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Molar Volumes and Heat Capacities of Aqueous Solutions of Short-Chain Aliphatic Sodium Carboxylates at 25 °C

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ABSTRACT: Densities and isobaric heat capacities of the aqueous solutions of the sodium salts of the four smallest straight-chain aliphatic carboxylates: sodium methanoate (formate), ethanoate (acetate) *n*-propanoate, and *n*-butanoate have been measured at 25 °C and 0.1 MPa by vibrating-tube densimetry and Picker flow calorimetry, respectively. All systems were investigated at concentrations ranging from approximately 0.02 $\text{mol}\cdot\text{kg}^{-1}$ to near saturation, which extends the existing database to higher concentrations for all of these salts. Apparent molar isobaric heat capacities and volumes derived from the data were fitted with an extended Redlich−Meyer equation to determine the standard state partial molar quantities. At concentrations where comparisons were possible, the present results generally agreed well with previous determinations. An exception was the heat capacities of sodium formate solutions, where the present results at low solute concentrations appear to be influenced by an unidentified thermal effect. The apparent molar quantities, especially the heat capacities, provide indirect evidence of aggregation by the longer-chain aliphatic carboxylates at high concentrations.

1. INTRODUCTION

Molar volumes and heat capacities of electrolyte solutions in water are of considerable scientific interest because they provide insight into the nature of ion−ion−solvent interactions.[1] Such measurements usually focus on relatively dilute solutions to provide the requisite apparent molar quantities, Y_ϕ ($Y = V$ or C_p), for extrapolation to infinite dilution. This yields the standard partial molar quantities, Y_ϕ^∞ ($= \overline{Y}_2^0$), which reflect only ion−solvent interactions. The magnitudes of V_ϕ and $C_{p\phi}$ (and Y_ϕ^∞) for carboxylate salts are of special interest because their anions serve as simple models for the negatively charged sites in amino acids, peptides, and proteins.[2]

On the other hand, technological interest in apparent molar heat capacities and volumes, which are required for engineering calculations of heat and mass transfer, respectively, is usually focused on the higher concentrations typical of most practical applications. For example, the well-known Bayer process, used for the extraction of alumina from bauxitic ores, typically operates at ionic strengths (I_m) up to ca. 8 $\text{mol}\cdot\text{kg}^{-1}$. Thermodynamic modeling of such solutions requires characterization of all components up to these ionic strengths, for example, for the application of Young's rule to calculate the properties of multicomponent mixtures.[3] Low-molecular-weight straight-chain aliphatic sodium carboxylates, particularly formate and acetate, are of special importance in the Bayer process because they are major end-products of the alkaline degradation of the organic matter typically present in bauxitic ores.[4] They also serve as useful model compounds to represent the effects of high-molecular-weight organics on the physicochemical properties of process solutions.[3] Unfortunately, gaps and uncertainties in the available V_ϕ and $C_{p\phi}$ data for simple straight-chain aliphatic carboxylate salts have hampered the development of Bayer liquor models.[3]

Accordingly, this paper presents measurements of the densities and isobaric heat capacities of the aqueous solutions of the four smallest straight-chain sodium carboxylates: sodium methanoate (formate), NaOOCH, NaOFm; sodium ethanoate (acetate) $NaOOCCH_3$, NaOAc; *n*-propanoate, $NaOOCCH_2CH_3$, NaOPr; and *n*-butanoate, $NaOOC(CH_2)_2CH_3$, NaOBu. The concentration range studied was as wide as practicable, ranging from ∼0.02 $\text{mol}\cdot\text{kg}^{-1}$ up to near saturation. This enabled reliable estimation of Y_ϕ^∞ using an extended form of the Redlich−Meyer equation and, for most of the systems studied, expanded considerably the available database, especially for the heat capacities.

2. EXPERIMENTAL SECTION

2.1. Reagents and Solutions. Sodium formate (99+ %) and sodium propanoate (> 99 %) were obtained from Sigma-Aldrich, while sodium acetate (99.0 %) was from Ajax. All three salts were used as received apart from drying overnight at 80 °C under dynamic vacuum ($p \approx 10$ Pa). In contrast, because of the commercial unavailability of a solid of suitable purity, stock solutions of sodium butanoate were prepared by the neutralization of butanoic acid (Sigma, 99%) with carbonate-free NaOH(aq). As discussed below some solutions of NaOFm(aq) were also made in a similar manner. All solutions were prepared with degassed ultrapure water (Millipore Milli-Q system) by weight, using an analytical balance, with buoyancy corrections. After preparation, solutions were filtered (0.45 μm) and stored in Pyrex glass bottles (Schott, Germany). Occasional checks by inductively-coupled plasma optical emission spectroscopy

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(ICPOES) indicated measurable but negligible contamination by Si even after prolonged storage.

2.2. Instrumentation. The present system for the measurement of isobaric volumetric heat capacities, σ_p, and solution densities, ρ, has been described on a number of occasions,[5,6] so only a brief outline is presented here. The system consists of Pt−Rh vibrating-tube densimeter (Sodev, Canada, model 03-D) connected in series with a Pt−Rh Picker flow microcalorimeter (Sodev, model CP-Cpr). Solutions were peristaltically pumped into the calorimeter at a flow rate of ∼0.7 $\mathrm{mL \cdot min^{-1}}$ and then passed directly to the densimeter so that both σ_p and ρ are determined on the same sample at virtually the same time. Temperatures in the calorimeter and the densimeter were controlled to ± 5 mK, with a National Institute of Standards and Technology (NIST)-traceable accuracy of about ± 10 mK, using two separate thermostats (Sodev, model CT-L). A temperature increment of ∼0.13 K (straddling 25.00 °C) was used for the heat capacity measurements. All solutions were measured relative to water. For reasons discussed in detail elsewhere,[5] all heat capacities were obtained from "first leg" (solution vs solvent) measurements in the Picker calorimeter. The densimeter was calibrated using the known densities of water[7] and nitrogen (from the NIST Web site: http://webbook.nist.gov/cgi/fluid.cgi?ID=C7727379&Action=Page). The measurement accuracy was checked occasionally by comparing the apparent molar quantities determined for various NaCl(aq) solutions with those calculated from Archer's model.[8] All data were collected using a desktop computer and processed as described elsewhere.[6] At 25 °C the heat capacities are thought to have an accuracy of about 0.05 % and the densities ± 10 ppm. The uncertainty in the latter is slightly worse than the best achievable with this type of densimeter because of its articulation with the calorimeter.

2.3. Data Analysis. Solution densities, ρ, were calculated from:

$$\rho - \rho_{\mathrm{w}} = k(\tau^2 - \tau_{\mathrm{w}}{}^2) \qquad (1)$$

where τ is the average oscillation period, k the mechanical constant of the vibrating tube, and the subscript w denotes a pure water value. Density data were used to calculate apparent molar volumes via the usual relationship:

$$V_\phi = (M/\rho) - [10^3(\rho - \rho_{\mathrm{w}})/m\rho\rho_{\mathrm{w}}] \qquad (2)$$

where M ($\mathrm{g \cdot mol^{-1}}$) is the molar mass of the solute, m (mol solute·(kg solvent)$^{-1}$) is its concentration (molality), and the density of water was taken to be 0.997047 $\mathrm{g \cdot cm^{-3}}$ throughout.[7]

Isobaric volumetric heat capacities σ_p ($\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$) were obtained as described elsewhere[5] and converted to the desired massic values, c_p ($\mathrm{J \cdot K^{-1} \cdot g^{-1}}$) via:

$$c_p = \sigma_p/\rho \qquad (3)$$

Apparent molar isobaric heat capacities $C_{p\phi}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) were calculated in the usual manner:

$$C_{p\phi} = (M/c_p) + [10^3(c_p - c_{p\mathrm{w}})/m] \qquad (4)$$

with the heat capacity of water, $c_{p\mathrm{w}}$, taken to be 4.1813 $\mathrm{J \cdot K^{-1} \cdot g^{-1}}$ throughout.[7]

For convenience the apparent molar quantities, Y_ϕ ($Y = V$ or C_p) were fitted to an extended form of the Redlich−Meyer (eRM) equation:[1]

$$Y_\phi = Y_\phi{}^\infty + A_{\mathrm{Y}}m^{0.5} + B_{\mathrm{Y}}m + C_{\mathrm{Y}}m^{1.5} + D_{\mathrm{Y}}m^2 \qquad (5)$$

where $Y_\phi{}^\infty$ is the value of Y_ϕ at infinite dilution, which is equal to $\overline{Y}{}_2^0$, the standard partial molar quantity for the solute in water. Note that in eq 5 A_{Y} is the appropriate Debye−Hückel theory limiting slope,[9] while B_{Y}, C_{Y}, and D_{Y} are empirical parameters. This type of equation has been shown[5] to produce values of $Y_\phi{}^\infty$ that are in excellent agreement with those obtained using the more complicated Pitzer equations.[10] The eRM equations are also satisfactory for correlating Y_ϕ data at higher solute concentrations, although they are often less precise for this purpose than the Pitzer equations.[5]

Table 1. Experimental Densities ($\rho/\mathrm{g \cdot cm^{-3}}$), Apparent Molar Volumes ($V_\phi/\mathrm{cm^3 \cdot mol^{-1}}$), Massic Isobaric Heat Capacities ($c_p/\mathrm{J \cdot K^{-1} \cdot g^{-1}}$), and Apparent Molar Isobaric Heat Capacities ($C_{p\phi}/\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) of NaOAc(aq) at 25 °C and p = 0.1 MPa as a Function of Solute Molality ($m/\mathrm{mol \cdot kg^{-1}}$), with $m^{\mathrm{o}} = 1\ \mathrm{mol \cdot kg^{-1}}$

m/m^{o}	ρ	V_ϕ	c_p	$C_{p\phi}$
0.01999	0.997898	39.44	4.1765	72.6
0.02177	0.997982	39.04	4.1759	67.3
0.03988	0.998731	39.75	4.1713	76.5
0.04259	0.998856	39.48	4.1703	69.8
0.06003	0.999574	39.81	4.1655	68.4
0.06004	0.999577	39.78	4.1657	72.2
0.08011	1.000408	39.93	4.1607	76.6
0.08018	1.000417	39.87	4.1605	74.5
0.1002	1.001247	39.94	4.1553	75.4
0.1002	1.001255	39.86	4.1554	75.9
0.2500	1.007380	40.28	4.1181	82.6
0.4956	1.017133	40.69	4.0621	91.5
0.4998	1.017288	40.71	4.0608	90.8
0.9999	1.036136	41.33	3.9618	104.9
1.997	1.070477	42.19	3.8111	127.0
2.003	1.070589	42.22	3.8098	126.7
4.532	1.141590	43.84	3.5887	163.5

3. RESULTS AND DISCUSSION

The results obtained for the densities and isobaric heat capacities and the apparent molar quantities derived from them for the four systems studied are summarized in Tables 1 to 4 and Figures 1 to 4. The partial molar quantities, $\overline{Y}{}_2^0$, obtained for each salt via application of eq 5 to the Y_ϕ values are listed in Table 5, together with the empirical parameters B_{Y}, C_{Y}, and D_{Y}. For reasons that will become obvious (Section 3.4) the results for sodium formate solutions will be discussed last.

3.1. Sodium Acetate. The numerical values of the densities and isobaric heat capacities obtained for sodium acetate solutions at concentrations $0.02 \lesssim m/\mathrm{mol \cdot kg^{-1}} \lesssim 4.5$ are listed in Table 1, along with the apparent molar quantities calculated from them. The latter are also plotted, along with literature data, in Figure 1.

Apparent molar volumes for aqueous solutions of NaOAc have been reported on numerous occasions (Figure 1a). The present V_ϕ values accord well with many of the previous studies,[11−14] but extend to higher concentrations. The rather large spread among the literature V_ϕ values at lower concentrations (Figure 1a) is, unfortunately, common even for well-studied and uncomplicated electrolyte systems; it reflects the difficulty of determining $\rho - \rho_{\mathrm{w}}$ (cf. eq 2) with sufficient accuracy in dilute solutions, where

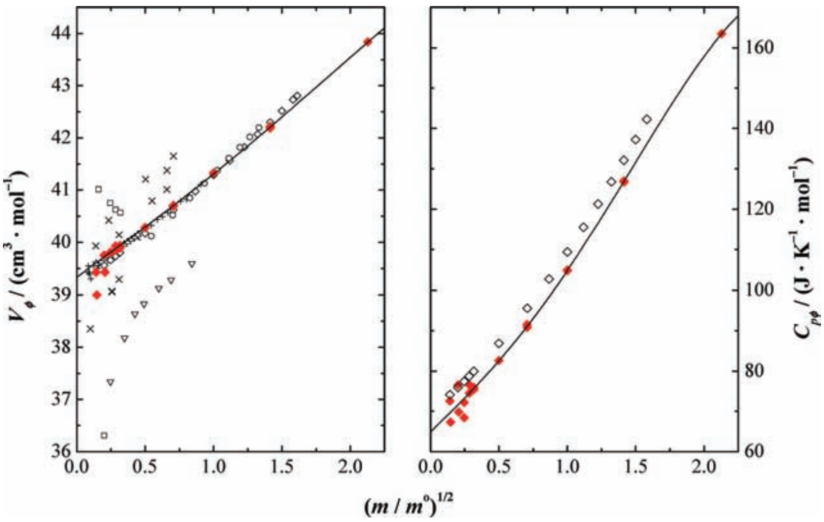

Figure 1. Apparent molar volumes (a) and apparent molar isobaric heat capacities (b) of NaOAc(aq) as a function of the square root of concentration at 25 °C and $p = 0.1$ MPa, together with literature data: red ◆, present work; □, ref 16; ○, ref 11; △, ref 14; ▽, ref 17; ◇, ref 13; ×, ref 15 (at $p = 0.35$ MPa); +, ref 12; —, extended Redlich-Meyer polynomials (eq 5).

Table 2. Experimental Densities (ρ/g·cm^{-3}), Apparent Molar Volumes (V_ϕ/cm^3·mol^{-1}), Massic Isobaric Heat Capacities (c_p/J·K^{-1}·g^{-1}), and apparent Molar Isobaric Heat Capacities ($C_{p\phi}$/J·K^{-1}·mol^{-1}) of NaOPr(aq) at 25 °C and p = 0.1 MPa as a Function of Solute Molality (m/mol·kg^{-1}), with m^o = 1 mol·kg^{-1}

m/m^o	ρ	V_ϕ	c_p	$C_{p\phi}$
0.01002	0.997478	52.99	4.1795	162.0
0.02029	0.997900	54.01	4.1771	164.0
0.04064	0.998740	54.35	4.1724	168.2
0.06027	0.999536	54.66	4.1680	170.3
0.08026	1.000385	54.33	4.1632	167.1
0.1002	1.001208	54.36	4.1588	169.2
0.1998	1.005242	54.63	4.1374	174.8
0.5005	1.016942	55.25	4.0780	184.2
0.7511	1.026374	55.44	4.0334	189.8
1.000	1.035327	55.71	3.9944	196.3
1.982	1.067677	56.50	3.8728	216.1
3.972	1.119872	58.08	3.7244	242.6
5.982	1.158323	59.59	3.6198	253.8
8.004	1.185887	61.05	3.5373	259.3

$\rho \rightarrow \rho_w$.[1] Interestingly, most of the divergent literature data (Figure 1a) are relatively recent determinations using vibrating-tube densimeters,[15−17] rather than the older pycnometric results,[11,12] which are usually thought to be less accurate.[1] Note that the small pressure difference between the data of Ballerat-Busserolles et al.,[15] measured at p = 0.35 MPa, and all the other studies, which were measured at p = 0.1 MPa, should be negligible at 25 °C.[18] The observed scatter in the independently determined V_ϕ values (Figure 1a) is a timely reminder that even such apparently straightforward measurements on a "well-behaved" system must be done with great care if reliable results are to be obtained.

In marked contrast to V_ϕ there appears to have been only one other modern study of the heat capacities of NaOAc(aq). The present values of $C_{p\phi}$ are systematically lower (Figure 1b) than that study,[13] also obtained by Picker flow calorimetry. However, the difference is only about 5 J·K^{-1}·mol^{-1}, which is probably within the realistic error limits of such measurements.[19]

3.2. Sodium *n*-Propanoate. Densities and isobaric heat capacities for NaOPr(aq), and the apparent molar quantities calculated from them, are summarized in Table 2; V_ϕ and $C_{p\phi}$ are plotted in Figure 2, along with the available literature data. The present concentration range of 0.01 $\lesssim m$/mol·kg^{-1} $\lesssim$ 8 considerably extends the existing database.

The V_ϕ values determined in this work for NaOPr(aq) are in good agreement with most previous studies (Figure 3a) especially ref 14, ref 20, and (at p = 0.35 MPa) ref 21. This agreement indicates that the earlier pycnometric data[11] for this system are somewhat low. The scatter in the data at low m is similar to, but somewhat smaller than, that observed for NaOAc(aq) (Figure 1a).

As for NaOAc(aq), there are far fewer literature data for $C_{p\phi}$ cf. V_ϕ available for NaOPr(aq) for comparison (Figure 2b). The present results are in quantitative agreement with those of McRae et al.[21] but differ significantly from the values of Rosenholm and Hepler,[22] especially at $m \lesssim 1$ mol·kg^{-1}.

3.3. Sodium *n*-Butanoate. Densities and heat capacities determined for NaOBu(aq) over the concentration range 0.02 $\lesssim m$/mol·kg^{-1} $\lesssim$ 6 are summarized in Table 3, along with the apparent molar quantities calculated from them.

The present values of V_ϕ (Figure 3a) are in good agreement with the older literature values[11] but differ (by ∼1 cm^3·mol^{-1}) at $m \lesssim 2$ mol·kg^{-1} from other studies.[20,21,23] At higher concentrations ($m \gtrsim 2$ mol·kg^{-1}) there is a marked discrepancy (of up to ∼4 cm^3·mol^{-1}) between the present results and those of Douhéret and Viallard,[20] the only other study that extends to very high concentrations. However, it may be noted that the present values for NaOBu at higher concentrations are broadly consistent with those obtained for NaOPr (compare Figures 2a and 3a).

The present $C_{p\phi}$ values are in good agreement (ca. ± 3 J·K^{-1}·mol^{-1}) with the only other study available,[21] measured at p = 0.35 MPa, but extend to much higher concentrations (Figure 3b). The curvature in $C_{p\phi}$ observed at very high concentrations ($m \gtrsim 3$ mol·kg^{-1}) in NaOBu(aq) is even more pronounced than that in NaOPr (Figure 2b). This is consistent

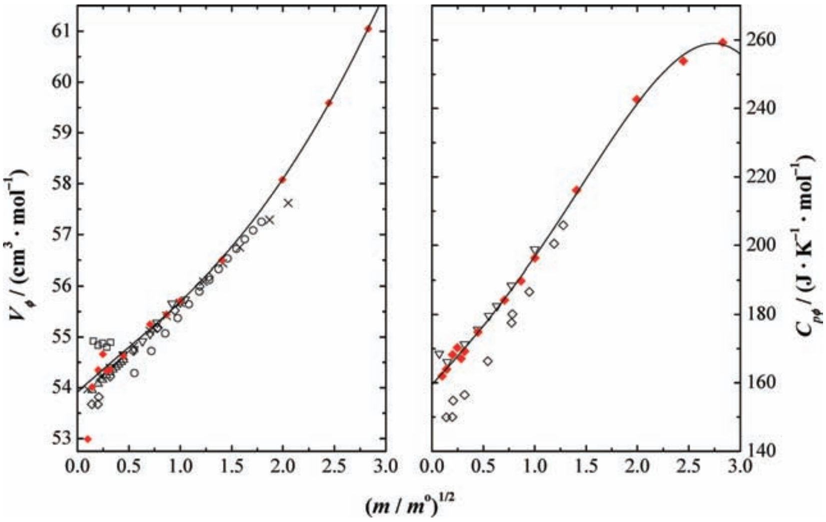

Figure 2. Apparent molar volumes (a) and apparent molar isobaric heat capacities (b) of NaOPr(aq) as function of the square root of concentration at 25 °C and p = 0.1 MPa, together with literature data: red ◆, this work; □, ref 16; ○, ref 11; △, ref 14; ×, ref 20; ◇, ref 22; ▽, ref 21 (at p = 0.35 MPa); —, extended Redlich−Meyer polynomials (eq 5).

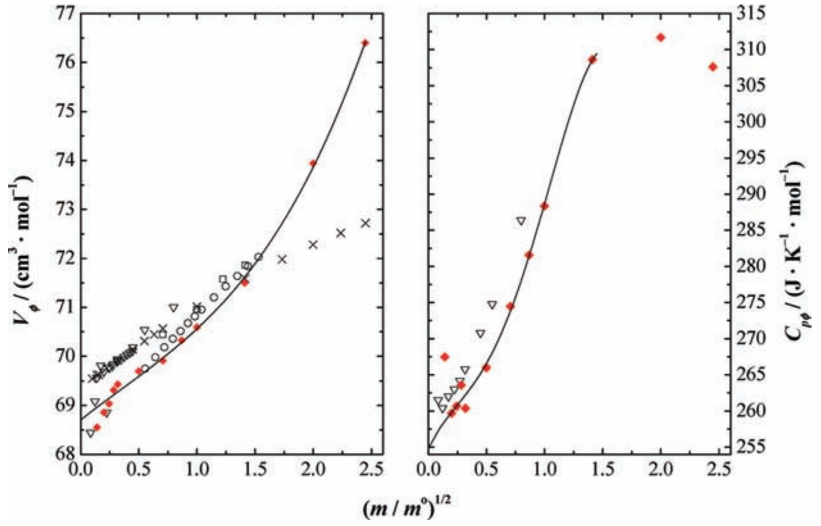

Figure 3. Apparent molar volumes (a) and apparent molar isobaric heat capacities (b) of NaOBu(aq) as function of the square root of concentration at 25 °C and p = 0.1 MPa, together with literature data: red ◆, this work; □, ref 23; ○, ref 11; △, ref 14; ▽, ref 21 (at p = 0.35 MPa); ×, ref 20; —, extended Redlich−Meyer polynomials (eq 5).

with micelle formation and/or ion clustering, which would be expected to be stronger for the more hydrophobic OBu$^-$(aq) ion.

3.4. Sodium Formate. The density data measured for NaOFm(aq) solutions at 25 °C over the concentration range $0.02 \lesssim m/\text{mol}\cdot\text{kg}^{-1} \lesssim 10$ are summarized in Table 4, along with the V_ϕ values derived from them, which are also plotted in Figure 4a together with the available literature data.

The present V_ϕ values are in excellent agreement with most of the previous studies.[14,24,25] The older values reported by Watson and Felsing[11] and the more recent ones of Chiemlewska et al.[16] are significantly lower and higher, respectively, than all of the other studies. Comparisons of the V_ϕ^∞ values for NaOFm(aq) with those obtained for the other systems studied here (Table 5) show a smooth dependence on anion chain length. Similar dependencies are interestingly also observed among the V_ϕ values at finite concentrations (Tables 1 to 4).

Unlike the volumetric data, and indeed all of the other data reported in this paper, the present isobaric heat capacities for NaOFm(aq) appear to be aberrant. For this reason no numerical values of $C_{p\phi}$ for sodium formate solutions are given in Table 4. Nevertheless, to assist in the discussion of the results obtained, the observed $C_{p\phi}$ values are plotted in Figure 4b along with unpublished results of Desnoyers et al.,[24] the only other $C_{p\phi}$ data that could be located for this system. At high concentrations ($m \gtrsim 2$ mol·kg^{-1}) the present data follow the trend of the results of Desnoyers et al.[24] but drop dramatically with decreasing concentration (Figure 4b).

These results are not only at variance with those of Desnoyers et al.[24] but also are quite implausible. None of the other carboxylate systems show such behavior, and the magnitude of $C_{p\phi}^\infty$ implied by the present data at low m is nonsensical. As a similar pattern does *not* occur in the V_ϕ data (Figure 4a) the

Table 3. Experimental Densities (ρ/g·cm^{-3}), Apparent Molar Volumes (V_ϕ/cm^3·mol^{-1}), Massic Isobaric Heat Capacities (c_p/J·K^{-1}·g^{-1}), and Apparent Molar Isobaric Heat Capacities ($C_{p\phi}$/J·K^{-1}·mol^{-1}) of NaOBu(aq) at 25 °C and p = 0.1 MPa as a Function of Solute Molality (m/mol·kg^{-1}), with m^o = 1 mol·kg^{-1}

m/m^o	ρ	V_ϕ	c_p	$C_{p\phi}$
0.01976	0.997868	68.55	4.1781	267.5
0.04005	0.998697	68.86	4.1739	259.7
0.06005	0.999507	69.04	4.1700	260.6
0.08053	1.000319	69.31	4.1662	263.6
0.1020	1.001172	69.43	4.1617	260.4
0.2495	1.006975	69.70	4.1347	266.0
0.4997	1.016488	69.91	4.0939	274.5
0.7508	1.025470	70.33	4.0579	281.6
1.000	1.034040	70.59	4.0269	288.4
1.993	1.064546	71.50	3.9339	308.6
4.000	1.109055	73.94	3.7690	311.7
5.997	1.136236	76.40	3.6301	307.6

Table 4. Experimental Densities (ρ/g·cm^{-3}) and Apparent Molar Volumes (V_ϕ/cm^3·mol^{-1}) of NaOFm(aq) at 25 °C and p = 0.1 MPa as a Function of Solute Molality (m/mol·kg^{-1}), with m^o = 1 mol·kg^{-1}

m/m^o	ρ	V_ϕ
0.02003[a]	0.997907	25.01
0.04064[a]	0.998753	25.95
0.06027[a]	0.999589	25.72
0.08026[a]	1.000449	25.49
0.1002[a]	1.001247	25.95
0.1998[a]	1.005363	26.11
0.5005[a]	1.017336	26.88
0.7500[a]	1.027242	26.89
1.008[a]	1.037006	27.24
2.576[a]	1.092067	28.40
3.968[a]	1.134814	29.25
6.036[a]	1.190197	30.17
8.011[a]	1.235127	30.93
10.011[a]	1.275624	31.43
0.02065[b]	0.997932	25.05
0.04058[b]	0.998750	25.94
0.06153[b]	0.999685	25.02
0.08098[b]	1.000466	25.66
0.1006[b]	1.001274	25.85
0.2500[b]	1.007389	26.32
0.5003[b]	1.017411	26.72
0.7507[b]	1.027174	27.02
1.000[b]	1.036614	27.32
2.000[b]	1.072425	28.17
4.000[b]	1.135381	29.34
5.998[b]	1.188906	30.22

[a] Stock solution prepared from NaOFm(s). [b] Stock solution prepared from formic acid and a ca. 1.3 mass % excess of NaOH(aq). Results corrected using Young's rule.[5] Note that numerical values for c_p and $C_{p\phi}$ are deliberately omitted (see text).

integrity of the solutions seems beyond question. Repeat measurements using an alternative source of NaOFm(s) and solutions prepared by neutralization of formic acid with NaOH(aq) gave essentially identical results (Figure 4b). Moreover, as the present calorimeter produced high quality data for all of the other systems studied, instrument malfunction seems unlikely.

A *possible* cause of these aberrant results is the presence of a temperature-sensitive chemical equilibrium, which is perturbed by the (small) temperature change required for the measurement of σ_p (densities, which are measured isothermally, would be unaffected). An effect of this nature occurs in the determination of $C_{p\phi}$ for Na_2CO_3(aq).[5] For that system the hydrolysis equilibrium:

$$CO_3^{\,2-}(aq) + H_2O \rightleftharpoons HCO_3^{\,-}(aq) + OH^-(aq) \qquad (6)$$

causes an "abnormal" increase in the observed $C_{p\phi}$ values at low concentrations. Computational correction for the hydrolysis or its suppression by the addition of NaOH(aq) returns the $C_{p\phi}$ (m) curve to its expected shape.[5]

For NaOFm(aq) the obvious candidate for a perturbing equilibrium is the hydrolysis:

$$OFm^-(aq) + H_2O \rightleftharpoons HOFm(aq) + OH^-(aq) \qquad (7)$$

However, the thermodynamic parameters for equilibrium 7 are similar to those of the other carboxylate ions investigated here, and this effect was not observed for them. Indeed, as formic acid is significantly stronger than the other straight-chain aliphatic carboxylic acids,[26] equilibrium 7 would be expected to have a *smaller* effect on the measured data. Nevertheless, to test for a possible effect from equilibrium 7, a slight excess (ie, beyond neutralization) of NaOH(aq) was added to NaOFm(aq) to suppress the anion hydrolysis. As previously,[5] allowance for the excess NaOH was made by application of Young's rule; however, no significant change in the measured values V_ϕ or $C_{p\phi}$ was observed (Figure 4).

Another possibility might be the ion-pairing equilibrium:

$$Na^+(aq) + OFm^-(aq) \rightleftharpoons NaOFm(aq) \qquad (8)$$

However, dielectric relaxation and potentiometric measurements indicate ion association is negligible in NaOFm(aq) and not significantly different from NaOAc(aq).[27]

While there is little doubt that the present values of $C_{p\phi}$ at $m \lesssim 2$ mol·kg^{-1} are aberrant, no plausible explanation presents itself. At this stage all that can be said is that there appears to be a formate-specific thermal effect associated with the dynamic measurement of σ_p in the Picker calorimeter. In this context it would be interesting to repeat these measurements in other Picker calorimeters and with other types of calorimeters (especially static ones) to resolve this anomaly. It is worth noting that a recent high precision conductivity study also reported anomalous (and uninterpretable) results for NaOFm(aq) solutions at low concentrations.[28]

3.5. General Comments. The present measurements have considerably extended the available database for V_ϕ and $C_{p\phi}$ to higher concentrations for all of the salts studied. Leaving aside the problematic $C_{p\phi}$ values for NaOFm(aq), a number of features of the data warrant comment.

First, the V_ϕ and $C_{p\phi}$ values show largely smooth variations with anion size. This is true at infinite dilution (Table 5), as might be expected, but persists up to solute concentrations as high as ca. 4 mol·kg^{-1} (Tables 1 to 4).

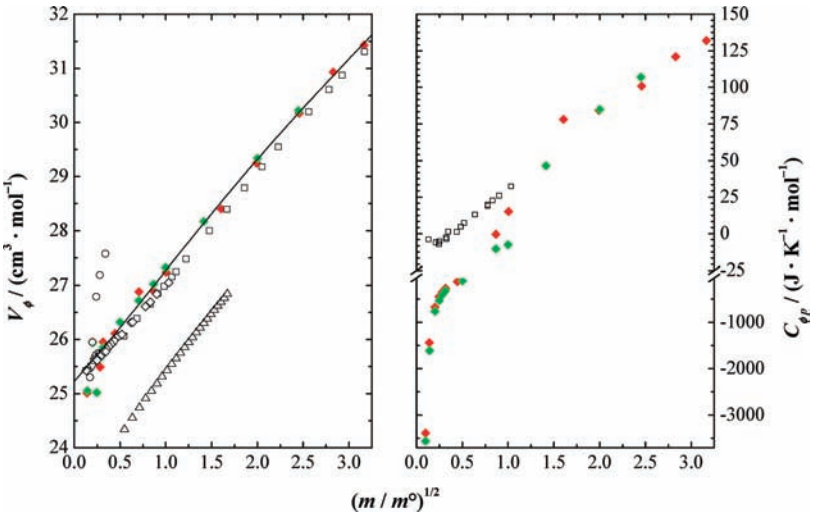

Figure 4. Apparent molar volumes (a) and apparent molar isobaric heat capacities (b) of NaOFm(aq) as function of the square root of concentration at 25 °C and $p = 0.1$ MPa, together with literature data: red ◆, this work, samples prepared from NaOFm(s) + H_2O; green ◆, this work, samples prepared from formic acid + NaOH(aq); ◇, ref 25 (V_ϕ); ○, ref 16; △, ref 11; ▽, ref 14; □, ref 24 ($C_{p\phi}$); —, extended Redlich−Meyer polynomial (eq 5; volumes only). Note that $C_{p\phi}$ values are unreliable (see text); also note the ordinate scale break for $C_{p\phi}$.

Table 5. Fitting Parameters for Equation 5 for Apparent Molar Volumes and Apparent Molar Isobaric Heat Capacities of Aqueous Solutions of Straight-Chain Aliphatic Sodium Carboxylates at 25 °C and p = 0.1 MPa[a]

	volumes		heat capacities	
NaOFm[b]	$V_\phi°$	25.127	$C_{p\phi}°$	
	B_V	0.535	B_C	
	C_V	−0.304	C_C	
	D_V	0.047	D_C	
NaOAc	$V_\phi°$	39.344	$C_{p\phi}°$	64.927
	B_V	0.001	B_C	1.207
	C_V	0.121	C_C	9.133
	D_V	−0.033	D_C	−3.152
NaOPr	$V_\phi°$	53.912	$C_{p\phi}°$	159.492
	B_V	−0.359	B_C	0.955
	C_V	0.297	C_C	5.521
	D_V	−0.031	D_C	−1.969
NaOBu	$V_\phi°$	68.703	$C_{p\phi}°$	254.830
	B_V	−0.373	B_C	−56.309
	C_V	0.354	C_C	93.480
	D_V	0.005	D_C	−36.067

[a] Note $X_\phi° = X_\phi^\infty$. Extra significant figures included for fitting purposes. [b] Model not fitted to heat capacities for NaOFm(aq) due to ambiguities in the data (see text).

Second, the spread of V_ϕ and $C_{p\phi}$ values among independent measurements of these relatively simple-to-determine properties is often quite large. At low concentrations this is mostly a reflection of the measurement difficulties as $y \rightarrow y_w$ ($y = \rho$ or σ_p; cf. eqs 2 and 4). In spite of these difficulties, the present estimations of the infinite dilution values of V_ϕ^∞ and $C_{p\phi}^\infty$ (Table 5), obtained from extrapolation of the experimental data via eq 5, are in good agreement with those tabulated by Marcus.[29] At higher concentrations, explanations for the sometimes large differences are less obvious: they probably reflect the presence of unsuspected impurities.

Third, if the V_ϕ and $C_{p\phi}$ values of NaOAc(aq) are taken as "normal" straight-chain aliphatic carboxylate ion behavior, then it is clear (Figures 1 to 3) that the larger straight-chain aliphatic carboxylate anions are very different at very high concentrations. Thus, whereas the values of Y_ϕ(NaOAc(aq)) show (Figure 1) a smooth, almost linear, dependence on $(m/m°)^{1/2}$, the corresponding curves (Figures 2 and 3, respectively) for NaOPr(aq) and NaOBu(aq) show increasingly strong variations with increasing $(m/m°)^{1/2}$, with V_ϕ curving upward and $C_{p\phi}$ even going through a maximum at very high concentrations. These features may be indicative of micelle formation and/or some type of ion clustering. Evidence for such effects has recently been obtained for these systems by dielectric relaxation spectroscopy.[27,30]

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