg$^{-1}$; ●, 0.5 mol·kg$^{-1}$; □, 1.0 mol·kg$^{-1}$.

As pointed out earlier, the volume−pressure−temperature relations are associated with the thermal properties of solutions; the products $f(T,m) = T(\partial^2V/\partial T^2)_{P,m}$ and $g(T,m) = T(\partial^2P/\partial T^2)_{V,m}$ are equal to the changes in heat capacities $f(T,m) = -(\partial C_P/\partial P)_{T,m}$ and $g(T,m) = (\partial C_V/\partial V)_{T,m}$ (eqs 6 and 21). Since the second derivative of the volume with respect to temperature is positive, $(\partial^2V/\partial T^2)_{P,m} > 0$, the isobaric heat capacit of pure water and that of solutions decrease with increasing pressure. On the other side, the isochoric heat capacities of pure water and solutions increase with increasing volume because the second derivative of the pressure with respect to temperature is positive $(\partial^2P/\partial T^2)_{V,m} > 0$. The products $g(T,m{=}\text{const.}) = T(\partial^2P/\partial T^2)_{V,m}$ as a function of temperature $T$ are plotted for pure water and

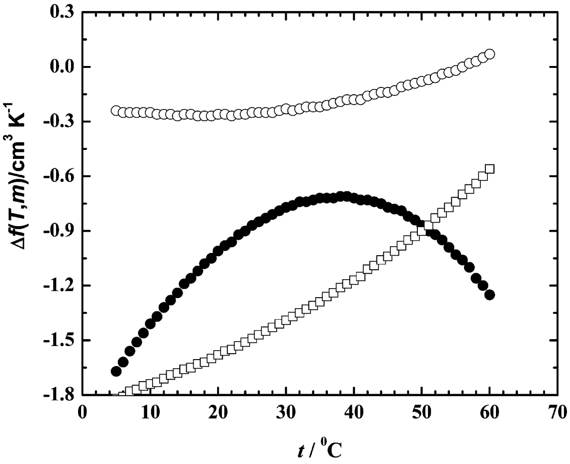

**Figure 8.** Differences in the change of molar heat capacities with pressure of sodium sulfate solutions and pure water $\Delta f(T,m) = [\partial(C_P - C_{P,1})/\partial P]_{T,m}$ as a function of temperature $t/°C = T/K - 273.15$. ○, 0.1 mol·kg$^{-1}$; ●, 0.5 mol·kg$^{-1}$; □, 1.0 mol·kg$^{-1}$.

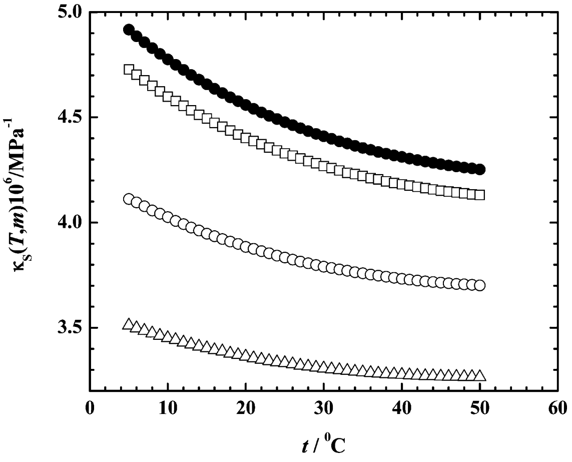

**Figure 9.** The isentropic compressibility coefficients $\kappa_S$ of water and sodium carbonate solutions as a function of temperature $t/°C = T/K - 273.15$. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

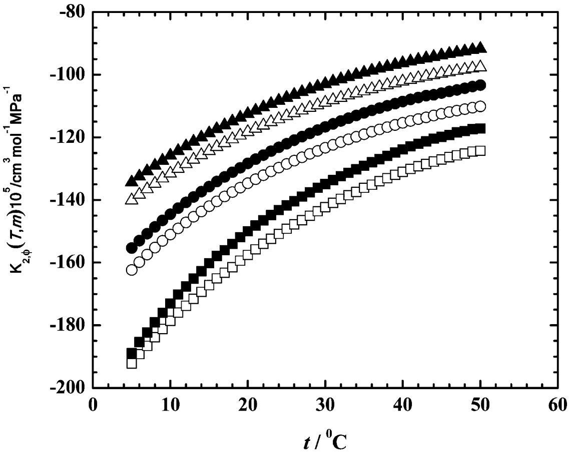

**Figure 10.** The apparent molar isentropic compressibilities $K_{2,\phi}(T,m)$ of sodium carbonate and sodium sulfate solutions as a function of temperature $t/°C = T/K - 273.15$. $Na_2CO_3$: □, 0.1 mol·kg$^{-1}$; ○, 0.1 mol·kg$^{-1}$; △, 0.1 mol·kg$^{-1}$. $Na_2SO_4$: ■, 0.1 mol·kg$^{-1}$; ●, 0.1 mol·kg$^{-1}$; ▲, 0.1 mol·kg$^{-1}$.

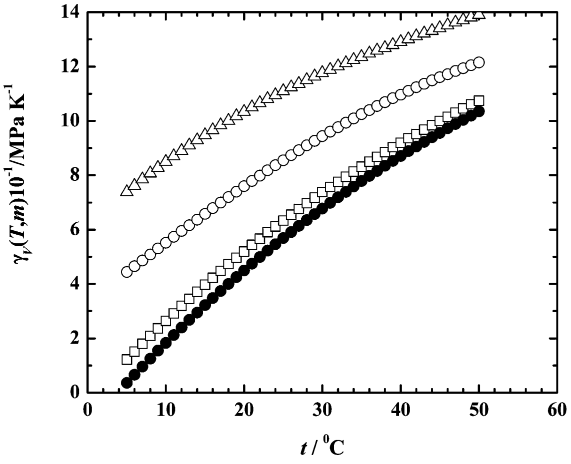

**Figure 11.** The isochoric thermal pressure coefficients, $\gamma_V(T,m) = (\partial P/\partial T)_{V,m}$ of water and sodium sulfate solutions as a function of temperature $t/°C = T/K - 273.15$. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

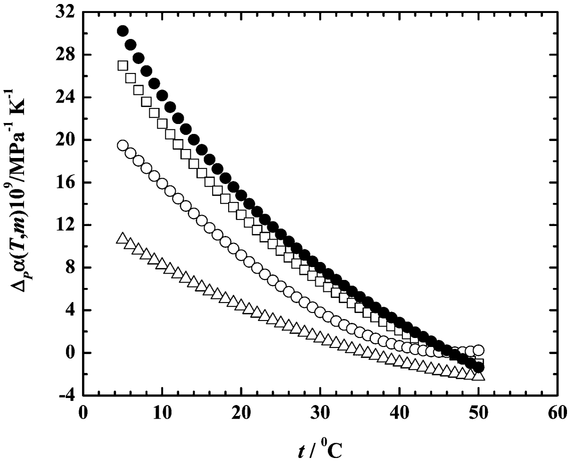

**Figure 12.** The change of the cubic expansion coefficients with pressure $\Delta_P\alpha(T,m) = (\partial\alpha/\partial P)_{T,m}$ of water and sodium carbonate solutions as a function of temperature $t/°C = T/K - 273.15$. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

investigated solutions in Figures 14 and 15. As can be observed, curves have the curvature concave downward ($g''(T,m=\text{const.}) < 0$) for sodium carbonate solutions and concave upward ($g''(T,m=\text{const.}) > 0$) for sodium sulfate solutions. However, similarly as with the volumetric properties, for moderately concentrated solutions, $m = 0.5$ mol·kg$^{-1}$, in both cases, they are concave downward.

In order to obtain indicative criteria about changes in the structure of water which will be similar to $\Delta f(T,m) = [f(T,m) - f(T,m=0)] = -[\partial(C_P - C_{P,1})/\partial P]_{T,m}$, the analogous functions $\Delta g(T,m) = [g(T,m) - g(T,m=0)] = [\partial(C_V - C_{V,1})/\partial V]_{T,m})$ were introduced, and they are plotted in Figures 16 and 17. Since $g(T,m=0) > g(T,m)$ (Figures 14 and 15), differences in the products $\Delta g(T,m)$ are always negative for sodium carbonate and sodium sulfate solutions, and their curvature is similar to that observed for corresponding curves of $\Delta f(T,m)$ in Figures 7 and 8. Thus, as was already illustrated in the case of lithium chloride solutions,[6] similarly as with negative values of $\Delta f(T,m)$, the negative values of $\Delta g(T,m)$ are associated with the structure-breaking solutes. A different magnitude of $\Delta g(T,m)$ values indicates that sodium carbonate is probably stronger than the sodium sulfate structure-breaking solute because $\Delta g(T,m;Na_2SO_4) < (\Delta g(T,m;Na_2CO_3)$, which is analogous to the inequality $(\Delta f(T,m;Na_2SO_4) < (\Delta f(T,m;Na_2CO_3))$ already mentioned above. However, it is evident that in terms of $\Delta f(T,m)$ or $\Delta g(T,m)$ functions, the determined volumetric and compressibility properties of electrolyte solutions can only be qualitatively interpreted.

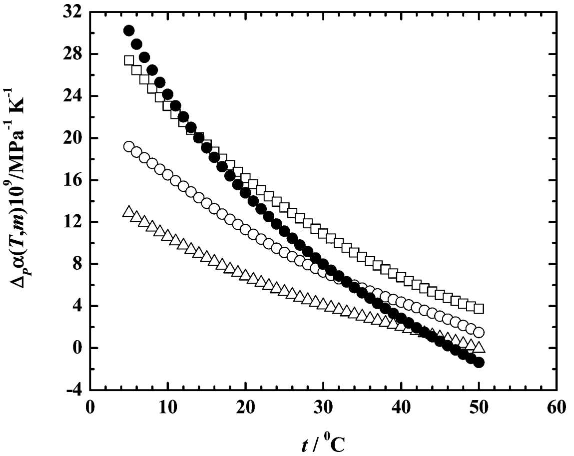

**Figure 13.** The change of the cubic expansion coefficients with pressure $\Delta_P\alpha(T,m) = (\partial\alpha/\partial P)_{T,m}$ of water and sodium sulfate solutions as a function of temperature $t$/°C = $T$/K − 273.15. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

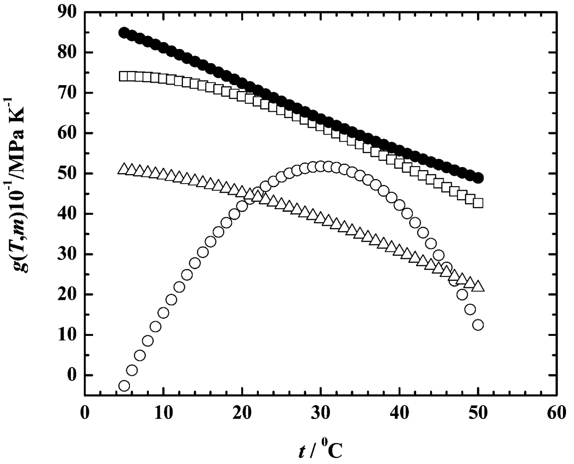

**Figure 14.** The change of molar heat capacity with volume of sodium carbonate solutions and pure water $g(T,m) = T(\partial^2P/\partial T^2)_{V,m} = (\partial C_V/\partial V)_{T,m}$ as a function of temperature $t$/°C = $T$/K − 273.15. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

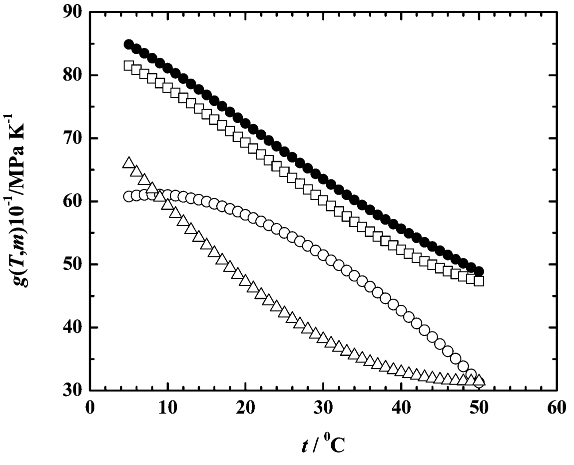

**Figure 15.** The change of molar heat capacity with volume of sodium sulfate solutions and pure water $g(T,m) = T(\partial^2P/\partial T^2)_{V,m} = (\partial C_V/\partial V)_{T,m}$ as a function of temperature $t$/°C = $T$/K − 273.15. ●, water; □, 0.1 mol·kg$^{-1}$; ○, 0.5 mol·kg$^{-1}$; △, 1.0 mol·kg$^{-1}$.

An addition of electrolyte to water is usually linked with the electrostriction of water in the vicinity of ions and changes in the water structure (hydrogen-bonding equilibrium among water molecules). These changes are also frequently expressed in terms

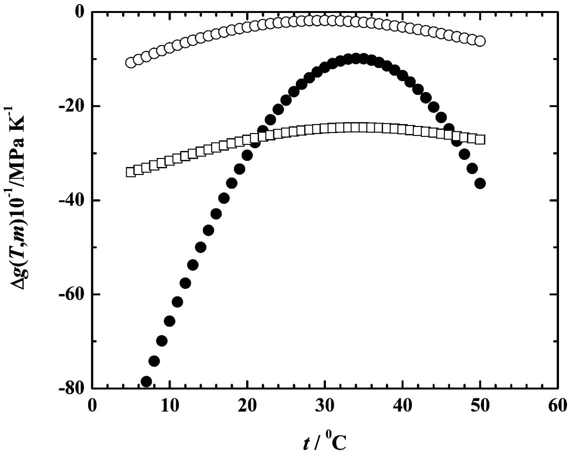

**Figure 16.** Differences in the change of molar heat capacities with volume of sodium carbonate solutions and pure water $\Delta g(T,m) = [\partial(C_V - C_{V,1})/\partial V]_{T,m}$ as a function of temperature $t$/°C = $T$/K − 273.15. ○, 0.1 mol·kg$^{-1}$; ●, 0.5 mol·kg$^{-1}$; □, 1.0 mol·kg$^{-1}$.

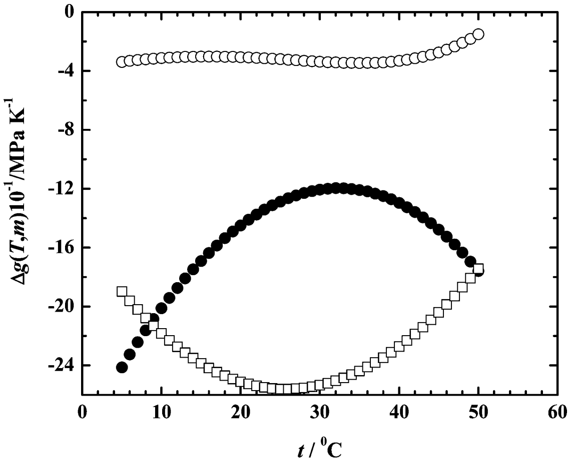

**Figure 17.** Differences in the change of molar heat capacities with volume of sodium sulfate solutions and pure water $\Delta g(T,m) = [\partial(C_V - C_{V,1})/\partial V]_{T,m}$ as a function of temperature $t$/°C = $T$/K − 273.15. ○, 0.1 mol·kg$^{-1}$; ●, 0.5 mol·kg$^{-1}$; □, 1.0 mol·kg$^{-1}$.

of the ion hydration.[46−52] With regard to compressibility properties, the maximum of sound velocity and the minimum of isothermal or adiabatic compressibilities are explained by various two-state models of pure water (mixture of a structured hydrogen-bonded liquid and an "ordinary" liquid). The equilibrium between different water species, which is temperature-dependent, produces at each temperature a different "composition" of water. Increase in temperature leads to the volume expansion but also to increase in the fraction of unassociated water molecules, that is, water behaves more and more like an ordinary unassociated liquid. These two processes are associated with the opposite temperature coefficients of sound velocity, and therefore, the extremal values represent the balance between them. Thus, the sound velocities as a function of temperature have the parabolic form and the compressibility coefficients an inverted parabolic form. The contraction effect resulting from the electrostatic fields of ions on surrounding water is responsible for the observed decrease in compressibility. This "electrostatic pressure" reduces the compressibility in the same way as an externally applied pressure does and produces an additional compression of water. An addition of electrolyte to water has the same effect as the application of an external pressure or raising the temperature in the case of pure water. The parabolic form of curves is preserved, but evidently, they are shifted depending on temperature and concentration. Thus, lower values of compressibility coefficients of electrolyte solutions result from two factors, the occurrence of more incompressible ions and the change of the water structure around of the ions. This reduction in compressibility is formally expressed by negative values of the apparent molar isentropic compressibilities $K_{2,\phi}(T,m)$, and these values permit comparison of different ions at different temperatures and concentrations. In an alternative treatment, a decrease in compressibility relates the ion−water interactions with the ion hydration. In this formulation, each ion is surrounded by a finite number of water molecules (in primary and secondary hydration shells), and it is assumed that some properties of the bulk water differ from those of water molecules which are in immediate contact with the ion. The hydration numbers of the electrolyte (or hydration numbers of constituent ions) can be estimated from different kinds of experiments (e.g., it is expected that compressibilities permit one to obtain primary and some secondary hydration), but the agreement between reported values is rather unsatisfactory.[49−52] In the case of compressibility measurements, the determination of the hydration numbers is frequently based on the assumption introduced by Passynski[53] that the water molecules in the hydration shells are compressed to their maximum extent by the electrical field of ions and only the bulk water is compressed by an external pressure. This molecular model leads to

$$\left(\frac{\partial V}{\partial P}\right)_{\mathrm{T}} \approx \frac{\partial}{\partial P}[V_1(n_1 - n_{1\mathrm{h}})] \qquad (32)$$

where $V$ is the volume of solution and $V_1$ is the molar volume of pure water. Numbers $n_1$ and $n_{1\mathrm{h}}$ denote moles of the total and hydrated water in the solution. In terms of the hydration numbers $h(T,m)$ and the isothermal compressibility coefficients $\kappa_{\mathrm{T},1}(T)$ and $\kappa_{\mathrm{T}}(T,m)$, eq 32 takes the form

$$h(T,m) = \frac{1000}{M_1 m}\left[1 - \frac{\kappa_{\mathrm{T}}(T,m)}{\kappa_{\mathrm{T},1}(T)}\left(\frac{\rho_1(T)}{\rho(T,m)}\right)\right] \qquad (33)$$

where the ratio of densities is usually omitted in dilute solutions.

Calculated from eq 33, hydration numbers at 298.15 K are $h(0.1\ \mathrm{mol \cdot kg^{-1}}) = 23.0$, $h(0.5\ \mathrm{mol \cdot kg^{-1}}) = 19.8$, and $h(1.0\ \mathrm{mol \cdot kg^{-1}}) = 17.2$ for sodium carbonate, and at infinite dilution, it is $h = 23.4$. The corresponding values for sodium sulfate are $h(0.1\ \mathrm{mol \cdot kg^{-1}}) = 23.9$, $h(0.5\ \mathrm{mol \cdot kg^{-1}}) = 20.5$, and $h(1.0\ \mathrm{mol \cdot kg^{-1}}) = 17.8$, and at infinite dilution, it is $h = 24.3$. The hydration numbers decrease with increasing concentration and temperature. If hydration numbers of ions at infinite dilution are assumed to be additive, then our $h$ values are consistent with those reported by Marcus[50,57] ($h(\mathrm{Na^+}) = 4$ to 8,[50] $h(\mathrm{CO_3^{2-}}) = 13.8$,[57] and $h(\mathrm{SO_4^{2-}}) = 7.2$ to 8[50,57]). However, the hydration numbers evaluated with the Passynski approach[53] were considered by Onori et al.[54] as incorrect (see also Afanasiev and Ustinov[55] and Afanasiev et al.[56]), and they proposed replacing them with those based on a quite different molecular model. However, hydration numbers derived in the Onori et al. approach are considerably larger than those reported in the literature. A similar situation exists also in our case; for example, for sodium sulfate solutions, Afanasiev and Ustinov[55] presented $h(0.1\ \mathrm{mol \cdot kg^{-1}}) = 55.3$, $h(0.45\ \mathrm{mol \cdot kg^{-1}}) = 45.3$, and, for the hydration number at infinite dilution, $h = 58.6$, that is, their $h$ values are more than twice larger than ours.

## Conclusions

Precise determination of the density and velocity of sound at closely spaced 1 K temperature intervals permitted thermodynamic analysis of volumetric and compressibility properties of aqueous solutions of sodium carbonate and sodium sulfate. Similarly as in the case of lithium chloride solutions,[6] it was found that the interpretation of the thermodynamic relation $-(\partial C_{\mathrm{P}}/\partial P)_{\mathrm{T,m}} = T(\partial^2 V/\partial T^2)_{\mathrm{P,m}}$, which was initiated by Hepler[44] in terms of the structure-making and the structure-breaking solutes, is consistent with the interpretation of the equivalent $(\partial C_{\mathrm{V}}/\partial V)_{\mathrm{T,m}} = T(\partial^2 P/\partial T^2)_{\mathrm{V,m}}$ relation. As a consequence, determination of volumetric properties (as a function of temperature at constant concentration) when combined with corresponding compressibility properties is able to give characterization of electrolytes dissolved in water. Sodium carbonate and sodium sulfate are both the structure-breaking solutes which have relatively large hydration numbers.

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