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HEAT CAPACITIES OF AQUEOUS MIXED ELECTROLYTE SOLUTIONS AT HIGH TEMPERATURE. THE RECIPROCAL SYSTEM K/Na/Cl/SO_4 BETWEEN 323 AND 493 K.

G.CONTI, P.GIANNI and M.R.TINE'
Istituto di Chimica Fisica, Via Risorgimento 35
Università di Pisa 56100 PISA (Italy)

ABSTRACT

The heat capacities of aqueous solutions containing the reciprocal system K/Na/Cl/SO_4 have been determined in the temperature range 333 - 493 K and for overall concentrations included between 0.5 and 5 molal. Experimental data are compared with those calculated both through the Pitzer's semiempirical equations, neglecting mixed interactions terms, and through the empirical Young's rule. A fair agreement is observed only for moderate values of T and m, at which the two procedures yield comparable results.

INTRODUCTION

Thermodynamic studies of aqueous salt systems at high temperatures, pressures and concentrations are very useful, particularly in view of the possibility of exploiting the energy and salt content of geothermal brines. Moreover, the developement of proper models (ref.1) which permit to predict the behaviour of these systems, require the availability of accurate thermodynamic data obtained at high concentrations and temperatures.

Making use of a drop calorimeter described previously (ref.2), we started a series of measurements of heat capacities of aqueous solutions containing the reciprocal system Na/K/Cl/SO_4. The solutions were realized by mixing in proper proportions three out of the four salts NaCl, KCl, Na_2SO_4 and K_2SO_4 with water and were studied at overall salt concentrations between 0.5 and 5 m and in the temperature range 333 - 493 K.

Experimental data were compared with those calculated using the semiempirical equations introduced by Pitzer (ref.3) (neglecting, as a first approximation, the mixed interaction terms ϑ and ψ) and also those calculated through the empirical method suggested many years ago by Young (ref.4).

GENERAL EQUATIONS

A general equation for computing the heat capacity at constant pressure, of the solutions, C_p , has been obtained by deriving with respect to temperature the expression proposed by Pitzer and Kim (ref.5) for the excess Gibbs free energy of solutions of mixed electrolytes:

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$$C_p = 1000\, c_w^o + \Sigma_i m_i \bar{C}^o_{p,i} + (A_J/3b) m \ln(1+b\sqrt{I})\, \Sigma_i\, \nu_i z_{Mi} |z_{Xi}|\, x_i - \\ - mRT^2 \Big[m(\mathbf{B}_J + \Theta_J) + m^2 (\mathbf{C}^\phi_J + \Psi_J) \Big] \qquad (1)$$

This equation expresses the heat capacity of a solution containing m moles of salts in 1 kg of water at temperature T. The index i refers to the single salt and the summations are extended to the four salts considered. $C^o_{p,i}$ is the partial molal heat capacity at infinite dilution, m_i and x_i the molality and internal molal fraction ($x_i = m_i/m$) respectively; ν_i is the number of ions of one molecule of dissolved electrolyte and z_{Mi} and z_{Xi} the cation and anion charge. Finally, c_w^o is the specific heat of water, A_J the Debye-Hückel constant for heat capacity (ref.6), I is the ionic strength, and b an empirical parameter which assumes in all cases a value of 1.2 (ref.3) .

The expressions of coefficients $\mathbf{B}_J$, Θ_J, $\mathbf{C}^\phi_J$ and Ψ_J as a function of the composition of the solution and of parameters of specific interactions B_J, ϑ_J, C^ϕ_J and ψ_J (ref.5 and 6), are as follows :

$$\mathbf{B}_J = 2\, \Sigma_a \Sigma_c\, y_a y_c\, B_{J,ca}$$

$$\Theta_J = \Sigma_c \Sigma_{c'}\, y_c y_{c'}\, \vartheta_{J,cc'} + \Sigma_a \Sigma_{a'}\, y_a y_{a'}\, \vartheta_{J,aa'}$$

$$\mathbf{C}^\phi_J = 2\, \Sigma_i x_i \Big[\nu_{Mi}\, \Sigma_a y_a (\Sigma zy)^{\frac{1}{2}} |z_{Mi} z_a|^{-\frac{1}{2}} C^\phi_{J,Mi,a} + \nu_{Xi}\, \Sigma_c y_c (\Sigma zy)^{\frac{1}{2}} |z_c z_{Xi}|^{-\frac{1}{2}} C^\phi_{J,cXi} + \\ + \Sigma_c \Sigma_a\, \nu_{Mi} z_{Mi} y_c y_a\, \tfrac{1}{2} |z_c z_a|^{-\frac{1}{2}} C^\phi_{J,ca} \Big] - 2\, \Sigma_c \Sigma_a\, y_c y_a (\Sigma zy) |z_c z_a|^{-\frac{1}{2}}\, C^\phi_{J,ca} \qquad (2)$$

$$\Psi_J = \Sigma_i x_i \Big[\Sigma_c \Sigma_a\, y_c y_a (\nu_{Mi}\, \psi_{J,Mi,ca} + \nu_{Xi}\, \psi_{J,caXi}) + \\ + \tfrac{1}{2} \Sigma_c \Sigma_{c'} y_c y_{c'}\, \nu_{Xi}\, \psi_{J,cc'Xi} + \tfrac{1}{2} \Sigma_a \Sigma_{a'} y_a y_{a'}\, \nu_{Mi}\, \psi_{J,Mi,aa'} \Big] + \\ + \Sigma_c \Sigma_{c'} y_c y_{c'} (\Sigma_a y_a \psi_{J,cc'a}) + \Sigma_a \Sigma_{a'} y_a y_{a'} (\Sigma_c y_c \psi_{J,caa'})$$

where the summations are extended to all cations c and c' and to all anions a and a', the values y_c, $y_{c'}$, y_a and $y_{a'}$ represent the ratio of the ion molality to the total molality of the salts ($y_j = m_j/m$) and $(\Sigma zy) = \Sigma z_c y_c = \Sigma |z_a| y_a$.

As mentioned before, eq.1 has been applied neglecting the terms Θ_J and Ψ_J relative to the pair and triplet mixed interactions.

The Young's empirical rule is expressed through the simple relation:

$$C_p = 1000\, c_w^o + m\, \Sigma_i\, x_i\, \Phi'_{Cp,i} \qquad (3)$$

where C_p, c_w^0, m and x_i have the meaning upper specified and $\Phi'_{Cp,i}$ is the apparent molal heat capacity of the salt i at the concentration value at which the salt, alone, has the same ionic strength as the mixed solution.

RESULTS AND DISCUSSION

Table 1 reports, at some temperatures and total salt concentrations, the specific heats at constant pressure, c_p, of solutions containing the reciprocal system under examination at a fixed ionic ratio (see table). For each concentration the experimental data are compared with those calculated through eqs. 1 and 2. The terms B_J, C_J^ϕ and $\bar{C}_p^o$ of single electrolytes, necessary for obtaining calculated data, were taken from Pitzer and coll. for NaCl (ref.6) and Na_2SO_4 (ref.7). As regards to KCl and K_2SO_4, the terms B_J and C_J^ϕ have been calculated

Table 1.
Experimental and calculated c_p ($J\ g^{-1}\ K^{-1}$) values for a solution containing the system $Na/K/Cl/SO_4$.$^{(a)}$

T/K m	333	373	413	453	493
0.6085	3.947	3.974	4.044	4.162	4.335
	3.958	3.988	4.038	4.124	4.257
	3.956	3.988	4.039	4.126	4.262
	3.958	3.988	4.038	4.125	4.265
1.2818	3.788	3.798	3.844	3.930	4.062
	3.761	3.788	3.824	3.882	3.977
	3.758	3.787	3.826	3.887	3.991
	3.762	3.788	3.823	3.886	4.000
2.8596	3.472	3.462	3.491	3.562	3.680
	3.444	3.439	3.444	3.468	3.546
	3.435	3.441	3.454	3.484	3.576
	3.445	3.437	3.442	3.480	3.607
5.0260	3.166	3.184	3.202	3.224	3.255
	3.188	3.134	3.098	3.100	3.212
	3.159	3.152	3.139	3.133	3.220
	3.197	3.115	3.076	3.113	3.341

(a) The solution is characterized by the following ionic ratios :
$m_{Na^+}/(m_{Na^+} + m_{K^+}) = 0.761$ and $m_{Cl^-}/(m_{Cl^-} + 2m_{SO_4^{--}}) = 0.594$.
For each molality the following values are reported : experimental results (1st line); values obtained from eq.1 using $\Theta_J = \Psi_J = 0$ (2nd line); values obtained from eq.3 using $x_1 = 0.446$, $x_2 = 0.300$, $x_3 = 0.254$, $x_4 = 0$ (3rd line) or using $x_1 = 0.745$, $x_2 = 0$, $x_3 = 0.105$, $x_4 = 0.150$ (4th line), being 1 = NaCl, 2 = KCl, 3 = Na_2SO_4 and 4 = K_2SO_4.

from our own experimental data (ref.2 and 8 respectively), while $\bar{C}_p^o$ values were taken from the literature for KCl (ref.9) or calculated using a criterion of additivity for K_2SO_4 (ref.8). The Young's rule furnishes two c_p values since the ionic composition of the mixture may be realized with two different triplets of salts (see note to the table).

It may be observed that the ability of the adopted procedures to reproduce the experimental data, within experimental uncertainty (± 0.02 J $g^{-1}K^{-1}$), results generally acceptable for moderate values of concentration and temperature. This last variable seems to be slightly more critical in determining the extent of the deviations. The application of Pitzer's procedure, when the ϑ_J and ψ_J terms are neglected, does not seem to yield much better results than the more simple Young's rule. The introduction of these mixed terms, whose experimental determination is however rather laborious, seems to be necessary for accurately reproducing the experimental data at high concentrations and temperatures.

It should be finally noted that the poor agreement between experimental and calculated data at the higher temperatures and concentrations may be partly due to the fact that the heat capacities of some salts,particularly Na_2SO_4 and K_2SO_4, have been experimentally determined up to values of ionic strength much lower than the largest value of the mixture here examined.

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