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MIXED INTERACTION TERMS IN THE USE OF PITZER EQUATIONS: APPLICATION TO THE HEAT CAPACITIES OF THE RECIPROCAL SYSTEM $Na^+/K^+/Cl^-/SO_4^{2-}/H_2O$ AT HIGH TEMPERATURES

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ABSTRACT

Changes of heat content of aqueous solutions of Na_2SO_4 and of $NaCl–Na_2SO_4$ mixtures have been measured between 60 and 220 °C by means of a drop calorimeter. Standard procedure yielded the corresponding heat capacity data. These data were analyzed in terms of Pitzer's theory which enables the calculation of the parameters β^0, β^1 and C^ϕ for Na_2SO_4(aq), which are valid up to 3 mol kg^{-1}, and the binary mixed interaction term ϑ_{ClSO_4}. These new data were utilized, in the framework of the ion interaction model, to reproduce experimental values of the heat capacity data of the quaternary system $Na^+/K^+/Cl^-/SO_4^{2-}/H_2O$. The critical points of this description are discussed.

INTRODUCTION

In previous papers [1,2], we have studied the specific heat c_p of aqueous solutions of the reciprocal system $Na^+/K^+/Cl^-/SO_4^{2-}$, which is the major component of some Italian geothermal reservoirs, at temperatures of up to 493 K and overall molal concentrations of up to 5 mol kg^{-1}. Comparison of these data with the values which may be calculated from the known behaviour of the single aqueous components NaCl, KCl, Na_2SO_4 and K_2SO_4, using the semiempirical model suggested by Pitzer [3], showed clear discrepancies at large sulphate contents which become more evident at higher temperatures [2]. The possible explanations which have been suggested, i.e. the poor validity of the heat capacity data for Na_2SO_4 at high concentrations and/or the neglected Pitzer mixed interaction coefficients ϑ and ψ, are critically examined here.

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The specific heat of aqueous solutions of sodium sulphate has been measured by Likke and Bromley [4] at concentrations below 1 mol kg^{-1} and up to 453 K, and by Pitzer [5] up to 1.5 mol kg^{-1} to 473 K. In the present paper, we extended these measurements up to a concentration of 3 mol kg^{-1} in the temperature range 333–493 K.

As far as we know, the mixed interaction terms of the Pitzer theory [3] have been determined only in some cases for such properties as activity and osmotic coefficients (see e.g. ref. 6) and heats of mixing (see e.g. ref. 7), usually at 298 K, but no data can be found in the literature relating to heat capacity. The mixed terms relevant to the aqueous system under investigation are the following: two pair (ϑ_{NaK} and ϑ_{ClSO_4}) and four triple (ψ_{NaKCl}, ψ_{NaKSO_4}, ψ_{NaClSO_4} and ψ_{KClSO_4}) interaction coefficients. These coefficients may be calculated from experimental data obtained from aqueous solutions of pairs of electrolytes with a common ion. The experimental and calculated data for c_p values of mixed solutions characterized by a large chloride content [2] are in good agreement, suggesting that the terms ϑ_{NaK} and ψ_{NaKCl} exert a negligible effect. This observation is supported by some direct experimental measurements [8] of c_p for KCl–NaCl aqueous mixtures between 303 and 353 K up to the total concentration of 3.5 mol kg^{-1}. On the other hand, the low solubility of K_2SO_4 (~ 0.7 m at 25 °C) prevented the direct investigation of the binary mixtures containing this electrolyte. We therefore studied aqueous mixtures of Na_2SO_4 and NaCl, which allow the determination of ϑ_{ClSO_4} and ψ_{NaClSO_4}.

The effect of these new data on the capability of the Pitzer model to describe the heat capacity data of the reciprocal system under examination is discussed.

EXPERIMENTAL

Specific heats at constant pressure were obtained using a drop calorimeter and the general procedure previously described in detail [9], with subsequent slight modifications [2]. The calorimeter furnishes the mean specific heat at the saturation pressure, $\bar{c}_{sat}$, averaged between a chosen temperature T and a reference temperature T_R, usually 298.15 K, for a solution of molality m. These data are transformed into the corresponding differential quantity c_{sat} through the following equation

$$c_{sat} = \bar{c}_{sat} + (T - T_R)(\partial \bar{c}_{sat}/\partial T)_m \quad (1)$$

and then into the specific heat at constant pressure c_p using

$$c_p = c_{sat} + T(\partial u/\partial T)_{P_s,m}(\partial P_s/\partial T)_m \quad (2)$$

where u and P_s are, respectively, the specific volume of the solution and the saturation pressure. The derivatives which appear in eqn. (2) have been estimated by means of an approximate procedure already described [2]. Reference 2 also describes the corrections for the presence of vapour space inside the cell; these corrections are lower than the experimental uncertainty, which is estimated as ±0.010 J g^{-1} K^{-1} on $\bar{c}_{sat}$ and ±0.015 J g^{-1} K^{-1} on c_p. All c_p measurements refer to the actual saturation pressure of each experiment, which may amount to 25 bar at the highest temperature. An estimate of the pressure effect on the heat capacity data of NaCl [10] and Na_2SO_4 [5] aqueous solutions indicates that, up to this pressure, the effect is below our experimental uncertainty, and the data may be safely attributed to the pressure of 1 bar.

The reference temperature T_R was always 298.15 K, except for experiments with aqueous Na_2SO_4 when the calorimeter was kept at 303.15 K in order to avoid precipitation of the more concentrated solutions.

The salts used were analytical grade commercial products which were recrystallized and dried before use. Deionized water was used throughout as the solvent.

THEORY

The heat capacity of a mixed electrolyte solution, according to Pitzer and Kim [6], can be obtained from

$$C_p = 1000 c_w^\ominus + \sum_i m_i \bar{C}_{p,i}^\ominus + (A_J/3b) m \ln(1 + bI^{1/2}) \sum_i \nu_i | z_{M_i} z_{X_i} | N_i$$
$$- RT^2 \left[m^2 (\boldsymbol{B}_J + \Theta_J) + m^3 (C_J^\phi + \Psi_J) \right] \tag{3}$$

This expression yields the heat capacity C_p of a solution containing m moles of salts in 1 kg of water at temperature T. The index J refers to the heat capacity property; the index i refers to the single salt MX and the summations are extended to the four salts considered. $\bar{C}_{p,i}^\ominus$ is the partial molar heat capacity at infinite dilution, m_i and N_i the molality and internal mole fraction ($N_i = m_i/m$), respectively, ν_i is the number of ions of one molecule of dissolved electrolyte, and z_{M_i} and z_{X_i} are the cation and anion charge. Finally, $c_w^\ominus$ is the specific heat of water, A_J is the Debye–Hückel slope for heat capacity [11], I is the ionic strength ($I = \Sigma_i m_i z_i^2$), and the empirical parameter $b = 1.2$ $mol^{-1/2}$ $kg^{1/2}$ in all cases [3].

The general expressions of overall coefficients $\boldsymbol{B}_J$, Θ_J, C_J^ϕ and Ψ_J as functions of composition and the specific ion interaction parameters B_J, ϑ_J, C_J^ϕ and ψ_J of the single salts are given elsewhere [2].

For solutions of a single electrolyte $M_M X_X$ eqn. (3) reduces to

$$C_p = 1000 c_w^\ominus + m\bar{C}_{p,i}^\ominus + \nu | z_M z_X | m (A_J/3b) \ln(1 + bI^{1/2})$$
$$- RT^2 \nu_M \nu_X \left[m^2 B_{J,MX} + 1/2 \nu_M z_M m^3 C_{J,MX} \right] \tag{4}$$

where B_J and C_J have the form [3]

$$B_{J,\mathrm{MX}} = \beta^0_{J,\mathrm{MX}} + 2\beta^1_{J,\mathrm{MX}}/(\alpha^2 I)\left[1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})\right]$$

$$C_{J,\mathrm{MX}} = C^{\phi}_{J,\mathrm{MX}} \mid z_\mathrm{M} z_\mathrm{X} \mid^{-1/2} \qquad (5)$$

and the parameter $\alpha = 2$ mol$^{-1/2}$ kg$^{1/2}$ for most electrolytes [11].

Measurements of heat capacity covering the correct ranges of temperature and concentration for solutions containing single electrolytes permit the unknown parameters in eqns. (4) and (5), $\bar{C}^{\ominus}_{p,i}$, $\beta_J^{\ominus}$, β_J^1 and $C^{\phi}\mathrm{d}J$ to be determined as a function of temperature. Introduction of these functions into the general expressions which give the overall parameters of eqn. (3) (see eqns. (6) of ref. 2), and the subsequent use of eqn. (3), permit the complete representation of the heat capacity data of the mixtures.

The mixed interaction parameters ϑ and ψ can be determined through experimental studies on solutions containing pairs of electrolytes having a common ion.

By properly rearranging eqn. (3) to isolate the interaction terms one obtains

$$\Theta_J + m\Psi_J = F(m, N, T) \qquad (6)$$

where for the system under examination

$$\Theta_J = 2(y_\mathrm{Cl} y_{\mathrm{SO}_4} \vartheta_{J,\mathrm{ClSO}_4} + y_\mathrm{Na} y_\mathrm{K} \vartheta_{J,\mathrm{NaK}})$$

$$\Psi_J = (y_\mathrm{K} y_\mathrm{Cl} y_{\mathrm{SO}_4} \psi_{J,\mathrm{KClSO}_4} + y_\mathrm{Na} y_\mathrm{K} y_{\mathrm{SO}_4} \psi_{J,\mathrm{NaKSO}_4} + y_\mathrm{Na} y_\mathrm{Cl} y_{\mathrm{SO}_4} \psi_{J,\mathrm{NaClSO}_4}$$
$$+ y_\mathrm{Na} y_\mathrm{K} y_\mathrm{Cl} \psi_{J,\mathrm{NaKCl}})$$

$$F = (C_p^\star - C_p)/(2RT^2 m^2) \qquad (7)$$

with $y_j = m_j/m$, where j indicates the single ion. Here C_p is the experimental heat capacity and $C_p^\star$ the value calculated through eqn. (3) neglecting Θ and Ψ.

In the case of NaCl–$\mathrm{Na_2SO_4}$ aqueous mixtures, at constant temperature, eqn. (6) reduces to

$$\vartheta_{\mathrm{ClSO}_4} + m/2(N_\mathrm{NaCl} + 2N_{\mathrm{Na_2SO_4}})\psi_{\mathrm{NaClSO}_4} = F/(N_\mathrm{NaCl} N_{\mathrm{Na_2SO_4}}) \qquad (8)$$

RESULTS

Sodium Sulphate

The direct experimental data of the average specific heat at the saturation pressure $\bar{c}_\mathrm{sat}$ as well as of the specific heat at constant pressure c_p are reported in Table 1 at the experimental concentrations and rounded values

TABLE 1

Average specific heats at saturation, $\bar{c}_{sat}$, and specific heats at constant pressure, c_p, of aqueous solutions of Na_2SO_4.[a]

m	T (K)								
	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15	493.15
$\bar{c}_{sat}$									
0.995	3.744	3.739	3.738	3.741	3.745	3.752	3.761	3.771	3.782
1.496	3.554	3.562	3.570	3.578	3.586	3.594	3.602	3.610	3.618
2.002	3.465	3.460	3.458	3.458	3.460	3.464	3.468	3.474	3.480
2.526	3.369	3.370	3.371	3.372	3.374	3.375	3.377	3.378	3.379
3.007	3.314	3.307	3.301	3.297	3.295	3.293	3.292	3.292	3.292
c_p									
0.995	3.733	3.732	3.741	3.758	3.781	3.810	3.843	3.882	3.927
1.496	3.566	3.582	3.599	3.616	3.633	3.652	3.673	3.697	3.725
2.002	3.455	3.452	3.456	3.465	3.478	3.495	3.516	3.541	3.570
2.526	3.370	3.373	3.376	3.379	3.384	3.389	3.396	3.405	3.417
3.007	3.301	3.291	3.285	3.284	3.285	3.289	3.295	3.306	3.319

[a] All values are in kJ kg^{-1} K^{-1}; $\bar{c}_{sat}$ average values between the temperature T and 303 K, were obtained by interpolating the $\bar{c}_{sat}$, calculated from eqn. (9), at rounded temperatures at each examined value of concentration m (mol kg^{-1}).

of temperature. The fitting-equation used for $\bar{c}_{\mathrm{sat}} = f(T)$ at each concentration was that used by Maier and Kelley [12]

$$\bar{c}_{\mathrm{sat}} = a_1 + a_2 T + a_3 T^{-2} \tag{9}$$

c_p values were obtained through eqns. (1) and (2) by inserting the correct value of the temperature derivative calculated from eqn. (9) into eqn. (1). Our c_p data were combined with Likke's data [4], available at the same temperatures (up to 453 K) in the region of low concentrations, and were then fitted to eqn. (4) at each temperature to obtain parameters $\beta^{\ominus}$, β^1 and C^{ϕ}. Data for $\bar{C}^{\ominus}_{p,i}$ were taken from Pitzer [5]. Values of the resulting parameters were then fitted with temperature, yielding the following relationships

$$\beta^{\ominus} = -4.8884\mathrm{E}-5 + 1.5506\mathrm{E}-7T - 1.0068\mathrm{E}-10T^2$$

$$\beta^1 = -1.0053\mathrm{E}-2 + 7.6826\mathrm{E}-5T - 1.9688\mathrm{E}-7T^2 + 1.6870\mathrm{E}-10T^3$$

$$\begin{aligned} C^{\phi} = {} & -4.8916\mathrm{E}-5 + 2.7137\mathrm{E}-7T - 4.6224\mathrm{E}-10T^2 + 1.9646\mathrm{E}-13T^3 \\ & -0.08989/(T(T-540)) + 1.0260\mathrm{E}-4/(T-260) \end{aligned} \tag{10}$$

Our experimental c_p values cannot be directly compared with data from other authors. Values reported by Likke and Bromley [4] cover the temperature range 353–453 K but reach the maximum concentration of 0.8 m. Rogers and Pitzer's data [5] were collected between 303 and 473 K, up to a concentration of 1.44 m. A few more measurements on more concentrated solutions, supersaturated at 298 K, are considered with caution by the authors themselves. A direct comparison is possible only for a series of measurements on a 0.999 m solution [5], studied between 305 and 453 K, which may be compared with our 0.995 m solution. The corresponding c_p values differ at most by 0.16%.

A more complete comparison can be made with reference to c_p values calculated using the ion interaction model. According to this model, virial coefficients for heat capacity of Na_2SO_4(aq) have also been obtained by Rogers and Pitzer [5] and by Holmes and Mesmer [13]. Both authors determined these coefficients using a least-squares fit which simultaneously took into consideration other thermodynamic data: the osmotic coefficients (Rogers, Holmes), the activity coefficients and the apparent relative enthalpies (Holmes). The functions $C_{p,\phi} = f(m)$ at two selected temperatures, calculated according to these authors and to our data, are compared in Fig. 1. The clear disagreement between Rogers and Holmes' functions at high temperatures and concentrations has already been discussed by the latter author [13] and was attributed to the fact that Rogers' fit in these experimental conditions was determined only by heat capacity data. Probably the fit realized by Holmes gives a high weight to the free energy data which are less critical than heat capacities. It has been observed [14] that acceptable free energy data at high temperatures may be obtained by good free energy

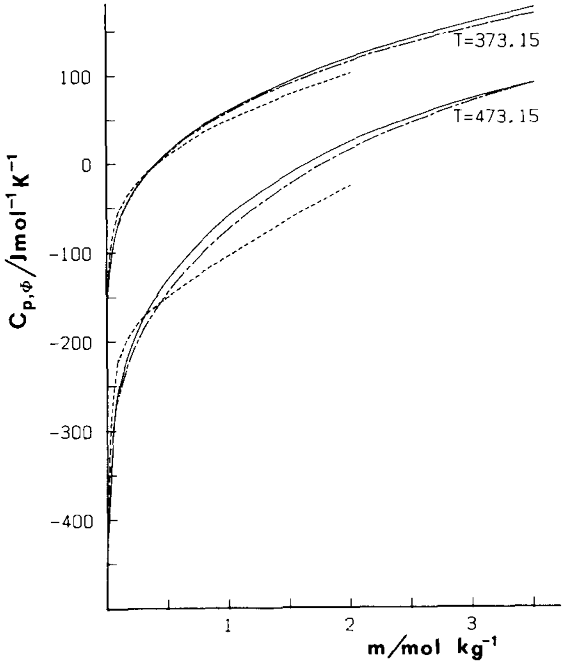

Fig. 1. Apparent molar heat capacities of Na_2SO_4(aq) ———, this work; — — —, Holmes, ref. 13; - —— - —— -, Rogers, ref. 5.

and enthalpy data at low temperatures combined with moderately precise high temperature heat capacities. The figure shows that our values are slightly higher than Rogers', though the two functions are substantially in agreement. A few values slightly higher than those given by Rogers, but within the uncertainties of the data of present work, were also obtained at high temperatures in our laboratory at up to 1 mol kg^{-1} making use of a more precise flow calorimeter [15]. Because our intention is to use these data to describe heat capacities of mixed solutions, and because our model and Rogers and Pitzer's model display a better consistency with direct experimental data, the model by Holmes and Mesmer was not taken into consideration. Equations (10) determined by us were therefore used in subsequent calculations. The agreement with Rogers and Pitzer's model up to 3 m is, however, surprising in view of the fact that these authors covered the high concentration region with only osmotic coefficient data up to 2.5 m and temperatures below 393 K.

$NaCl$–Na_2SO_4 mixtures

The aqueous solutions of these mixed salts were studied in the temperature range 333–493 K, for total concentrations between 2 and 4.5 m, and for molar ratios of the two salts changing from 1 : 2 to 2 : 1. The composition

TABLE 2

Composition of the Na_2SO_4–NaCl aqueous binary mixtures investigated [a]

Mixture	$N_{Na_2SO_4}$	N_{NaCl}	m [b]
BA	0.3330	0.6670	2.950
BB	0.6667	0.3333	3.004
BC	0.5005	0.4995	3.003
BD	0.5028	0.4972	2.018
BE	0.3214	0.6786	4.446

[a] The composition is given in terms of the internal mole fraction, N_{MX}, of the salt MX.
[b] m = overall solute molality (mol kg^{-1}).

and concentration of the single solutions investigated is shown in Table 2. Values of $\bar{c}_{sat}$ and c_p, calculated in a manner analogous to that already described for Na_2SO_4 solutions, are reported in Table 3.

Using eqn. (8) at each temperature investigated c_p values of these mixtures were used to obtain the values of the interaction parameters ϑ_{ClSO_4} and ψ_{NaClSO_4}. Virial coefficients for the single electrolytes were taken from this work for Na_2SO_4 and from Silvester and Pitzer [11] for NaCl. The fitting yielded values for the three-body interaction coefficient ψ_{NaClSO_4} which were of the same order of magnitude as their corresponding standard deviations. Evidently, in the concentration range explored the influence of this term is not very significant and the parameter results are ill-defined. The c_p data for these mixtures were, therefore, used to define the sole two-body interaction parameter ϑ_{ClSO_4}. Values of this parameter at the various temperatures are reported in Table 4. These values were finally fitted to a simple polynomial equation as a function of temperature (K) leading to the expression

$$\vartheta_{ClSO_4} = -1.31147E-3 + 9.6834E-6T - 2.3581E-8T^2 + 1.8885E-11T^3 \qquad (11)$$

The trend of this parameter with temperature is reported in Fig. 2 where it is also compared with the experimental values.

DISCUSSION

Values of heat capacity Pitzer parameters determined in this work, i.e. the single $\beta^{\ominus}$, β^1 and C^{ϕ} for aqueous Na_2SO_4 and the binary interaction parameter ϑ_{ClSO_4}, were used to represent the heat capacity of aqueous solutions for the reciprocal system $Na^+/K^+/Cl^-/SO_4^{2-}$. Experimental data relative to a series of solutions of this system have already been collected [2]. For convenience, the composition of these solutions is reported in Table 5. Table 6 summarizes the experimental c_p values together with those calcu-

TABLE 3

Average specific heats at saturation, $\bar{c}_{sat}$, and specific heats at constant pressure, c_p, of aqueous solutions of Na_2SO_4–NaCl mixtures [a]

Solution	T (K)								
	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15	493.15
$\bar{c}_{sat}$									
BA	3.471	3.470	3.471	3.473	3.476	3.480	3.483	3.488	3.493
BB	3.393	3.388	3.384	3.383	3.382	3.383	3.384	3.386	3.389
BC	3.443	3.432	3.425	3.422	3.421	3.422	3.425	3.429	3.435
BD	3.607	3.600	3.597	3.597	3.600	3.604	3.610	3.618	3.627
BE	3.314	3.300	3.291	3.286	3.284	3.284	3.286	3.291	3.296
c_p									
BA	3.469	3.471	3.477	3.485	3.496	3.509	3.525	3.544	3.567
BB	3.383	3.377	3.376	3.379	3.385	3.394	3.406	3.422	3.441
BC	3.423	3.410	3.408	3.413	3.424	3.441	3.462	3.489	3.520
BD	3.593	3.588	3.593	3.605	3.622	3.645	3.672	3.705	3.743
BE	3.289	3.272	3.267	3.271	3.281	3.298	3.319	3.346	3.378

[a] All values are in kJ kg^{-1} K^{-1}; $\bar{c}_{sat}$, average values between the temperature T and 298 K, were obtained by interpolating the $\bar{c}_{sat}$ calculated from eqn. (9), at rounded temperatures for each solution examined. For composition and concentration of the mixtures see Table 2.

TABLE 4

Values of the Pitzer pair interaction coefficients ϑ_{ClSO_4} [a]

T (K)	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15	493.15
$-\vartheta_{ClSO_4} \times 10^6$	4.60	0.44	0.51	2.08	4.13	6.34	8.28	8.79	5.96

[a] Values of ϑ_{ClSO_4} were obtained by applying eqn. (8) to the experimental data in Tables 2 and 3.

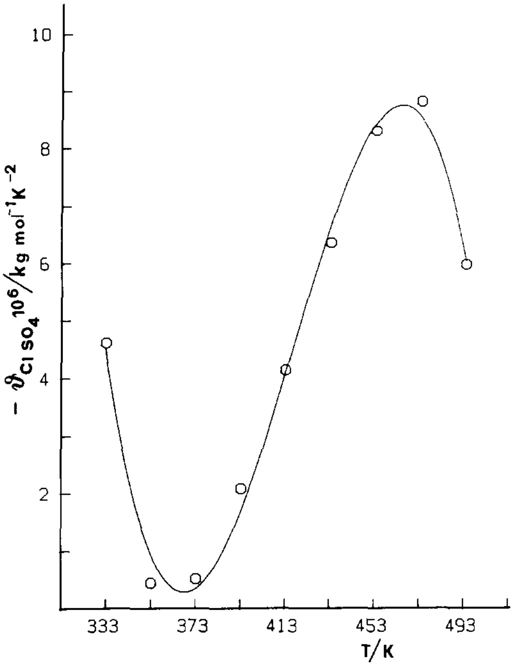

Fig. 2. Binary mixed interaction term $\vartheta_{\mathrm{ClSO_4}}$ as a function of temperature. ———, eqn. (11); o, experimental.

lated according to the Pitzer's model. The latter were obtained by introducing into eqn. (3) (a) the Pitzer coefficients of the single salts NaCl(aq), KCl(aq), Na_2SO_4(aq) and K_2SO_4(aq) already reported [2], and (b) the same coefficients for NaCl(aq) and KCl(aq) together with the new parameters measured in this work for Na_2SO_4(aq) (and those which follow for

TABLE 5

Composition of the aqueous solutions of the mixed system $Na^+/K^+/Cl^-/SO_4^{2-}$

Solution	X [a]	Y [a]	m [b]	I [c]
MA	0.800	0.101	2.282	2.52
MB	0.200	0.201	3.080	3.77
MC	0.239	0.406	0.608	0.92
			1.282	1.93
			2.860	4.32
			5.026	7.58
ME	0.188	0.691	3.490	7.17
MF	0.438	0.833	3.051	7.40

[a] Coordinates of the Janecke projection defined as $X = m_K/(m_K + m_{Na})$ and $Y = 2m_{SO_4}/(2m_{SO_4} + m_{Cl})$.

[b] Overall salt molality (mol kg^{-1}).

[c] Ionic strength, $I = 1/2\,\Sigma_i m_i z_i^2$.

TABLE 6

Specific heats at constant pressure, c_p, of aqueous solutions of the system $Na^+/K^+/Cl^-/SO_4^{2-}$ [a]

Solution	T (K)								
	333.15	353.15	373.15	393.15	413.15	433.15	453.15	473.15	493.15
MA	3.513	3.512	3.519	3.533	3.555	3.585	3.625	3.674	3.734
	3.484	3.498	3.517	3.540	3.565	3.590	3.615	3.643	3.674
	3.486	3.498	3.517	3.542	3.569	3.596	3.623	3.652	3.683
MB	3.464	3.473	3.482	3.491	3.501	3.512	3.525	3.541	3.560
	3.468	3.473	3.476	3.478	3.480	3.485	3.499	3.530	3.590
	3.473	3.474	3.477	3.483	3.493	3.507	3.527	3.560	3.616
MC	3.947	3.955	3.974	4.003	4.044	4.097	4.162	4.241	4.335
	3.958	3.972	3.989	4.010	4.039	4.076	4.124	4.187	4.257
	3.959	3.972	3.989	4.011	4.040	4.079	4.128	4.191	4.263
	3.788	3.789	3.798	3.816	3.844	3.882	3.930	3.990	4.062
	3.761	3.774	3.788	3.804	3.824	3.849	3.882	3.925	3.977
	3.764	3.775	3.789	3.807	3.830	3.859	3.895	3.940	3.993
	3.472	3.462	3.462	3.471	3.491	3.521	3.562	3.614	3.680
	3.444	3.441	3.439	3.440	3.444	3.453	3.468	3.497	3.546
	3.450	3.442	3.442	3.451	3.467	3.489	3.515	3.546	3.588
	3.166	3.175	3.184	3.192	3.202	3.212	3.224	3.238	3.255
	3.188	3.160	3.134	3.113	3.098	3.093	3.100	3.133	3.212
	3.213	3.167	3.142	3.138	3.154	3.181	3.213	3.247	3.284
ME	3.290	3.266	3.256	3.260	3.279	3.313	3.362	3.428	3.510
	3.300	3.271	3.248	3.232	3.226	3.231	3.248	3.284	3.348
	3.308	3.274	3.256	3.257	3.274	3.302	3.333	3.364	3.395
MF	–	–	–	3.129	3.169	3.243	3.349	3.488	3.662
	–	–	–	3.133	3.136	3.158	3.200	3.264	3.352
	–	–	–	3.156	3.176	3.215	3.263	3.317	3.375

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[a] All values are in kJ kg^{-1} K^{-1}; the three values given for each solution–temperature pair are, in order: the experimental value (see ref. 2), the value calculated using Pitzer's data for Na_2SO_4(aq) and the value calculated using new data for Na_2SO_4(aq) and ϑ_{ClSO_4} (this work). The composition of the solutions is given in Table 5.

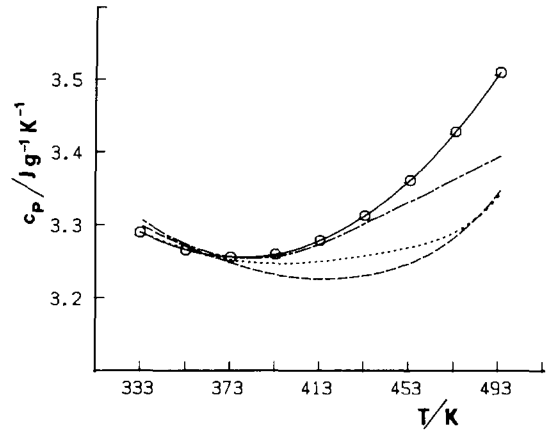

Fig. 3. Specific heat of solution ME (see Table 5) as a function of temperature. o——o, Experimental; — — —, calculated in ref. 2; - - - - - -, calculated using data of this work for $C_{p,\phi}$ of Na_2SO_4(aq); - —— - —— -, calculated using data of this work for $C_{p,\phi}$ of Na_2SO_4(aq) and ϑ_{ClSO_4}.

K_2SO_4(aq) from the additive procedure adopted in ref. 2) and the parameter for the mixed interaction Cl^-–SO_4^{2-}. Very recent high quality c_p data for KCl [16] were not used because they refer to a much higher pressure (17.9 MPa).

Experimental and calculated data are compared in Figs. 3 and 4. Figure 3 takes into consideration solution ME, which has the largest Na_2SO_4 content, and shows the separate effect of introducing new data for Na_2SO_4 and data for ϑ_{ClSO_4}. The figure shows that the new data for Na_2SO_4, based on high concentration experimental c_p measurements performed in this work, do not lead to a significant improvement in the fit. In effect, as noted above, the virial coefficients previously given by Rogers and Pitzer [5] are able to extrapolate c_p data of Na_2SO_4(aq) in good agreement with ours.

From Fig. 4, it can be seen that the introduction of new parameters produces a very slight improvement in the capability of the ion interaction model to describe the c_p behaviour of solutions characterized by a low sulphate content, whether this low content is due to the specific ionic composition (solution MB) or to the low overall concentration (solution MC_2, $m = 1.282$). In fact, the heat capacity of these mixtures was acceptably reproduced by the old data [2]. If we now considered the solutions characterized by a larger SO_4^{2-} fraction (solutions ME and MF) or even by a larger overall concentration (solution MC_4, $m = 5.026$), we realize that the introduction of new data, mainly of the mixed interaction term ϑ_{ClSO_4}, leads to clearly smaller differences between experimental and calculated values. However, the newly calculated functions exhibit a trend which suggests an incorrect consistency of the interpretative model with the experimental

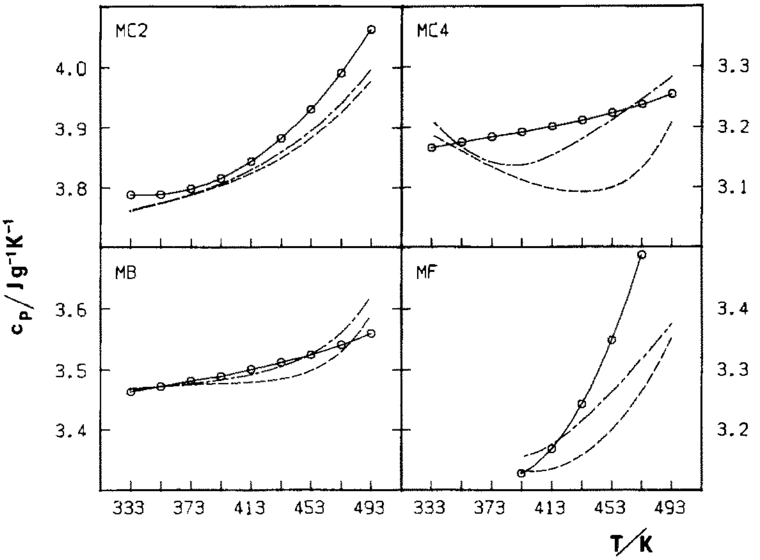

Fig. 4. Specific heat of aqueous solutions of the reciprocal system $Na^+/K^+/Cl^-/SO_4^{2-}$ as a function of temperature (for the composition of the solutions see Table 5). o——o, Experimental; — — —, calcualted in ref. 2; -——-, calculated using present data for $C_{p,\phi}$ of Na_2SO_4(aq) and ϑ_{ClSO_4}.

behaviour. It is, in fact, clear that the steep rise of experimental c_p values at high temperatures for solutions ME and MF is not reproduced by the calculated function. On the other hand, at the same temperatures the calculated function shows an overcorrection (while an undercorrection at the lower temperatures) for solution MC_4 with $m = 5.026$, where the large and comparable concentration of the ions Cl^- and SO_4^{2-} provides the conditions under which the ϑ_{ClSO_4} term displays its maximum effect. The latter term appears, therefore, to act more as an empirical correction, which only lowers the sum of the squares of the residuals without correctly interpreting the c_p variations which follow specific changes in the composition of the solutions.

It should also be noted that the solutions which display the larger discrepancies between experimental and calculated values, are all characterized by a high value of ionic strength ($I > 7$), independently of their actual ionic composition.

It is, apparently, not easy to provide a logical and exhaustive explanation of the c_p trend of the aqueous solutions of the mixed system under examination. We identify as the possible causes: (1) the extrapolation of Pitzer's parameters for the single salts to the large ionic strengths of the mixtures; (2) the poor validity of the additivite hypothesis used for calculating Pitzer's parameters for K_2SO_4(aq); and (3) the form of the temperature-fitting function chosen for the experimental $\bar{c}_{sat}$ values and for the Pitzer parameters.

As to the first point, the parameters β^0, β^1 and C^Φ for NaCl(aq) have been calculated from a general fit which used experimental c_p measurements on solutions with, at most, $I = 4.5$ mol kg^{-1}, and only few data from osmotic coefficients measured at high temperatures and concentrations (see Table III of ref. 11). The complex mixtures examined here reach I values larger than 7 mol kg^{-1}. The calculation of $\vartheta_{\mathrm{ClSO_4}}$ values themselves might be biased by use of extrapolated data for NaCl(aq).

As far as the second point is concerned, the additivite nature of Pitzer's coefficients should prove less valid at high concentrations; in fact, the largest differences between calculated and experimental values are shown by mixture MF which is characterized by the largest K_2SO_4 content.

The third point, finally, might lead to highly uncertain data at the extreme values of the temperature range investigated, when the derivative of eqn. (1) has its maximum uncertainty. Moreover, the strong correlation existing among Pitzer's parameters for a single salt makes their separate description with temperature very critical.

Other effects, such as neglecting the electrostatic contribution for unsymmetrical electrolytes [17], though pertinent to the reciprocal system under consideration, are certainly negligible compared with the uncertainties of the present experimental data.

We feel that the use of virial coefficients of single electrolytes for representing the characteristics of complex mixtures in conditions of temperature and concentration different from those in which they were calculated, is the major factor responsible for the observed discrepancies. Thus, the use of Pitzer's model for the description of the thermodynamic properties of complex ionic mixtures, while being a powerful and versatile tool, may reveal very critical discrepancies because of this factor. As a consequence, the physical meaning itself of parameters such as $\vartheta_{\mathrm{ClSO_4}}$ may be questionable, in view also of the fact that quantities calculated as excess properties are biased owing to the accumulation, on their values, of all the possible errors in the primary parameters.

As far as the possibility of reproducing the heat capacity data of the complex mixtures examined here is concerned, we think it is necessary to check whether the c_p values of NaCl(aq) are correctly described by the Silvester model [11], even under the experimental conditions of present work, and then to dispose of the experimental virial coefficients for the species K_2SO_4(aq) and for the mixed interaction terms neglected here. To achieve this, owing to the low water solubility of this salt, very precise experimental c_p data is required in order to reveal the effect of two-body and three-body interactions in even more dilute solutions. These data would probably prove less critical when applied to complex mixtures at higher ionic strengths. Pursuing this goal, we have constructed a flow calorimeter [15] capable of measuring the c_p of solutions, homogeneous at ambient temperature, at up to 600 K and 40 MPa with a precision which is ten times that of the drop calorimeter used here.

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