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Partial Molar Heats of Solution of Hydrated Electrolytes in Saturated Solutions

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Partial molar heats of solution of several hydrated electrolytes in saturated solutions ($\Delta H_s(sat) \equiv \bar{H}_2(sat) - H_2{}^s$) have been determined calorimetrically. From the results obtained, the following two subjects have been discussed: (1) the correlation between the values of $\Delta H_s(sat)$ and the dissolution process of hydrated electrolytes, and (2) the legitimacy of calculating a derivative $(\partial \ln \gamma_\pm / \partial \ln m)_{T,P}$ in a saturated solution from the value of $\Delta H_s(sat)$ and the temperature dependence of the solubility.

A solid sample of a hydrated electrolyte, sealed in an ampoule, was dissolved into 45 m*l* of a solvent, which consisted of an aqueous solution of the same electrolyte, the concentration of which was greater than 60% of its solubility. For each salt, $\Delta H_s(sat)$ has been obtained by extrapolating the observed heats of solution to saturation solubility. These values are listed in the second column of Table 1. They may be in error by as much as 3—4%.

Generally, for a hydrated electrolyte with the formula of $A_{\nu_+}X_{\nu_-} \cdot n H_2O$, the solubility in water, m'_{sat},[1] is expressed by the following equation:[2]

$$-\nu \boldsymbol{R} \ln\left(\frac{m'_{sat}}{m'_{sat}+M/(n+\nu)}\right) - n\boldsymbol{R} \ln\left(\frac{m'_{sat}+M/n}{m'_{sat}+M/(n+\nu)}\right) = \frac{\Delta H_s(sat)}{T} - \Delta S_m{}^F + \Delta C_p \ln\left(\frac{T_m}{T}\right) - S^E \qquad (1)$$

where $\nu = \nu_+ + \nu_-$, $\boldsymbol{R}$ is the gas constant, ΔS_m^F is the molar entropy of fusion at the melting point (T_m), ΔC_p is the difference in molar-heat capacities at a constant pressure between a liquid (fused) state and a solid state, and S^E is the entropy of mixing of a liquid (fused) electrolyte other than the cratic term (the left-hand side of Eq. (1)).

For $CaCl_2 \cdot 6H_2O$, for which all the experimental data are available,[3,4] the terms of the above equation become, at 25°C:

$$-\nu \boldsymbol{R} \ln\left(\frac{m'_{sat}}{m'_{sat}+M/(n+\nu)}\right) - n\boldsymbol{R} \ln\left(\frac{m'_{sat}+M/n}{m'_{sat}+M/(n+\nu)}\right) = 0.048\boldsymbol{R},$$

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[1] m' is molality suitable for a hydrated electrolyte; *i.e.*, an m' solution of the hydrated electrolyte with a general formula $A_{\nu_+}X_{\nu_-} \cdot nH_2O$ contains $m'\nu_+$ moles of cation A, $m'\nu_-$ moles of anion X, and $m'n$ moles of water in 1000 g of solvent (water). Hence $m' = m/(1 - nm/M)$, where m is usual molality and $M = 55.51$.

[2] H. Nakayama, *Bull. of the Faculty of Engineering, Yokoyama National University*, **19**, 29 (1970). The derivation of Eqs. (1) and (2) is briefly given in appendix.

[3] "Solubilities of Inorganic and Organic Compounds," Vol. 1, ed. by H. Stephen and T. Stephen, Pergamon Press, London (1963).

[4] "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill Book Comp., New York (1928).

$\Delta H_s(sat)/T = 15.16\boldsymbol{R}$ (this work, Table 1), $\Delta S_m^F = 14.81\,\boldsymbol{R}$, $\Delta C_p \ln(T_m/T) = 0.41\boldsymbol{R}$; consequently, from Eq. (1), $S^E = 0.71\,\boldsymbol{R}$. A notable feature of this example is that the terms having significant values are $\Delta H_s(sat)/T$ (entropy of solution in a saturated solution) and ΔS_m^F, and that these two terms are of approximately the same magnitude. This situation is typical of aqueous solutions of hydrated electrolytes for the following reasons.

Thermodynamically, the dissolution of a solid solute may be divided into two processes: (1) the melting of a solid solute, and (2) the mixing of the melt with a solvent. In the case of an aqueous solution of a hydrated electrolyte, the change in entropy (and also in enthalpy) due to the latter mixing process will be small since the melt of a hydrated electrolyte already contains considerable amounts of water.[5] The $\Delta C_p \ln(T_m/T)$ term in Eq. (1) will also be small because of the low melting point of the hydrated electrolyte. Consequently, it may be concluded that the dissolution process of a hydrated electrolyte is essentially specified by the melting process of a solid state.

On the other hand, $\Delta H_s(sat)$ is connected with the temperature dependence of the solubility $(\partial \ln m'_{sat}/\partial(1/T))_P$ by the following equation:[2]

$$\Delta H_s(sat) = -\nu \boldsymbol{R}\left(1-\frac{nm_{sat}}{M}\right)^2 \times \left(1+\left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{sat,T,P}\right)\cdot\left(\frac{\partial \ln m'_{sat}}{\partial(1/T)}\right)_P, \quad (2)$$

where $\gamma_\pm$ is the mean activity coefficient based on the m unit. From this relation, we may expect that the derivative $(\partial \ln \gamma_\pm/\partial \ln m)_{T,P}$ in a saturated solution can be calculated from the thermal data ($\Delta H_s(sat)$ and $(\partial \ln m'_{sat}/\partial(1/T))_P$) only. In Table 1, the values of $(\partial \ln \gamma_\pm/\partial \ln m)_{sat,T,P}$ obtained in this procedure are compared with those obtained by the graphical differentiation of the existing $\gamma_\pm - m$ data. They are in good agreement within the limits of experimental accuracy. This proposed method may also be applied to other electrolytes.

TABLE 1. THE PARTIAL MOLAR HEATS OF SOLUTION OF HYDRATED ELECTROLYTES IN SATURATED SOLUTIONS AT 25°C. AND THE COMPARISON OF THE VALUES OF $(\partial \ln \gamma_\pm/\partial \ln m)_{sat,T,P}$ CALCULATED FROM THERMAL DATA AND THOSE OBSERVED DIRECTLY

Electrolytes	ΔH_s (sat) (kcal/mol)	$(\partial \ln \gamma_\pm/\partial \ln m)_{sat,T,P}$	
		Calcd from Eq. (2)[a]	Observed[b]
$BaCl_2 \cdot 2H_2O$	4.35	+0.30	+0.39[7]
$NaBr \cdot 2H_2O$	3.15	+0.78	+0.62[8]
$MgCl_2 \cdot 6H_2O$	2.85	+5.50	+5.02[9]
$CaCl_2 \cdot 6H_2O$	8.98	+2.42	+2.55[10]
$Na_2SO_4 \cdot 10H_2O$	14.90	−0.40	−0.40[11]

a) The slope $(\partial \ln m'_{sat}/\partial(1/T))_P$ is obtained by graphical differentiation of the solubility data.[3]

b) The values obtained by graphical differentiation using $\gamma_\pm$ data cited.

Experimental

The calorimeter used was a twin-type micro-calorimeter manufactured by Ōyōdenki Kenkyujo (CM-502). The hydrated electrolytes, which were separated from their saturated solutions at 25°C, were left in an atmosphere of a constant vapor pressure of water (the dissociation pressure of each salt) until no more change in weight was observed.

Appendix

If we choose the pure liquid (fused) state as the standard state, the activity of a solid solute, $a_2{}^s$, may be given by the following equation:[6]

$$\boldsymbol{R}T\cdot\ln a_2{}^s = -\Delta H_m{}^F(1-T/T_m) + \Delta C_p(T_m - T - T\cdot\ln(T_m/T)). \quad \text{(A-1)}$$

On the other hand, when a solid solute is in equilibrium with its saturated solution, $\boldsymbol{R}T\cdot\ln a_2{}^s$ can be expressed as:

$$\boldsymbol{R}T\cdot\ln a_2{}^s = (\bar{H}_2(sat) - H_2{}^l) - T(\bar{S}_2(sat) - S_2{}^l), \quad \text{(A-2)}$$

where the superscript l stands for a liquid state. We may rewrite the enthalpy term of Eq. (A-2) as:[6]

$$\begin{aligned}\bar{H}_2(sat) - H_2{}^l &= (\bar{H}_2(sat) - H_2{}^s) - \Delta H_m{}^F + \Delta C_P(T_m - T)\\ &= \Delta H_s(sat) - \Delta H_m{}^F + \Delta C_P(T_m - T). \quad \text{(A-3)}\end{aligned}$$

The entropy term of Eq. (A-2) can be expressed as:

$$\bar{S}_2(sat) - S_2{}^l = -\boldsymbol{R}\left\{\nu_+ \ln\left(\frac{X_+^{sat}}{X_+^l}\right) + \nu_- \ln\left(\frac{X_-^{sat}}{X_-^l}\right) + n\ln\left(\frac{X_{H_2O}^{sat}}{X_{H_2O}^l}\right)\right\} + S^E, \quad \text{(A-4)}$$

with

$$X_+^{sat} = \frac{\nu_+ m'_{sat}}{M + m'_{sat}(n+\nu)}, \quad X_+^l = \frac{\nu_+}{n+\nu},$$

$$X_-^{sat} = \frac{\nu_-{}' m_{sat}}{M + m'_{sat}(n+\nu)}, \quad X_-^l = \frac{\nu_-}{n+\nu},$$

$$X_{H_2O}^{sat} = \frac{M + nm'_{sat}}{M + m'_{sat}(n+\nu)}, \quad X_{H_2O}^l = \frac{n}{n+\nu},$$

where X^{sat} and X^l represent the mole fraction in a saturated solution and in a liquid (fused) state respectively. By combining these four equations, we finally get Eq. (1).

The entropy of solution of a solid solute is connected with the temperature dependence of the solubility by the following equation:[6]

$$\bar{S}_2(m') - S_2{}^s = \left(\frac{\partial(\mu_2(m') - \mu_2{}^s)}{\partial \ln m'}\right)_{T,P}\cdot\left(\frac{\partial \ln m'_{sat}}{\partial T}\right)_P. \quad \text{(A-5)}$$

The chemical potential of a hydrated electrolyte ($A\nu_+X\nu_-\cdot nH_2O$) becomes:

$$\mu_2(m') = \mu^{0\prime}(T,P) + \boldsymbol{R}T\ln(m\gamma_\pm) + n\boldsymbol{R}T\ln a_1, \quad \text{(A-6)}$$

in which a_1 is the activity of water. By inserting Eq. (A-6) into Eq. (A-5) and using the Gibbs-Duhem relation, $M\mathrm{d}\ln a_1 + m\mathrm{d}\ln a_2 = 0$, we obtain for a saturated solution:

$$\bar{S}_2(sat) - S_2{}^s = \nu\boldsymbol{R}T\left(1-\frac{nm_{sat}}{M}\right)^2\cdot\left\{1+\left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{sat,T,P}\right\} \times \left(\frac{\partial \ln m'_{sat}}{\partial T}\right)_P. \quad \text{(A-7)}$$

This equation is identical with Eq. (2), since $\Delta H_s(sat) = T(\bar{S}_2(sat) - S_2{}^s)$.

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5) For instance, for $CaCl_2 \cdot 6H_2O$ the water content is 49.3% in the melt and 54.7% in the saturated solution (at 25°C).

6) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall Inc., Englewood Cliffs, New Jersey (1962).

7) R. A. Robinson, *Trans. Faraday Soc.*, **36,** 735 (1940).

8) L. L. Makarov, Yu. G. Vlasov, and V. A. Azarko, *Zh. Fiz. Khim.*, **40,** 1134 (1966).

9) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," McGraw-Hill Book Comp., New York (1961).

10) R. H. Stokes, *Trans. Faraday Soc.*, **41,** 637 (1945).

11) R. A. Robinson, J. M. Wilson, and R. H. Stokes, *J. Amer. Chem. Soc.*, **63,** 1011 (1941).