Apparent Molar Heat Capacities of Aqueous Solutions of Acetic, Propanoic and Succinic Acids, Sodium Acetate and Sodium Propanoate from 300 to 525 K and a Pressure of 28 MPa

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The apparent molar heat capacities of dilute aqueous solutions of acetic, propanoic and succinic acid and sodium salts of the two monofunctional acids were measured at 300 K < T < 525 K and p = 28 MPa. Corrections for ionization/ hydrolysis and relaxation effects were applied and the results were extrapolated to infinite dilution to calculate $C_{p,2}^o$. After subtracting the heat capacity of a point mass, the remaining heat capacity was successfully decomposed into functional group contributions at all temperatures. Together with the results of our previous paper on alcohols and diols[(2)] the heat capacity contributions of the CH_2, CH_3, OH, COOH, $(COOH)_2$, and COONa groups are now available and these allow reasonably accurate predictions of the heat capacities of all compounds composed of these groups in this temperature range.

1. INTRODUCTION

Estimation of the chemical potentials of organic solutes in aqueous solutions at temperatures above 398 K is important to an understanding of

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a variety of natural phenomenon; for instance, the transformation of natural hydrocarbon deposits at high temperatures, and the mineral formation in hydrothermal systems. In addition, there are many industrial processes in which the equilibria of organic species dissolved in hot water are of great importance; for instance, pH control in electric power boilers, and wet oxidation at both moderate and supercritical temperatures. Recent papers from this laboratory[1,2] reported the apparent molar volumes of a variety of organic solutes[1] and the heat capacities of alcohols and diols[2] in water at temperatures to 525 K and showed that group contribution methods were applicable from 300 to 525 K for both properties. This paper is the second of a series on the heat capacities of aqueous solutions of organic compounds at high temperatures. We report here the heat capacity of several carboxylic acids and sodium carboxylates and then explore the utility of decomposing these heat capacities into functional group contributions. These heat capacities allow the accurate calculation of the chemical potentials of compounds built with these groups from chemical potentials and entropies at $T = 298.15$ K.

2. EXPERIMENTAL

Acetic acid (Fluka guarantee, puriss p.a. >99.5%), propanoic acid (Fluka puriss p.a. >99.5%) and succinic acid (Fluka guarantee, puriss p.a. >99.5%) were used directly without further purification. Two stock aqueous solutions were prepared for acetic acid, propanoic acid, (target molalities 0.4 and 0.9 mol-kg^{-1}) and succinic acid (target molalities 0.15 and 0.25). The concentrations of these stock solutions were determined both by mass and by titration with a volumetric standard sodium hydroxide solution using phenolphthalein as indicator. Two titrations were made for each stock solution and the two titrations agreed to better than 0.12% for all acids. The average molalities obtained by the mass of the components were higher (by 0.4% to 1%), presumably due to small amounts of water in the acids. The accepted molalities given in Tables I–III were those obtained by titration.

Two stock aqueous solutions of sodium propanoate (target molalities 0.4 and 0.9) were prepared by mass from a sample (Fluka purum > 99%) carefully dried for four days in a vacuum oven at 50°C. On the basis of mass the molalities were 0.3948 and 0.8974.

The sodium acetate solution (0.1209 mol-kg^{-1}) was that prepared by Criss[1] using sodium acetate trihydrate (Aldrich 99+ %). The procedure described by Criss is: "A sample taken from the bottle was weighed and dried in a vacuum oven at 50°C over night. Mass loss was 39.709%. Theoretical mass loss for the trihydrate salt transforming to the anhydrous salt is 39.716%. Further heating for 24 hours at 150°C showed no further mass loss. Consequently it was

Table I. Apparent Molar Heat Capacities of Acetic Acid in Aqueous Solutions

$T(K)$	p^a	m^b	$c_{p,s}/c_{p,w}$	$C_{p,\Phi}^{exp\ c}$	α^d	$\Delta C_{p,\Phi}{}^e$	$C_{p,\Phi}{}^c$
303.08	28.11	0.4180	0.9923	169.7	0.0073	1.0	170.7
303.08	28.11	0.4180	0.9923	168.8	0.0073	1.0	169.8
303.08	28.08	0.4180	0.9920	166.2	0.0073	1.0	167.2
303.08	28.08	0.4180	0.9921	167.5	0.0073	1.0	168.5
303.08	28.04	0.8511	0.9848	169.8	0.0052	0.7	170.5
303.08	28.04	0.8511	0.9846	168.8	0.0052	0.7	169.5
303.08	28.04	0.8511	0.9843	167.0	0.0052	0.7	167.7
303.08	28.04	0.8511	0.9844	167.5	0.0052	0.7	168.2
374.27	27.90	0.4180	0.9947	195.5	0.0059	0.7	196.2
374.27	27.90	0.4180	0.9939	187.2	0.0059	0.6	187.8
374.27	27.86	0.8511	0.9873	184.8	0.0042	0.4	185.2
374.27	27.86	0.8511	0.9871	183.7	0.0042	0.4	184.1
448.26	28.02	0.4180	0.9952	207.4	0.0037	0.1	207.5
448.26	28.02	0.4180	0.9949	204.1	0.0037	0.1	204.2
448.26	28.01	0.4180	0.9948	202.8	0.0037	0.1	202.9
448.26	28.01	0.4180	0.9951	206.1	0.0037	0.1	206.2
448.26	28.02	0.8511	0.9895	201.8	0.0026	0.1	201.9
448.26	28.02	0.8511	0.9895	201.6	0.0026	0.1	201.7
448.26	28.02	0.8511	0.9889	198.9	0.0026	0.1	199.0
448.26	28.02	0.8511	0.9893	200.7	0.0026	0.1	200.8
523.64	28.04	0.4180	0.9953	224.0	0.0018	−0.2	223.8
523.64	28.04	0.4180	0.9954	224.6	0.0018	−0.2	224.4
523.64	28.03	0.4180	0.9952	223.3	0.0018	−0.2	223.1
523.64	28.03	0.4180	0.9950	221.1	0.0018	−0.2	220.9
523.64	28.04	0.8511	0.9908	224.7	0.0013	−0.1	224.6
523.64	28.04	0.8511	0.9901	220.5	0.0013	−0.1	220.4
523.64	28.05	0.8511	0.9903	221.8	0.0013	−0.1	221.7
523.64	28.05	0.8511	0.9906	223.7	0.0013	−0.1	223.6

^{a} Units: MPa.
^{b} Units: mol-kg^{-1}.
^{c} Units: J-K^{-1}-mol^{-1}.
^{d} Degree of ionization of the acid.
^{e} Correction to $C_{p,\Phi}^{exp}$ due to ionization and chemical relaxation.

assumed that the original salt contained insignificant surface water and other impurities. The anhydrous salt was used to make solutions".

The instrument and the experimental procedure used to measure the heat capacities of solutions have been described in detail by Carter and Wood[3] with some modifications due to Sharygin and Wood.[4] The apparent molar heat capacities were calculated from

$$C_{p,\Phi}^{exp} = C_{p,w}\{(M + 1/m)c_{p,s}/c_{p,w} - 1/m\} \tag{1}$$

Table II.   Apparent Molar Heat Capacities of Propanoic Acid in Aqueous Solutions[a]

T	p	m	$c_{p,s}/c_{p,w}$	$C_{p,\Phi}^{exp}$	α	$\Delta C_{p,\Phi}$	$C_{p,\Phi}$
303.08	28.02	0.4173	0.9947	250.8	0.0064	0.8	251.6
303.08	28.02	0.4173	0.9947	251.0	0.0064	0.8	251.8
303.08	28.02	0.4173	0.9945	249.0	0.0064	0.8	250.7
303.08	28.02	0.4173	0.9951	254.7	0.0064	0.9	255.6
303.13	28.03	0.8900	0.9891	250.8	0.0044	0.6	251.4
303.13	28.03	0.8900	0.9896	253.1	0.0044	0.6	253.7
303.13	28.03	0.8900	0.9896	253.2	0.0044	0.6	253.8
303.13	28.03	0.8900	0.9893	251.7	0.0044	0.6	252.3
373.85	27.83	0.4173	0.9954	260.9	0.0051	0.5	261.4
373.85	27.83	0.4173	0.9958	265.1	0.0051	0.5	265.6
373.85	27.83	0.4173	0.9955	261.6	0.0051	0.5	262.1
373.85	27.86	0.8900	0.9899	258.0	0.0035	0.4	258.4
373.85	27.86	0.8900	0.9900	258.5	0.0035	0.4	258.9
373.85	27.88	0.8900	0.9903	259.7	0.0035	0.4	260.1
373.85	27.88	0.8900	0.9903	260.0	0.0035	0.4	260.4
448.35	27.98	0.4173	0.9947	261.3	0.0031	0.0	261.3
448.35	27.98	0.4173	0.9948	262.7	0.0031	0.0	262.7
448.35	27.95	0.4173	0.9947	261.6	0.0031	0.0	261.6
448.35	27.95	0.4173	0.9952	267.0	0.0031	0.1	267.1
448.35	27.92	0.8900	0.9907	269.9	0.0022	0.0	269.9
448.35	27.92	0.8900	0.9904	268.2	0.0022	0.0	268.2
523.64	28.03	0.4173	· 0.9960	296.4	0.0016	−0.2	296.2
523.64	28.03	0.4173	0.9960	296.1	0.0016	−0.2	295.9
523.64	28.03	0.4173	0.9962	299.1	0.0016	−0.2	298.9
523.64	28.03	0.4173	0.9961	297.0	0.0016	−0.2	296.8
523.64	28.05	0.8900	0.9914	294.2	0.0011	−0.1	294.1
523.64	28.05	0.8900	0.9915	294.8	0.0011	−0.1	294.7
523.64	28.05	0.8900	0.9916	295.2	0.0011	−0.1	295.1
523.64	28.05	0.8900	0.9919	297.2	0.0011	−0.1	297.1

[a] For units and description of symbols see footnote Table I.

where $c_{p,s}$ and $c_{p,w}$ are the specific heat capacities ($J\text{-}K^{-1}\text{-}kg^{-1}$) of solution and water, respectively, M is the molecular weight of solute ($kg\text{-}mol^{-1}$) and m is the molality of the solution ($mol\text{-}kg^{-1}$). The ratio of specific heat capacities, $c_{p,s}/c_{p,w}$, is related to the ratio of powers in the heater by the relation

$$c_{p,s}/c_{p,w} = (\rho_w/\rho_s)_{TSL}\{1 + f(p_s - p_w)/p_w\} \tag{2}$$

where $(\rho_w/\rho_s)_{TSL}$ is the ratio of densities of water and solution at the temperature and pressure of the sample loop, f is the calibration factor for heat loss; and p_s and p_w are the powers that keep constant ΔT_{exp} when water is replaced by the solution in the sample cell.

Table III. Apparent Moral Heat Capacities of Succinic Acid in Aqueous Solutions[a]

T	p	m	$c_{p,s}/c_{p,w}$	$C_{p,\Phi}^{exp}$	α_1	$10^6\alpha_2$	$\Delta C_{p,\Phi}$	$C_{p,\Phi}$
303.13	28.01	0.1499	0.9908	227.7	0.0232	23	4.6	232.3
303.13	28.01	0.1499	0.9904	218.8	0.0232	23	4.4	223.2
303.13	28.01	0.1499	0.9910	235.7	0.0232	23	4.8	240.5
303.13	28.01	0.1499	0.9912	241.1	0.0232	23	4.9	246.0
303.13	28.02	0.2317	0.9860	230.2	0.0188	15	3.8	234.0
303.13	28.02	0.2317	0.9860	230.3	0.0188	15	3.8	234.1
303.13	28.02	0.2317	0.9861	231.5	0.0188	15	3.8	235.3
303.13	28.02	0.2317	0.9895	228.6	0.0188	15	3.7	232.3
373.84	27.85	0.1499	0.9925	278.6	0.0197	15	2.8	281.4
373.86	27.88	0.1499	0.9918	260.4	0.0197	15	2.5	262.9
373.86	27.88	0.1499	0.9923	272.8	0.0197	15	2.7	275.5
373.84	27.94	0.2317	0.9885	279.7	0.0160	10	2.3	282.0
373.84	27.94	0.2317	0.9881	270.9	0.0160	10	2.2	273.1
374.04	27.91	0.2317	0.9882	273.2	0.0160	10	2.2	275.4
374.04	27.91	0.2317	0.9881	272.0	0.0160	10	2.2	274.2
448.26	28.04	0.1499	0.9933	309.8	0.0118	6	0.3	310.1
448.26	28.04	0.1499	0.9931	304.8	0.0118	6	0.3	305.1
448.40	27.98	0.1499	0.9935	317.2	0.0118	6	0.4	317.6
448.40	27.96	0.1499	0.9927	294.1	0.0118	6	0.1	294.2
448.40	27.96	0.2317	0.9903	321.0	0.0096	4	0.3	321.3
448.40	27.96	0.2317	0.9897	311.1	0.0096	4	0.3	311.4
448.40	27.98	0.2317	0.9890	297.1	0.0096	4	0.1	297.2
448.40	27.96	0.2317	0.9896	308.9	0.0096	4	0.2	309.1
523.99	28.02	0.1499	0.9925	309.3	0.0047	1	−1.0	308.3
523.99	28.02	0.1499	0.9927	315.1	0.0047	1	−1.0	314.1
523.99	28.02	0.1499	0.9916	281.2	0.0047	1	−1.2	280.0
523.99	28.03	0.2317	0.9877	293.9	0.0038	1	−0.8	293.1
523.99	28.03	0.2317	0.9873	284.9	0.0038	1	−0.9	284.0
523.99	28.03	0.2317	0.9881	300.9	0.0038	1	−0.8	300.1

[a] For units and description of symbols see footnotes Table I.

The calibration factor for heat loss f in Eq. (2) was determined by changing (with an auxiliary ISCO pump) the base flow rate in the sample cell in order to mimic a change in heat capacity. The resulting values of f have been reported by Inglese and Wood.[2]

The temperature rise of the liquid in the sample cell, ΔT_{exp}, was determined by measuring the temperatures after the sample cell heater, before and after turning on the heater. The temperature reported is $T(block) + (1/2)\Delta T_{exp}$. The ratio of densities, Eq. (2), at the temperature and pressure of the sample loop $(\rho_w/\rho_s)_{TSL}$ was calculated as follows. For the two acetic acid aqueous solutions ($m = 0.4180$ and 0.8511) the density results obtained by Majer[5] were used; the values of $(\rho_w/\rho_s)_{TSL}$ were 0.9968 and 0.9937. The densities

of the aqueous solutions of propanoic acid and succinic acid at 298.15 K and 28.0 MPa were calculated from the apparent molar volumes V_Φ determined by Criss[1] for aqueous solutions of molalities 0.1180 (propanoic acid) and 0.1209 (succinic acid). V_Φ was assumed constant in the investigated range of concentration. The values of $(\rho_w/\rho_s)_{TSL}$ obtained at 298.15 K and 28.0 MPa were: 0.9977 ($m = 0.4173$), 0.9953 ($m = 0.8900$) for propanoic acid, and 0.9948 ($m = 0.1499$), 0.9921 ($m = 0.2317$) for succinic acid. In the same way the densities of the two aqueous solutions of sodium propanoate at 298.15 K and 28.0 MPa were calculated, from the apparent molar volume determined by Criss[1] for a solution of molality 0.1197. The calculated values of $(\rho_w/\rho_s)_{TSL}$ were: 0.9848 ($m = 0.3948$) and 0.9670 ($m = 0.8974$). For the sodium acetate aqueous solution the density results obtained by Criss were used ($m = 0.1208$, $(\rho_w/\rho_s)_{TSL} = 0.9951$).

At high enough temperatures it is expected that aqueous solutions of these compounds will decompose. Criss and Wood[1] have measured the densities of aqueous solutions of all the present compounds except acetic acid. They report no detectable decomposition at 523 K using GCMS analysis of the exit stream. At each temperature the calorimeter was tested by measuring the heat capacity of NaCl aqueous solution of molality 3.0007. The experimental results obtained for this solution were in satisfactory agreement with the earlier measurements[2] and the literature results.[6]

3. RESULTS

The ratio of specific heat capacities $c_{p,s}/c_{p,w}$ [Eq. (2)] and the experimental apparent molar heat capacities $C_{p,\Phi}^{exp}$ [Eq. (1)] at constant pressure for aqueous solutions of acetic acid, propanoic acid, succinic acid, sodium acetate, and sodium propanoate are given in Tables I–V, respectively. Results obtained when the calorimeter occasionally exhibited a noisy baseline are not reported. Values of $C_{p,\Phi}^{exp}$ were calculated using initial and final baselines, and both are reported in Tables I–V. When the baseline shift was large (≥ 12 J-K^{-1}-mol^{-1} for a 0.4m solution), only values that agreed with the other measurements were reported. Because the ionization/hydrolysis reactions of carboxylic acids and carboxylate ions might make appreciable contributions to $C_{p,\Phi}^{exp}$ at the conditions of our measurements, we applied corrections due to these reactions and also due to a chemical relaxation effect.[7] Calculated corrections, $\Delta C_{p,\Phi}$, the degree of dissociation (for acids) or hydrolysis (for carboxylate ions), α, and the final corrected apparent molar heat capacity $C_{p,\Phi}$ are reported in Tables I–V. The method of calculating the corrections is described in detail in the Appendix. The corrections were found usually to be small. The resulting

Table IV. Apparent Molar Heat Capacities of Sodium Acetate in Aqueous Solutions[a]

T	p	m	$c_{p,s}/c_{p,w}$	$C_{p,\Phi}^{exp}$	α	$\Delta C_{p,\Phi}^{b}$	$C_{p,\Phi}$
303.13	27.96	0.1209	0.9929	93.1	0.0013	0.2	93.3
303.13	27.96	0.1209	0.9933	105.9	0.0013	0.2	106.1
303.13	27.96	0.1209	0.9931	100.9	0.0013	0.2	101.1
303.13	27.96	0.1209	0.9928	89.5	0.0013	0.2	89.7
373.84	27.94	0.1209	0.9933	108.8	0.0014	−0.1	108.7
373.84	27.93	0.1209	0.9934	111.2	0.0014	−0.1	111.1
373.84	27.93	0.1209	0.9934	112.4	0.0014	−0.1	112.3
448.27	28.02	0.1209	0.9931	105.4	0.0027	−1.6	103.8
448.27	28.02	0.1209	0.9926	87.9	0.0027	−1.6	86.3
448.27	28.02	0.1209	0.9927	90.6	0.0027	−1.6	89.0
448.27	28.02	0.1209	0.9921	68.2	0.0027	−1.7	66.5
523.28	28.08	0.1209	0.9878	−93.0	0.0075	−4.0	−97.0
523.28	28.08	0.1209	0.9874	−106.3	0.0075	−4.1	−110.4
523.28	28.08	0.1209	0.9878	−92.2	0.0075	−4.0	−96.2
523.28	28.08	0.1209	0.9876	−99.9	0.0075	−4.0	−103.9

[a] For units see Table I.
[b] Correction to $C_{p,\Phi}$ due to hydrolysis and chemical relaxation.

apparent heat capacities for acids were used to calculate the infinite dilution partial molar heat capacities by

$$C_{p,\Phi} = C_{p,2}^{o} + b(1 - \alpha)m \qquad (3)$$

to get the values of the partial molar heat capacity at infinite dilution, $C_{p,2}^{o}$, its estimated uncertainty, and the slope b (see Table VI). The Pitzer ion-interaction treatment[8] with $\beta_C^{(1)} = 0$ was used for the extrapolation of the heat capacities of sodium 1-1 salts

$$C_{p,\Phi} = C_{p,2}^{o} + (A_J/1.2) \ln(1 + 1.2\sqrt{I}) + 2RT\beta_C^{(o)}(1 - \alpha)m \qquad (4)$$

where $I = (1/2)\Sigma_i m_i z_i^2$ is the ionic strength (m_i and z_i are the actual molality and charge of ion i, respectively), A_J is the Debye-Hückel limiting slope (calculated here from Archer and Wang[14] with water properties given by Hill's equation of state[9]) and $\beta_C^{(o)}$ is a constant. Fitting our data to Eq. (4) we found that the estimated 95% confidence limits of $\beta_C^{(o)}$ were always larger than the value itself and the fits were essentially the same with or without this parameter; therefore, we decided to set $\beta_C^{(o)} = 0$ in all extrapolations. Resulting infinite dilution partial molar heat capacities of sodium acetate and propanoate and their estimated uncertainties are given in Table VII.

To compare our data with some previous experiments, we considered $C_{p,2}^{o}$ at 298.15 K and $p = 0.1$ MPa for two of our compounds. In the recent

Table V. Apparent Molar Heat Capacities of Sodium Propanoate in Aqueous Solutions[a]

T	p	m	$c_{p,s}/c_{p,w}$	$C_{p,\phi}^{exp}$	α	$\Delta C_{p,\phi}$	$C_{p,\phi}$
303.02	27.97	0.3948	0.9809	188.7	0.0006	0.2	188.9
303.02	27.97	0.3948	0.9813	192.8	0.0006	0.2	193.0
303.02	27.97	0.3948	0.9815	195.2	0.0006	0.2	195.4
303.02	27.97	0.3948	0.9811	190.1	0.0006	0.2	190.3
303.00	27.93	0.8974	0.9624	207.9	0.0003	0.1	208.0
303.00	27.93	0.8974	0.9627	209.1	0.0003	0.1	209.2
303.02	27.96	0.8974	0.9615	203.1	0.0003	0.1	203.2
303.02	27.96	0.8974	0.9626	208.6	0.0003	0.1	208.7
303.00	28.06	0.8974	0.9626	208.6	0.0003	0.1	208.7
303.00	28.06	0.8974	0.9621	206.5	0.0003	0.1	206.6
373.81	27.88	0.3948	0.9816	198.8	0.0007	−0.1	198.7
373.81	27.88	0.3948	0.9823	206.4	0.0007	0.0	206.4
374.35	27.93	0.3948	0.9807	188.3	0.0007	−0.1	188.2
374.35	27.93	0.3948	0.9813	195.4	0.0007	−0.1	195.3
373.81	27.94	0.8974	0.9637	216.7	0.0004	−0.1	216.6
373.81	27.94	0.8974	0.9638	217.1	0.0004	−0.1	217.0
373.81	27.90	0.8974	0.9632	214.4	0.0004	−0.1	214.3
373.81	27.90	0.8974	0.9639	217.5	0.0004	−0.1	217.4
374.35	27.94	0.8974	0.9642	219.5	0.0004	−0.1	219.4
374.35	27.94	0.8974	0.9635	215.7	0.0004	−0.1	215.6
448.27	28.00	0.3948	0.9765	147.3	0.0017	−1.1	146.2
448.27	28.00	0.3948	0.9767	148.7	0.0017	−1.1	147.6
448.26	27.95	0.3948	0.9770	152.1	0.0017	−1.0	151.1
448.26	27.95	0.3948	0.9761	142.2	0.0017	−1.1	141.1
448.26	28.10	0.8974	0.9528	166.8	0.0011	−0.7	166.1
448.26	28.10	0.8974	0.9531	168.3	0.0011	−0.7	167.6
448.26	28.00	0.8974	0.9537	171.4	0.0011	−0.7	170.7
448.26	28.00	0.8974	0.9542	173.9	0.0011	−0.7	173.2
523.99	27.98	0.3948	0.9655	24.5	0.0046	−2.1	22.4
523.99	27.98	0.3948	0.9661	31.8	0.0046	−2.0	29.8
523.99	27.98	0.3948	0.9657	27.8	0.0046	−2.0	25.8
523.99	27.98	0.3948	0.9658	28.8	0.0046	−2.0	26.8
523.99	27.99	0.8974	0.9335	72.2	0.0031	−1.2	71.0
523.99	27.99	0.8974	0.9339	74.0	0.0031	−1.2	72.8
523.99	27.99	0.8974	0.9339	74.2	0.0031	−1.2	73.0
523.99	27.99	0.8974	0.9336	72.5	0.0031	−1.2	71.3

[a] For units and description of symbols see Table I.

review, Hepler and Hovey[22] state $C_{p,2}^o = 170$ J-K^{-1}-mol^{-1} for acetic acid and $C_{p,2}^o = 68$ for sodium acetate, which is in excellent and reasonable agreement, respectively, with our extrapolations at 303 K and $p = 28$ MPa ($C_{p,2}^o = (169 \pm 4)$ for acetic acid and 88 ± 12 for sodium acetate).

Table VI. Standard Apparent Molar Heat Capacities of Acetic, Propanoic, and Succinic Acids in Aqueous Solutions[e]

T	p	$C^{\circ}_{p,2}$	b^a	Δ^b
		Acetic acid		
303.08	28.07	169 ± 4^c	0	-2
374.27	27.88	199 ± 28	-16	-9
448.26	28.02	209 ± 5	-10	0
523.64	28.04	224 ± 5	-1	0
		Propanoic acid		
303.10	28.02	252 ± 5	1	3
373.85	27.86	266 ± 5	-8	0
448.35	27.95	258 ± 8^d	12	18
523.64	28.04	298 ± 4	-3	0
		Succinic acid		
303.13	28.01	237 ± 30	-13	-1
373.87	27.90	267 ± 33	40	2
448.35	27.98	301 ± 41	38	-3
523.99	28.02	312 ± 78	-88	2

[a] Eq. (3).
[b] Difference between $C^{\circ}_{p,2}$ calculated from functional group additivity scheme, Eq. (7), and experimental value of $C^{\circ}_{p,2}$.
[c] The uncertainties are estimated 95% confidence limits of $C^{\circ}_{p,2}$ from the fit.
[d] This value of $C^{\circ}_{p,2}$ was excluded from the functional group evaluation.
[e] For units see Table I.

Table VII. Standard Apparent Molar Heat Capacities of Sodium Acetate and Sodium Propanoate in Aqueous Solutions

T	p	$C^{\circ}_{p,2}$	Δ^a
		Sodium acetate	
303.13	27.96	88 ± 12^b	8
373.84	27.93	95 ± 5	2
448.27	28.02	50 ± 30^c	-19
523.28	28.08	-186 ± 21^c	2
		Sodium propanoate	
303.01	27.98	183 ± 5	-1
374.00	27.92	177 ± 6	-4
448.26	28.00	97 ± 9^c	3
523.99	27.98	-109 ± 13^c	-2

[a] Δ is the difference between $C^{\circ}_{p,2}$ calculated from functional group additivity scheme, Eq. (7), and experimental value of $C^{\circ}_{p,2}$.
[b] The uncertainties are estimated 95% confidence limits of $C^{\circ}_{p,2}$ from the fit.
[c] Due to the neglect of the second virial coefficient in the extrapolation, extra uncertainties ($\pm$ 5 at $T = 448$ K and $\pm$ 10 at $T = 523$ K) were added to the 95% confidence limits.

It has been shown in the two previous papers from this laboratory[1,2] that functional group methods work quite well for V_2^0 and $C_{p,2}^o$ at temperatures to 525 K. The functional group equation is

$$C_{p,2}^o = \upsilon C_{p,\Phi}(\text{std. state}) + \sum_j n_j C_j \tag{5}$$

where υ is the number of particles (1 for a nonelectrolyte, 2 for a 1 $-$ 1 electrolyte . . .), $C_{p,\Phi}(\text{std. state})$ is the standard state heat capacity of a single particle, and C_j is the contribution to the heat capacity of the functional group j. The standard state heat capacity is the partial molar heat capacity produced by adding a point mass to a kg of solution at constant pressure[10–12]

$$C_{p,\Phi}(\text{std. state}) = 2RT\alpha_w + RT^2(\partial\alpha_w/\partial T)_p + (3/2)RT \tag{6}$$

where $\alpha_w = (1/V)(\partial V_m/\partial T)_p$ for pure water. After some trial runs, the temperature dependence of the functional group parameters C_j was set to a different form than the quadratic function used for alcohols.[2] The final form for prediction of $C_{p,2}^o$ was

$$C_{p,2}^o = \upsilon\{2RT\alpha_w + RT^2(\partial\alpha_w/\partial T)_p + (3/2)RT\} \tag{7}$$

$$+ \sum_j n_j[a_j + b_j T + c_j/\{T - 800\}^2]$$

Table VIII gives the functional group parameters resulting from a weighted least-squares fit of Eq. (7) to the present values of $C_{p,2}^o$ of all acids and carboxylates, together with the previous values for alcohols and diols at 28 MPa.[2] After discarding one measurement (propanoic acid at 448 K), the average $[C_{p,2}^o(\text{exp}) - C_{p,2}^o(\text{calc})]/\sigma$ was 0.56 and the maximum was 1.9. The average relative error was 2.6%, which was mainly due to the high relative error in the sodium acetate measurement at 448 K. Nevertheless the estimated uncertainty of this particular measurement is large, and it is higher than the calculated deviation (the average relative error without this point is 1.3% and the changes in regression parameters are negligible). The fit was clearly

Table VIII. Functional Group Parameters in Eq. (7)

Group j	a_j	b_j	$10^6 c_j$
CH$_2$	142.4	−0.245345	4.613676
CH$_3$	310.4	−0.685317	14.554561
COOH	−265.1	1.130190	−22.535267
(COOH)$_2$	−219.9	1.130164	−19.563661
COONa	−399.1	2.138357	−87.583863
OH	−139.7	0.591111	−11.631665

better than that with the quadratic temperature function used in the previous paper.[2] The reason for separate evaluation of the $(COOH)_2$ group was the important improvement of the fit, compared to evaluation of a COOH group only. This indicates nonnegligible steric and/or near neighbor effects in succinic acid, which presumably become large as the alkyl chain becomes shorter. Unfortunately, not enough data are available to unambiguously establish this effect. For diols with longer chain this effect was found to be much less than the experimental uncertainty. Cabani et al.[21] found at 298 K that many compounds with two or more functional groups required extra parameters to accurately fit the experimental data. We find corrections for two COOH groups are large while corrections for two OH groups are small whereas Cabani et al. find the opposite. Clearly results on more compounds are needed. Deviations of the calculated values of $C_{p,2}^o$ from experimental values for alcohols and diols are given in Table IX, which shows the general improvement of these calculations compared to the previous results.[2] Figure 1 displays the group contributions C_j as a function of temperature. The curves for CH_2, CH_3, and OH groups agree well with those in the previous paper.[2] Decreasing trends of C_j at high temperatures for the two new polar groups, COOH and $(COOH)_2$, are very similar to that of the OH group and are in

Table IX. Standard Apparent Molar Heat Capacities of 1-Propanol, 1,4-Butanediol, and 1,6-Hexanediol in Aqueous Solutions[c]

T	p	$C_{p,2}^o$	Δ^a
		1-Propanol	
374.32	27.96	326 ± 13^b	0(-19)
448.22	28.02	321 ± 9	0(-10)
523.37	28.07	358 ± 8	0(4)
		1,4-Butanediol	
302.99	28.02	351 ± 5	1(2)
373.85	27.85	363 ± 6	-2(3)
448.35	28.01	370 ± 7	1(2)
523.39	28.03	389 ± 22	-6(-10)
		1,6-Hexanediol	
302.99	28.04	508 ± 25	17(18)
374.30	27.81	522 ± 11	-9(-18)
448.22	28.02	499 ± 12	11(4)
523.30	28.08	534 ± 19	-3(6)

[a] Δ is the difference between $C_{p,2}^o$ calculated from functional group additivity scheme, [Eq. (7),] and experimental value of $C_{p,2}^o$ numbers in parenthesis are differences calculated in the previous paper.[2]
[b] The uncertainties are estimated 95% confidence limits of $C_{p,2}^o$ from the fit.
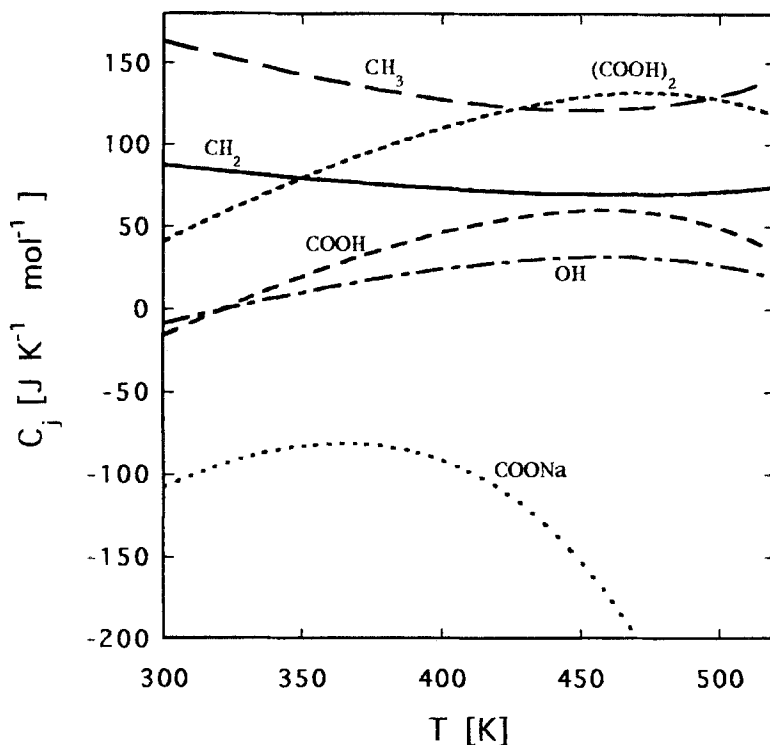[c] For units see Table I.

Fig. 1. Functional group heat capacities, C_j, as a function of temperature.

agreement with theory.[13] The difference between COOH and $(COOH)_2$ group contributions is quite large. However, the 95% confidence limits of the $(COOH)_2$ group are also large, because the $(COOH)_2$ group was evaluated from the measurements of a single compound. As a result the 95% confidence intervals of the COOH and $(COOH)_2$ group contributions are in touch. The COONa group is composed of two ionic functional groups (Na^+ and COO^-). For this group the decrease of C_j with temperature is as expected from the long-range attractive forces between the ions and water.[13] Figure 2 (the plot of the calculated $C_{p,2}^o$ against the experimental value) gives an overall indication of the accuracy of our fit. Figure 2 indicates that reasonably accurate predictions of $C_{p,2}^o$ at temperatures up to 525 K may be obtained with Eq. (7) for alcohols, polyols, mono- and polyfunctional carboxylic acids and sodium carboxylates. The accuracy of the predictions should be slightly less than the precision of our fit, with a little less accuracy in the case of polyfunctional compounds and compounds with strong steric and/or near neighbor effects.
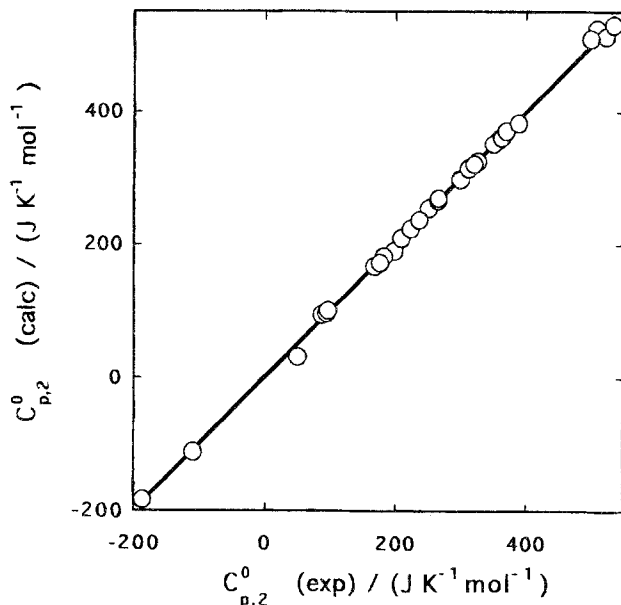
Fig. 2. Plot of $C_{p,2}^o$ calculated from functional group additivity, Eq. (7), *vs.* $C_{p,2}^o$ experimental.

ACKNOWLEDGMENT

APPENDIX

The weak electrolytes treated in this study dissociate or hydrolyze to an appreciable extent at experimental conditions and the ions contribute to the measured heat capacities. Another contribution to the experimental values comes from "chemical relaxation" effect caused by a shift in the degree of reaction due to the temperature increment in the course of measuring the heat capacity. As an example of these reactions we can write the acid ionization

$$HA \rightleftharpoons H^+ + A^-$$

<div align="right">(A1)</div>

and carboxylate ion hydrolysis

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{A2}$$
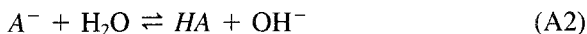
Following Woolley and Hepler,[7] the apparent molar heat capacity for reaction (A1) is expressed by

$$C_{p,\Phi}^{exp} = C_{p,\Phi}^{sp} + \Delta C_p^{rel} = (1 - \alpha)C_{p,\Phi}(HA) + \alpha[C_{p,\Phi}(H^+) \tag{A3}$$

$$+ C_{p,\Phi}(A^-)] + \Delta H_r(\partial\alpha/\partial T)_p$$

where $C_{p,\Phi}^{sp}$ is the sum of the heat capacities of all species, $\Delta C_p^{rel} = \Delta H_r(\partial\alpha/\partial T)_p$ is the relaxation contribution and ΔH_r is the reaction enthalpy. Because the degree of ionization is generally small, ion concentrations are also low, and Pitzer's equation[8] with only the first term can be adopted as an excellent approximation

$$C_{p,\Phi}(H^+) + C_{p,\Phi}(A^-) = C_{p,2}^o(H^+) + C_{p,2}^o(A^-) + \upsilon|z_H z_A|(A_J/2.4)(1 + 1.2\sqrt{I}) \tag{A4}$$

$$\Delta H_r = \Delta H_r^o + \upsilon|z_H z_A|(A_H/2.4)(1 + 1.2\sqrt{I}) \tag{A5}$$

where υ is the stoichiometric sum of the number of ions, A_J and A_H are the Debye-Hückel limiting slopes, calculated from Archer and Wang's equation[14] and the Hill equation of state for water.[9] Calculations of the heat capacities of ions at infinite dilution were performed using temperature interpolations of the data at $p = 28$ MPa for HCl (Sharygin[15]) and NaCl (Archer[6]). Simonson's[16] results for NaOH at the pressure $p = 7$ MPa were corrected to $p = 28$ MPa using the equation $(\partial C_{p,2}^o/\partial p)_T = -T(\partial^2 V_2^o/\partial T^2)_p)$. For all the compounds included in this study, we used the group contribution estimate from Eq. (7), with initial values calculated without any corrections for ionization or hydrolysis. Reaction enthalpies at infinite dilution were calculated from

$$\Delta H_r^o(T_o, p) = \Delta H_r^o(T_o, p_o) + \int_{p_o}^{p} \left[\Delta V_r^o(T_o, p_1) - T_o\left(\frac{\partial\Delta V_r^o(T_o, p_1)}{\partial T}\right)_p \right] dp_1 \tag{A6}$$

$$\Delta H_r^o(T, p) = \Delta H_r^o(T_o, p) + \int_{T_o}^{T} \Delta C_{p,r}^o(T_1, p)dT_1 \tag{A7}$$

where $T_o = 298.15$ K, $p_o = 0.1$ MPa, $\Delta V_r^o(T_o, p_1)$ is the volume change of reaction at standard temperature, approximated here by the average of these volumes at $p = 0.1$ MPa (calculated from volumetric data of Høiland[17])

and $p = 28$ MPa (taken again from Sharygin,[15] Archer,[6] and Simonson *et al.*[16] for HCl, NaCl and NaOH), and from Criss[1] for our compounds. $\Delta C_{p,r}^{o}(T_1, p)$ is the change of heat capacity of the reaction at $p = 28$ MPa. For all reactions, $\Delta H_r^o(T_o, p_o)$ was taken from Robinson and Stokes,[18] except that for water dissociation (Olofsson and Hepler[19]) and succinic acid (Kettler *et al.*[20]). The degree of dissociation α was obtained from solving the equation for the equilibrium constant

$$K(T, p) = \frac{\alpha^2 m \gamma_{\pm}^2}{(1 - \alpha)} \tag{A8}$$

for acids and

$$K(T, p) = \frac{\alpha^2 m}{(1 - \alpha)} \tag{A9}$$

for salts, where the approximation $\gamma = 1$ has been adopted for all uncharged species, and

$$\ln \gamma_{\pm} = -|z_H z_A| A_{\Phi} \left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + (2/1.2)\ln(1 + 1.2\sqrt{I}) \right] \tag{A10}$$

where A_{Φ} is the osmotic slope in the Debye–Hückel limiting law, again from Archer and Wang.[14] Equilibrium constants were calculated from

$$\ln K(T_o, p) = \ln K(T_o, p_o) - \int_{p_o}^{p} \frac{\Delta V_r^o(T_o, p_1)}{RT_o} dp_1 \tag{A11}$$

$$\ln K(T, p) = \ln K(T_o, p) + \int_{T_o}^{T} \frac{\Delta H_r^o(T_1, p)}{RT_1^2} dT_1 \tag{A12}$$

where $\Delta V_r^o(T_o, p_1)$ comes from the same estimate as in Eq. (A6), $\Delta H_r^o(T_1, p)$ is calculated using Eqs. (A6, A7) and $\ln K(T_o, p_o)$ were from Robinson and Stokes[18] for all reactions except for water dissociation (Olofsson and Hepler[19]). For clearness and to reduce ambiguity, the notation adopted in the preceding paragraphs was more comprehensive than in the rest of the paper, where the functional dependencies are evident.

Because we used uncorrected values of the apparent heat capacities of our compounds initially, we had to iterate all the procedure described above, including the group contribution evaluations. Corrections were unchanged after two iterations; the values of $\Delta C_{p,\Phi}$ and α in Tables I–V refer to these final calculations. Relaxation contributions for ionization/hydrolysis reactions were found to be quite small in general. For succinic acid, the only polyfunctional compound included in this study, the first and second dissociation

corrections were calculated in the same manner as for monofunctional acids; Eq. (A8) and a similar equation for the second dissociation were solved simultaneously for both degrees of ionization, α_1 and α_2, and Eq. (A3) and the ionic strength calculation were modified in accordance with the more complicated equilibrium composition.

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