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Heat Capacities and Volumes of Aqueous Dicarboxylate Salt Solutions of Relevance to the Bayer Process

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Apparent molar volumes (V_ϕ) and heat capacities at constant pressure ($C_{p\phi}$) of aqueous solutions of sodium oxalate (Na_2Ox), sodium succinate (Na_2Suc), sodium malonate (Na_2Mal), and potassium oxalate (K_2Ox) were determined at 25 °C up to their saturation limits using vibrating tube densitometry and flow calorimetry. These data were fitted using the Redlich−Rosenfeld−Meyer and Pitzer models. It was established using literature data that V_ϕ and $C_{p\phi}$ of Na^+ and K^+ salts with a common anion are additive within well-defined limits even up to high concentrations. This was used to estimate hypothetical values of $C_{p\phi}$ and V_ϕ at high ionic strengths for the sparingly soluble Na_2Ox, which are required for the thermodynamic modeling of concentrated electrolyte mixtures such as Bayer process solutions. These values were in reasonable agreement with those estimated using a Pitzer model with parameters for Na_2SO_4(aq).

Introduction

The Bayer process, which involves the selective dissolution of $Al(OH)_3$ (gibbsite) and/or AlOOH (boehmite) in hot caustic (NaOH) solution, followed by the precipitation of purified $Al(OH)_3$ upon cooling, is the only method used worldwide for the large-scale extraction of alumina from bauxitic ores.[1] The industrial process is complicated by the variable composition of the bauxite including organic contaminants. This organic material typically includes high molecular weight compounds such as cellulose and lignin. Under Bayer plant conditions such material is decomposed, forming a great variety of sodium "organate" salts including dicarboxylates such as sodium succinate (Na_2Suc) and especially sodium oxalate (Na_2Ox). As the process stream is continuously recycled, these decomposition products build up, which can alter the thermodynamic and other solution properties that are required for various process engineering calculations.

The thermodynamic properties of complex mixtures of electrolytes can be calculated approximately by way of the properties of binary solutions (those containing just one electrolyte and the solvent) using Young's pro-rata additivity rule. This rule states that the partial molar property of a mixture of electrolytes in solution is equal to the sum of the partial molar properties of its constituent binary solutions, weighted according to their concentrations, at the (stoichiometric) total ionic strength of the mixture.[2] To describe the thermodynamic properties of Bayer liquors in this way, appropriate data are required for binary solutions of all the major components, including the significant organic impurities, up to high ionic strengths.

The present paper reports density and heat capacity measurements at 25 °C on two compounds, sodium malonate (Na_2Mal) and Na_2Suc, that are useful as model organic impurities in Bayer liquors. Measurements on the industrially important impurity Na_2Ox were also undertaken but were limited by its sparing solubility (0.266 $mol\cdot kg^{-1}$ in water at 25 °C).[3] Since estimates of the partial molar properties of Na_2Ox at high ionic strengths are required for modeling purposes, measurements were also made on the more soluble (≈1.6 $mol\cdot kg^{-1}$ in water at 25 °C)[3] potassium oxalate, K_2Ox.

Experimental Section

Reagents. Sodium malonate monohydrate ($Na_2Mal\cdot H_2O$, ≥99.0 % w/w) and sodium succinate hexahydrate ($Na_2Suc\cdot 6H_2O$, ≥99.0 % w/w) were obtained from Sigma-Aldrich. Sodium oxalate (Na_2Ox) and potassium oxalate (K_2Ox) were from Ajax, Australia, with purity of 99.9 % w/w or greater, while NaCl was from BDH (U.K.) with purity of 99.5 % w/w. All reagents were used as received. Solutions were prepared gravimetrically with buoyancy corrections using high-purity water (Millipore Milli-Q system), boiled under nitrogen, and then degassed under vacuum.

Densimetry. Solution densities were measured using an Anton Paar DMA 602 vibrating tube density meter connected to an Anton Paar mPDS 4000 data module. The temperature was set to (25.00 ± 0.02) °C (NIST traceable) with a temperature control of better than ± 0.01 °C using a Julabo F-33 thermostat circulator.

Densities (ρ) were calculated using

$$\rho - \rho^0 = k(\tau^2 - (\tau^0)^2) \tag{1}$$

where τ symbolizes the period of oscillation of the sample tube, and the superscript 0 signifies the reference solution, usually pure water. The densimeter constant k was determined before each set of measurements by calibration with two fluids of known density. Degassed high-purity water ($\rho = 0.997047\ g\cdot cm^{-3}$)[4] and dry cylinder air ($\rho = 0.001185\ g\cdot cm^{-3}$)[5] were used for this purpose.

Apparent molar volumes (V_ϕ) were derived from the density data according to

$$V_\phi = \frac{M_2}{\rho} - \frac{\rho - \rho^0}{m\rho\rho^0} \tag{2}$$

where solution compositions are in molality (m, mol of solute/kg of solvent), M_2 is the molar mass of the solute,

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and SI units are assumed. The precision of the density readings is estimated to be ca. ± 5 μg/mL but the overall uncertainty in densities is probably an order of magnitude greater.

Microcalorimetry. Heat capacities of solutions at constant pressure were measured with a Sodev model CP-C Picker flow calorimeter.[6] The calorimeter temperature was set to 24.935 °C with a precision of ± 5 mK using a Sodev CT-L circulator-thermostat. A temperature rise of 1.30 °C was used throughout. Solutions were introduced into the calorimeter through a four-way chromatography valve (Hamilton, USA, model HVP) connected to a peristaltic pump (Gilson, minipuls 3) with a 0.6 $\text{cm}^3\cdot\text{min}^{-1}$ flow rate. The voltage output from the calorimeter was monitored with a chart recorder. The out-of-balance signal, however, was measured with an integrating voltmeter (Hewlett-Packard model 34401A) for periods of 30 to 60 s.

When the test solution is in the working cell and the reference liquid is in the reference cell of the Picker calorimeter, the relative volumetric heat capacity difference between the two liquids at constant pressure is[7]

$$\Delta\sigma/\sigma^0 = (\sigma - \sigma^0)/\sigma^0 = \Delta W_A/W^0 \tag{3}$$

where σ^0 is the heat capacity per unit volume of the reference liquid, ΔW_A is the applied power necessary to maintain the "final" temperature of both liquids equal, and W^0 is the baseline power applied to both cells to heat the flowing liquids.

The values of c_p, the heat capacity per unit mass of solution, were calculated from the volumetric heat capacities using the expression[7]

$$c_p = c_{p,1}^0(1 + \Delta\sigma/\sigma^0)\rho^0/\rho \tag{4}$$

where $c_{p,1}^0$ and ρ^0 are the heat capacity and density of the reference solution, respectively.

The apparent molar heat capacity at constant pressure ($C_{p\phi}$) was calculated using the formula

$$C_{p\phi} = M_2 c_p + \left[\frac{1000(c_p - c_{p,1}^0)}{m}\right] \tag{5}$$

where c_p is the experimentally derived heat capacity of the electrolyte solution and $c_{p,1}^0$ is the heat capacity of pure water (4.1819 $\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$).[4]

Results

Calorimeter Calibration. Picker flow calorimeters are subject potentially to heat losses, which can introduce systematic errors into the measured heat capacities.[6–8] Several authors have investigated this, but their findings have been inconclusive, with the heat loss errors appearing to be of the same order of magnitude as the overall uncertainty. Accordingly, the present calorimeter set up was tested with various NaCl solutions. The results obtained without correction for heat losses are summarized in Table 1, along with reliable critically reviewed literature data.[9,10] The agreement is close to the likely limits of uncertainty of (1 to 2) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in $C_{p\phi}$.[11] Thus correction for heat losses in the calorimeter was considered unnecessary.

Calorimeter Asymmetry. In their usual operating mode, Picker calorimeters produce two measurements of heat capacity.[6] Ideally the heat capacity obtained from the two measurement "legs" should be the same. Several authors[7,12] have reported small discrepancies between the two values, which increase with concentration and are probably due to the incomplete flushing of the concentrated sample from the measurement cell by the reference solution.[12]

Table 1. Experimental Densities (*ρ*), Heat Capacities (*c_p*), and Apparent Molar Heat Capacities (*$C_{p\phi}$*), of Aqueous Solutions of NaCl at Molality (*m*) at 25 °C

m	ρ	c_p	$C_{p\phi}$[a]	$C_{p\phi}$[b]	$C_{p\phi}$[c]
$\text{mol}\cdot\text{kg}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0.9998	1.036181	3.9153(4)	−37.8	−40.9	−41.4
1.999	1.072216	3.7194(4)	−13.2	−15.4	−16.2
3.000	1.105705	3.5713(7)	5.2	3.4	2.4

[a] This study. [b] Interpolated values of Clarke and Glew.[9] [c] Interpolated values from Archer.[10]

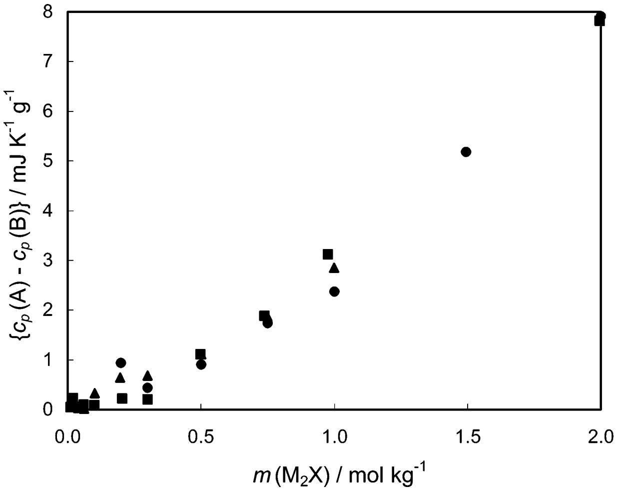

Figure 1. Difference between "first leg", c_p(A), and "second leg", c_p(B), heat capacities: ●, Na_2Suc; ■, Na_2Mal; ▲, K_2Ox.

For the more soluble salts, Figure 1 summarizes the differences between the heat capacities determined from the first leg, c_p(A), and the second leg, c_p(B). There is a remarkable consistency in the discrepancy as a function of concentration, as has been observed for other systems.[12] Accordingly, all heat capacities were derived from first leg measurements, c_p(A), where the solution is displacing water in the calorimeter, as discussed in detail previously.[12]

The apparent molar volumes and heat capacities of the aqueous solutions of Na_2Suc, Na_2Mal, Na_2Ox, and K_2Ox as a function of concentration are summarized in Tables 2 and 3.

Modeling Apparent Molar Properties

Redlich−Rosenfeld−Meyer Model. Apparent molar volumes and heat capacities are adequately represented up to moderate concentrations ($m \approx 1$ $\text{mol}\cdot\text{kg}^{-1}$) by the Redlich−Rosenfeld−Meyer (RRM) equations:[13]

$$V_\phi = V_2^0 + \omega^{3/2}A_V m^{1/2} + B_V m \tag{6}$$

$$C_{p\phi} = C_{p,2}^0 + \omega^{3/2}A_J m^{1/2} + B_J m \tag{7}$$

where V_2^0 and $C_{p,2}^0$ are respectively the standard state partial molar volume and heat capacity of the electrolyte in the solvent, $\omega^{3/2}$ is a valency factor, A_V and A_J are the molality-based Debye−Hückel coefficients for volume and heat capacity respectively, B is an empirical parameter fitted to the data to extend the RRM model to higher concentrations, and the remaining symbols have their usual meanings. In this study the values of A_V and A_J were

Table 2. Apparent Molar Volumes of Aqueous Solutions of Alkali Metal Dicarboxylates at 25 °C[a]

m	ρ	V_ϕ	m	ρ	V_ϕ
$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{g\cdot cm^{-3}}$	$\mathrm{cm^3\cdot mol^{-1}}$	$\mathrm{mol\cdot kg^{-1}}$	$\mathrm{g\cdot cm^{-3}}$	$\mathrm{cm^3\cdot mol^{-1}}$
	Na_2Suc			Na_2Mal	
0.0099519	0.998141	51.90(77)	0.010204	0.998203	34.46(49)
0.020381	0.999243	54.03(30)	0.020188	0.999271	37.56(25)
0.041867	1.001535	54.46(16)	0.040229	1.001444	38.35(12)
0.060543	1.003529	54.48(4)	0.059967	1.003607	38.17(8)
0.10032	1.007698	55.15(4)	0.099517	1.007822	39.13(5)
0.20028	1.017997	56.13(3)	0.20489	1.018850	41.69(2)
0.30014	1.028045	56.87(1)	0.30051	1.028551	41.69(4)
0.50055	1.047460	58.27(1)	0.49847	1.048206	43.02(1)
0.74971	1.070410	59.70(1)	0.73563	1.070786	44.35(1)
1.00028	1.092289	60.93(1)	0.97461	1.092131	45.94(1)
1.4943	1.132322	62.93(1)	1.4812	1.134796	48.25(1)
1.9993	1.169445	64.62(1)	1.9950	1.173577	50.51(1)
			2.9931	1.241777	53.16(1)
			3.9907	1.296362	56.16(1)
	K_2Ox			Na_2Ox	
0.010287	0.998319	42.27(49)	0.0099860	0.998164	21.85(50)
0.019926	0.999506	42.47(25)	0.019895	0.999268	22.05(25)
0.039951	1.001904	44.21(13)	0.039979	1.001477	22.83(13)
0.061184	1.004415	45.24(8)	0.060298	1.003675	23.67(8)
0.10109	1.009207	45.17(5)	0.1000	0.099988	24.32(5)
0.19713	1.020459	46.17(3)	0.15023	1.013276	25.31(3)
0.29963	1.032086	47.42(2)	0.19961	1.018424	26.11(2)
0.50100	1.054203	49.14(1)	0.24940	1.023554	26.77(2)
0.74829	1.080170	50.74(1)			
0.99871	1.105267	52.06(1)			
1.1970	1.124387	52.94(1)			
1.3964	1.142785	53.86(1)			
1.4970	1.151715	54.35(1)			

[a] Values in parentheses are standard deviations in last significant figure.

taken[14] as 1.875 $\mathrm{cm^3\cdot mol^{-3/2}\cdot kg^{1/2}\cdot K^{-1}}$ and 32.75 $\mathrm{J\cdot mol^{-3/2}\cdot kg^{1/2}\cdot K^{-1}}$, respectively, which are in good agreement (within 3 %) with more recent evaluations as discussed previously.[12] The valency factor is given by

$$\omega = \frac{1}{2}\sum_i \nu_i z_i^{\,2} \tag{8}$$

where ν_i and z_i are the stoichiometric and charge numbers of the solute ions, i. The experimental data for V_ϕ and $C_{p\phi}$ were fitted using the RRM model, and the results are shown in Figures 2 and 3 for each salt.

Pitzer Model. The RRM model is often found to be unsatisfactory for fitting data at high concentrations.[12] For this purpose the Pitzer ion-interaction approach is usually better. The equations used in this study were, where $\nu = \nu_M + \nu_X$:[15]

$$V_\phi = V_2^0 + \nu|z_M z_X| A_V \frac{\ln(1 + 1.2\sqrt{I})}{2.4} + 2\nu_M \nu_X RT[mB_{MX}^V + m^2(\nu_M z_M)C_{MX}^V] \tag{9}$$

$$C_{p\phi} = C_{p,2}^0 + \nu|z_M z_X| A_J \frac{\ln(1 + 1.2\sqrt{I})}{2.4} - 2\nu_M \nu_X RT^2[mB_{MX}^J + m^2(\nu_M z_M)C_{MX}^J] \tag{10}$$

The second virial coefficients (B_{MX}^Y) are empirical functions of the ionic strength and, for 1:1 and 1:2 electrolytes, are given by

$$B_{MX}^Y = \beta_{MX}^{(0)Y} + 2\beta_{MX}^{(1)Y}[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})](\alpha^2 I)^{-1} \tag{11}$$

Table 3. Apparent Molar Heat Capacities of aqueous Solutions of Alkali Metal Dicarboxylates at 25 °C[a]

m		c_p	$C_{p\phi}$
$\mathrm{mol\cdot kg^{-1}}$	$10^3\,\Delta\sigma/\sigma_o$	$\mathrm{J\cdot K^{-1}\cdot g^{-1}}$	$\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$
	Na_2Suc		
0.0099519	−0.579(79)	4.17490(66)	−27(66)
0.020381	−1.123(57)	4.16802(48)	−5(24)
0.041867	−2.289(20)	4.15363(17)	−2.1(41)
0.060543	−3.232(20)	4.14146(17)	3.2(28)
0.10032	−5.193(17)	4.11621(14)	12.3(14)
0.20028	−9.343(45)	4.05757(37)	36.8(19)
0.30014	−12.837(24)	4.00374(19)	55.2(7)
0.50055	−18.141(20)	3.90842(16)	87.0(3)
0.74971	−22.198(10)	3.80882(8)	119.6(1)
1.00028	−24.151(24)	3.72507(18)	147.0(2)
1.4943	−23.252(15)	3.59668(11)	191.2(1)
1.9993	−17.927(14)	3.50149(10)	227.1(1)
	Na_2Mal		
0.010204	−0.596(1)	4.17468(73)	−90(72)
0.020188	−1.053(4)	4.16820(163)	−62(81)
0.040229	−2.0700(5)	4.15492(24)	−55.6(60)
0.059967	−3.034(9)	4.14196(73)	−52.9(122)
0.099517	−4.781(12)	4.11741(20)	−38.6(20)
0.20489	−8.717(1)	4.05674(82)	−10.4(41)
0.30051	−11.590(14)	4.00683(11)	10.5(4)
0.49847	−15.856(12)	3.91473(10)	43.5(2)
0.73563	−17.706(7)	3.82497(44)	81.0(7)
0.97461	−19.58(27)	3.74307(204)	103.8(2)
1.4812	−17.706(74)	3.60922(54)	147.6(4)
1.9950	−12.277(1)	3.50924(11)	182.3(1)
	K_2Ox		
0.010287	−0.822(9)	4.17314(75)	−158(73)
0.019926	−1.676(2)	4.16462(17)	−175.0(84)
0.039951	−3.270(2)	4.14802(13)	−158.6(34)
0.061184	−4.914(7)	4.13082(50)	−148.1(82)
0.10109	−7.871(9)	4.09899(74)	−138.8(74)
0.19713	−14.652(4)	4.02609(33)	−121.2(17)
0.29963	−21.189(3)	3.95432(21)	−102.2(7)
0.50100	−32.817(8)	3.82537(67)	−75.8(15)
0.74829	−45.337(5)	3.68508(41)	−51.4(6)
0.99871	−56.301(8)	3.56005(60)	−30.9(7)
1.1970	−64.078(5)	3.47067(37)	−17.3(4)
1.3964	−71.353(10)	3.38825(73)	−5.1(6)
1.4970	−74.749(2)	3.34968(15)	1.14(1)
	Na_2Ox		
0.0099860	−0.481(5)	4.17521(42)	−110(42)
0.019895	−0.982(6)	4.16851(50)	−115(25)
0.039979	−1.815(8)	4.15584(67)	−94.8(17)
0.060298	−2.683(5)	4.14314(42)	−87.7(69)
0.099988	−4.199(14)	4.11925(12)	−74.6(12)
0.15023	−5.912(31)	4.09059(26)	−59.7(17)
0.19961	−7.350(49)	4.06403(40)	−45.9(21)
0.24940	−8.640(21)	4.03841(17)	−34.2(7)

[a] Values in parentheses are standard deviations in last significant figure.

where Y denotes J or V, $\beta^{(0)Y}$ and $\beta^{(1)Y}$ are empirical parameters fitted to the experimental data, and α is a constant set to 2.0 $\mathrm{kg^{1/2}\cdot mol^{-1/2}}$. The third virial coefficients (C_{MX}^Y) were taken to be independent of ionic strength.

No Pitzer parameters for Na_2Ox have been reported in the literature, probably because the limited solubility of Na_2Ox makes it very difficult to determine them. On the other hand, Na_2SO_4(aq) is both highly soluble and well-studied.[16,17] Accordingly, it was decided to model Na_2Ox(aq) by assuming that its Pitzer parameters were identical to those of Na_2SO_4(aq) (Table 4) under all conditions.[20]

Figures 2 and 3 show that the Pitzer model fits the volumetric and heat capacity data well for all of the present electrolytes up to their saturation limits. The fits with the RRM model are also highly satisfactory although, as would be expected, some departures are observed for $C_{p\phi}$ at high

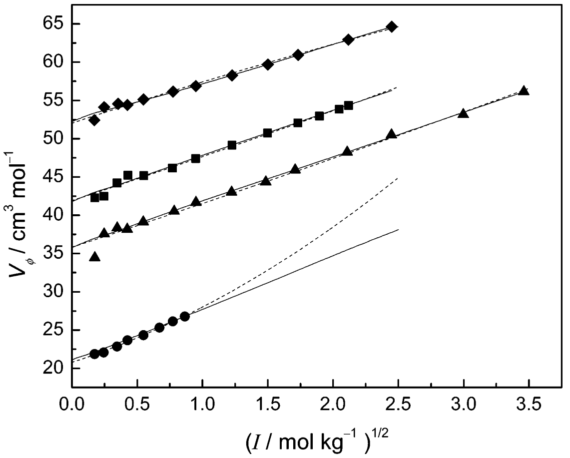

Figure 2. Apparent molar volumes of alkali metal dicarboxylate solutions as a function of ionic strength at 25 °C: ●, Na_2Ox; ■, K_2Ox; ▲, Na_2Mal; ◆, Na_2Suc; solid line, Pitzer model; dashed line, Redlich−Rosenfeld−Meyer model.

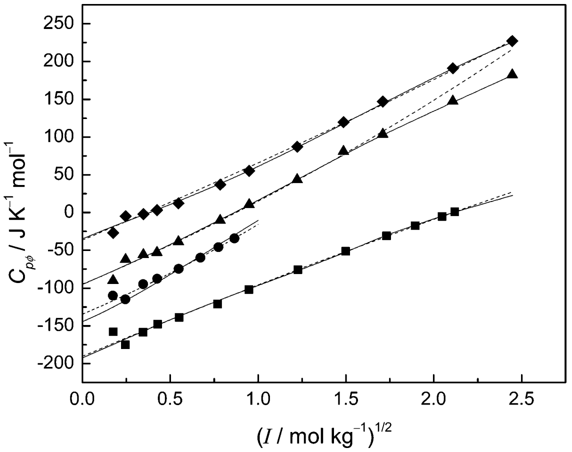

Figure 3. Apparent molar heat capacities of alkali metal dicarboxylate solutions as a function of ionic strength at 25 °C: ●, Na_2Ox; ■, K_2Ox; ▲, Na_2Mal; ◆, Na_2Suc; solid line, Pitzer model; dashed line, Redlich−Rosenfeld−Meyer model.

I (Figure 3). As has been noted for a number of other electrolytes,[12] close examination of $C_{p\phi}$ as a function of concentration reveals a slight "S" shape. The Pitzer model fits this shape for Na_2Mal and Na_2Suc up to high ionic strengths. The fit is slightly worse for the rather more inflected Na_2Ox data, possibly due to their small concentration range and the use of Na_2SO_4 parameters.

Standard State Values of $C^0_{p,2}$ and V^0_2. Both the RRM and Pitzer models were used to extrapolate the apparent molar properties of the electrolytes to infinite dilution ($I = 0$). The V^0_2 and $C^0_{p,2}$ values so obtained are summarized in Table 5; B_J and B_V values of the RRM model are given in Table 6. The Pitzer model parameters were determined by fitting the data over the complete range of ionic strengths. For the purpose of determining the infinite dilution quantities the RRM model was fitted to the experimental data for solutions with $I \leq 1.0$ mol·kg^{-1}. The V^0_2 values calculated by the RRM and the Pitzer models show good agreement for all salts, with differences less than 0.2 cm^3·mol^{-1}. The calculated values of $C^0_{p,2}$ are also in excellent agreement for both models with all of the salts differing by less than 2.5 J·K^{-1}·mol^{-1}, with the exception of Na_2Ox. This is almost certainly a consequence of assuming the Pitzer parameters of $Na_2Ox(aq)$ were identical to those of $Na_2SO_4(aq)$. For this reason, the RRM-derived $C^0_{p,2}$ value of (−134.60 ± 2.24) J·K^{-1}·mol^{-1} is preferred. No literature data with which to compare to the present results appear to exist for the salts examined in this study.

Estimation of Apparent Molar Properties at High Ionic Strengths

The partial molar thermodynamic properties (Y^0) of electrolyte solutions are strictly additive at infinite dilution. Thus, for example

$$Y^0(\mathrm{MX}) - Y^0(\mathrm{M'X}) = Y^0(\mathrm{MX'}) - Y^0(\mathrm{M'X'}) = Y^0(\mathrm{M^+}) - Y^0(\mathrm{M'^+}) \quad (12)$$

can be demonstrated to be obeyed within the limits of experimental uncertainty for a variety of thermodynamic properties. The differences, being characteristic of the ions and solvent alone, are constant at constant T and p.

At finite concentrations such additivities are expected to breakdown due to increasing ion−ion interactions that by definition are absent at infinite dilution. However, not all thermodynamic properties are equally sensitive to such interactions. In the present context of seeking a means to estimate $Y_\phi(Na_2Ox)$ at concentrations well above its solubility limit, it was decided to investigate the additivities of Y_ϕ up to high concentrations. For this purpose literature data for apparent molar volumes and heat capacities for a range of sodium and potassium salts were used.

For volumes, Figure 4, the difference $\{V_\phi(K_yX) - V_\phi(Na_yX)\}/y$ (corrected for the charge type with $y = 1$ or 2) is remarkably constant and independent of concentration (or ionic strength) with a value of (10.5 ± 0.5) cm^3·mol^{-1}. This unexpected result is probably due to the large contribution that is made to V_ϕ values by the intrinsic (crystallographic) ion size.[19] Interestingly, the variation in $\{V_\phi(K_yX) - V_\phi(Na_yX)\}/y$ is greater at $I = 0$, where the differences should truly be constant, than at finite I. This may reflect the extra uncertainties associated with the extrapolation to $I = 0$.

The situation is slightly different for heat capacities (Figure 5). Here the differences $\{C_{p\phi}(Na_yX) - C_{p\phi}(K_yX)\}/y$ are again almost independent, to a remarkable degree (± 2 J·K^{-1}·mol^{-1}), of the electrolyte type, at least up to $I \approx 2.5$ mol·kg^{-1}. However, in contrast to the V_ϕ values the differences are linearly dependent on $I^{1/2}$, at least up to this ionic strength. At still higher concentrations the differences become salt-dependent, presumably reflecting specific differences in ion−ion interactions and possibly solvent structure (to which heat capacities are rather sensitive[20]). It is notable that the values for chloride salts appear to diverge from linearity more than those of the other anions. In contrast to the volumes, the differences in $\{C_{p\phi}(Na_yX) - C_{p\phi}(K_yX)\}/y$ (where y is defined above) are smallest at $I = 0$.

Despite the divergence at high I, the differences in $C_{p\phi}$ values for all the Na$^+$ and K$^+$ salts shown in Figure 5 for $I \leq 2.5$ mol·kg^{-1} can be described adequately by the simple function:

$$\{C_{p\phi}(K_yX) - C_{p\phi}(Na_yX)\}/(y\text{·J·K}^{-1}\text{·mol}^{-1}) = 8.19\,(I/\text{mol·kg}^{-1})^{1/2} + 28.62 \quad (13)$$

The correlations in Figures 4 and 5 provide a simple method for estimating V_ϕ and $C_{p\phi}$ for salts for which no experimental data are available. The values so calculated appear to be reasonably accurate even up to quite high concentrations. This approach also provides a means for

Table 4. Pitzer Model Parameters for Apparent Molar Volumes and Heat Capacities of Aqueous Solutions of Alkali Metal Dicarboxylates at 25 °C Derived from This Work[a]

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$(2\sqrt{2})\boldsymbol{C}$
		V_ϕ	
Na_2Ox[b]	5.309×10^{-5}	3.200×10^{-3}	1.752×10^{-6}
K_2Ox	$(3.76 \pm 0.92) \times 10^{-5}$	$(1.15 \pm 0.66) \times 10^{-4}$	$(-4.27 \pm 4.64) \times 10^{-6}$
Na_2Mal	$(3.25 \pm 0.41) \times 10^{-5}$	$(1.21 \pm 0.56) \times 10^{-4}$	$(-2.08 \pm 1.05) \times 10^{-6}$
Na_2Suc	$(3.86 \pm 0.14) \times 10^{-5}$	$(1.43 \pm 15.12) \times 10^{-6}$	$(-6.11 \pm 0.57) \times 10^{-6}$
		$C_{p\phi}$	
Na_2Ox[c]	-4.230×10^{-5}	-1.206×10^{-4}	3.613×10^{-6}
K_2Ox	$(-2.42 \pm 0.40) \times 10^{-5}$	$(-2.09 \pm 2.07) \times 10^{-5}$	$(6.20 \pm 2.33) \times 10^{-6}$
Na_2Mal	$(-3.93 \pm 0.64) \times 10^{-5}$	$(-4.33 \pm 3.28) \times 10^{-5}$	$(1.11 \pm 0.36) \times 10^{-5}$
Na_2Suc	$(-4.00 \pm 0.29) \times 10^{-5}$	$(1.96 \pm 1.51) \times 10^{-5}$	$(9.33 \pm 1.63) \times 10^{-6}$

[a] Uncertainties are ± 1 σ. [b] Na_2SO_4 data from Monnin.[17] [c] Na_2SO_4 data from Holmes and Mesmer.[16]

Table 5. V_2^0 and $C_{p,2}^0$ for Alkali Metal Dicarboxylate Salts in Aqueous Solution at 25 °C Extrapolated from Experimental Data Using the RRM and Pitzer Models[a]

	RRM model		Pitzer model	
	V_2^0	$C_{p,2}^0$	V_2^0	$C_{p,2}^0$
electrolyte	$cm^3 \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$
Na_2Ox	20.77 ± 0.07	-134.60 ± 2.24[b]	21.087[c]	-144.52[b,d]
K_2Ox	41.90 ± 0.17	-190.37 ± 2.16	41.79 ± 0.39	-190.15 ± 2.21
Na_2Mal	35.81 ± 0.26	-95.05 ± 2.49	35.89 ± 0.44	-95.78 ± 3.53
Na_2Suc	52.03 ± 0.15	-36.51 ± 1.80	52.22 ± 0.12	-34.92 ± 1.62

[a] Additional (non-)significant figure retained to emphasize differences and preserve computational precision (uncertainties are ± 1 σ). [b] RRM value preferred, see text. [c] To be used in conjunction with volumetric Pitzer parameters for Na_2SO_4 reported by Monnin.[17] [d] To be used in conjunction with Pitzer parameters for Na_2SO_4 reported by Holmes and Mesmer.[16]

Table 6. B_V and B_J Values for Alkali Metal Dicarboxylate Salts in Aqueous Solution at 25 °C Obtained from Fits to Experimental Data Using the RRM Model[a]

	B_V	B_J
electrolyte	$cm^3 \cdot kg \cdot mol^{-2}$	$J \cdot kg \cdot K^{-1} \cdot mol^{-2}$
Na_2Ox	4.83 ± 0.56	61.82 ± 16.94
K_2Ox	0.379 ± 0.225	-11.92 ± 2.77
Na_2Mal	0.266 ± 0.166	35.46 ± 5.73
Na_2Suc	-0.708 ± 0.177	12.08 ± 1.88

[a] Additional (non-)significant figure retained to emphasize differences and preserve computational precision (uncertainties are ± 1 σ).

estimating the hypothetical V_ϕ and $C_{p\phi}$ values of Na_2Ox solutions above their solubility limit. Such values are required for the application of Young's rule to the estimation of the thermodynamic properties at high ionic strength of Bayer process solutions that may contain Na_2Ox.[13]

For a mixed electrolyte solution containing i binary components Young's rule may be written as

$$Y_\phi(\text{mixture}) = \sum_i (m_i/\Sigma_i m_i) Y_{\phi i} \tag{14}$$

The application of Young's rule requires knowledge of the relevant apparent molar property ($Y_{\phi i}$) of the component binary electrolyte solutions (real or hypothetical) at the stoichiometric ionic strength of the mixture. For many complex electrolyte mixtures this requires nothing more than access to the relevant binary solution data. However, for some components in Bayer liquors such values are not available. This is either because the component binary solution is unstable (as for *pure* $NaAl(OH)_4(aq)$) or because the electrolyte has insufficient solubility (e.g., Na_2Ox). In such cases $Y_{\phi i}$ must be estimated.

For Na_2Ox the desired Y_ϕ values ($Y = V$ or C_p) were estimated using the correlations encompassed in Figures 4 and 5. By taking the measured properties of K_2Ox and assuming a constant (for V_ϕ) or linearly varying (for $C_{p\phi}$) difference between the K^+ and Na^+ salts (corresponding to the trends in Figures 4 and 5 respectively) the values of V_ϕ and $C_{p\phi}$ for Na_2Ox were estimated up to $I \approx 4.5\ mol \cdot kg^{-1}$.

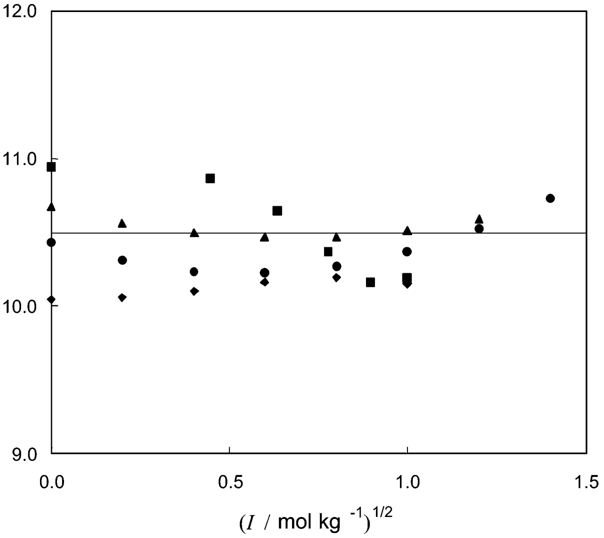

Figure 4. Differences between apparent molar volumes of Na^+ and K^+ salts containing various common anions at 25 °C: ●, Cl^-; ■, Br^-; ▲, I^-; ◆, $^1/_2SO_4^{2-}$; solid line, $\Delta V_\phi = 10.5\ cm^3 \cdot mol^{-1}$.

Values of V_ϕ and $C_{p\phi}$ for Na_2Ox at high I can also be estimated by the Pitzer equations using the empirical parameters derived for Na_2SO_4 by Holmes and Mesmer.[16] In a similar manner, a Pitzer model based on recent literature values[12] of $C_{p\phi}$ for Na_2SO_4 was also used to estimate $C_{p\phi}$ for Na_2Ox. In all cases, the models were adjusted for the difference $Y^0(SO_4^{2-}) - Y^0(Ox^{2-})$ such that the present experimental Na_2Ox data were well-reproduced. Since the Pitzer parameters for Na_2SO_4 provide a good fit of the measured Y_ϕ for Na_2Ox up to its solubility limit (Figures 2 and 3), it is reasonable to assume they might also provide satisfactory estimates for Y_ϕ in supersaturated solutions, at least up to the solubility limit of

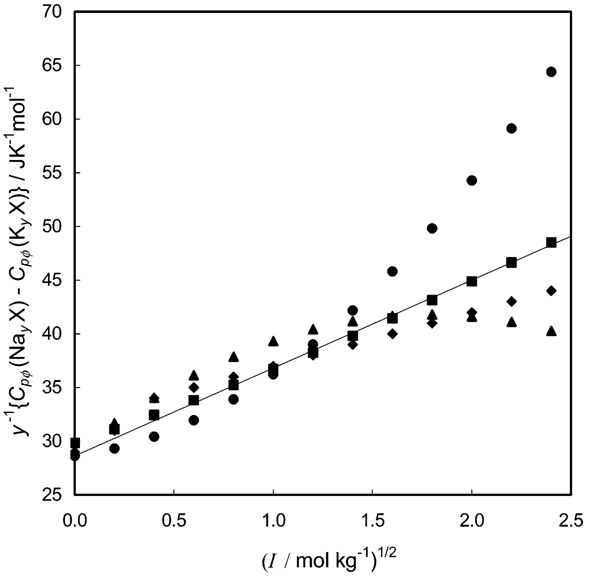

Figure 5. Differences between apparent molar heat capacities of Na^+ and K^+ salts containing various common anions at 25 °C: ●, Cl^-; ■, Br^-; ▲, I^-; ◆, $\frac{1}{2}SO_4^{2-}$; solid line, eq 13.

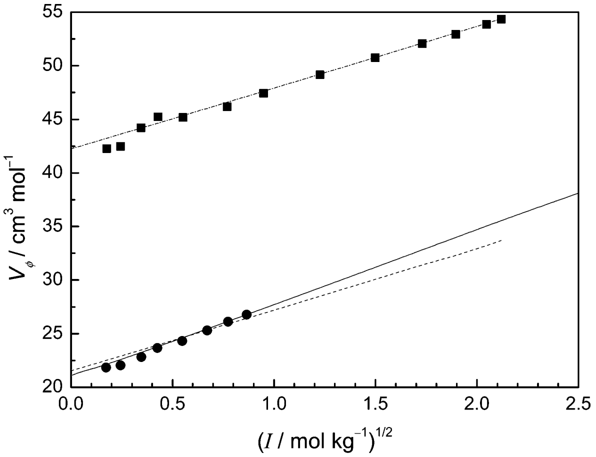

Figure 6. Estimation of hypothetical apparent molar volumes of Na_2Ox(aq) at high ionic strengths: ●, Na_2Ox experimental values; ■, K_2Ox experimental values. Solid line, volumetric model for Na_2SO_4(aq) of Monnin[17] shifted by a constant value of 9.3 cm^3·mol^{-1}; dashed line, extrapolation based on K_2Ox (RRM correlation minus 21.0 cm^3·mol^{-1}).

Na_2SO_4 ($\approx$1.9 mol·kg^{-1}).[3] On the other hand it should be noted that the $C^0_{p,2}$ value predicted for Na_2Ox in this way is possibly in error (see above and Table 5), and it is well-established that the extrapolation of Pitzer models to concentrations beyond the experimental correlation range frequently results in erroneous predictions.[21]

The estimated values of V_ϕ and $C_{p\phi}$ for Na_2Ox(aq) obtained by all three methods are illustrated in Figures 6 and 7, respectively, and show modest agreement among the various predictions up to moderate ionic strengths. At $I = 4.0$ mol·kg^{-1} for instance, the values from the various models vary by ca. 2.5 cm^3·mol^{-1} in V_ϕ and 50 J·K^{-1}·mol^{-1} in $C_{p\phi}$.

Whichever method of estimation is adopted, the likely uncertainties seem to be such that reasonable estimates can be made of the densities and heat capacities of complex mixed electrolyte solutions containing Na_2Ox even at high *I*. Due to their directness, the values obtained by the present observation of the additivity of V_ϕ and $C_{p\phi}$ values up to high ionic strengths are preferred in the current context. Indeed, the extent of this phenomenon warrants further investigation. If found to be true for other salts and other properties it will represent a useful means of estimating the apparent partial molar thermodynamic properties of unmeasured (or unmeasurable) binary electrolyte solutions and, via Young's rule, of complex mixtures of electrolyte solutions.

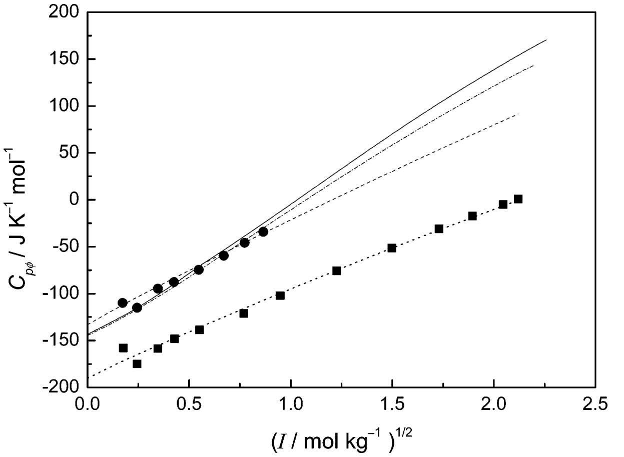

Figure 7. Estimation of hypothetical apparent molar heat capacities of Na_2Ox(aq) at high ionic strengths: ●, Na_2Ox experimental values; ■, K_2Ox experimental values. Solid line, Pitzer model based on experimental Na_2SO_4 data[9] shifted by a constant value of 55.0 J·K^{-1}·mol^{-1}; dot−dash line, Pitzer model of Holmes and Mesmer for Na_2SO_4[16] shifted by a constant value of 55.0 J·K^{-1}·mol^{-1}; dashed line, extrapolation based on K_2Ox data (RRM correlation plus eq 13) from this study.

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