Enthalpy of Solution for Anhydrous $VOSO_4$ and Estimated Enthalpy of Reaction for Formation of the Ion Pair $[VOSO_4]^0$

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The molal enthalpies of solution of $VOSO_4 \cdot nH_2O$ (n = 4.21, 3.90, 3.00, and 2.63) at various molalities in water, $\Delta_{sol}H_m$, were measured by a solution−reaction isoperibol calorimeter at (298.15 ± 0.01) K. The standard molal enthalpies of solution of $VOSO_4 \cdot nH_2O(s)$, $\Delta_{sol}H_m^0(n)$, were determined according to Archer's method. The standard molal enthalpies of solution for anhydrous VOSO4(s), $\Delta_{sol}H_m^0 = (-49.19 \pm 0.65)$ $kJ \cdot mol^{-1}$, were obtained using extrapolation, and relative apparent molal enthalpies, φ_L, of aqueous $VOSO_4$ were calculated. In terms of the Bjerrum theory for ion association and the values of φ_L, the enthalpy of reaction for the formation of the ion pair $[VOSO_4]^0$, $\Delta_{as}H_m^0 = (3.42 \pm 0.04)$ $kJ \cdot mol^{-1}$, was estimated using a semiempirical method.

1. Introduction

The vanadium redox flow battery (VRB) is showing great promise as an efficient new energy-storage system for a wide range of applications.[1−4] The thermochemical data of vanadyl sulfate should be of considerable interest for the VRB because vanadyl sulfate is one of the most important components; it is not only the conductor of the ions but also the energy-storage medium in this battery. Fundamental knowledge of thermochemistry may help to optimize the cell operation and to realize high energy efficiency.

Recently, there has been a developing trend in the literature toward estimation of thermodynamic quantities, which is to be commended because it provides valuable insight into the origins of the behavior of materials.[5−8] In particular, physicochemical properties of some unstable compounds are difficult to measure so that predicting these properties using semiempirical methods is an important goal in research. To our knownledge, no measurement of the enthalpy of solution for $VOSO_4(s)$ is at present available because $VOSO_4(s)$ is easily hydrated and the preparation of anhydrous $VOSO_4(s)$ is quite difficult. Therefore, this article reports on the molal enthalpy of solution of $VOSO_4 \cdot nH_2O$ (n = 4.21, 3.90, 3.00, and 2.63) at various molalities in water, $\Delta_{sol}H_m(n)$, measured by a solution−reaction isoperibol calorimeter at (298.15 ± 0.01) K. According to Archer's method,[9] the standard molal enthalpies of solution of $VOSO_4 \cdot nH_2O$, $\Delta_{sol}H_m^0(n)$, can be obtained. Then, the value of the standard molal enthalpies of solution, $\Delta_{sol}H_m^0$, for anhydrous $VOSO_4(s)$ was obtained using an extrapolation method, and the relative apparent molal enthalpy, φ_L, of aqueous $VOSO_4$ was calculated. Lastly, in terms of the Bjerrum theory for ion association and the values of φ_L, the enthalpy of reaction for formation of the ion pair $[VOSO_4]^0$, $\Delta_{as}H_m^0$, was estimated using a semiempirical method.

2. Experimental Section

2.1. Chemicals. $VOSO_4 \cdot nH_2O(s)$ was recrystallized twice from water.[10] Several samples of $VOSO_4 \cdot nH_2O(s)$ were dried under reduced pressure at various temperatures,[10] and the values of n (n = 4.21, 3.90, 3.00, and 2.63) were determined by thermogravimetry (TG) with a ThermoMax 700 apparatus (Thermo Carhn). The temperature range of the TG was (273 to 673) K with a heating rate of 20 $K \cdot min^{-1}$ under a nitrogen atmosphere. KCl with a purity greater than 99.99 % was dried in a vacuum oven at 408 K for 6 h, and THAM (tris(hydroxymethyl)aminomethane), a GR grade reagent, was dried in a vacuum oven before use. Double-distilled water was used.

2.2. Determination of the Molal Enthalpies of Solution. On the basis of other calorimetric apparatuses,[11,12] a solution−reaction isoperibol calorimeter was constructed. It consists of a water thermostat, a 200 mL pyrex-glass plated silver Dewar, a 4 mL glass sample cell, a calibration heater, a glass-sheathed thermistor probe, an amplifier, a circuit used as an A/D converter, and a personal computer for data acquisition and processing. 150 g of water (or 150 mL of 0.1 $mol \cdot dm^{-3}$ HCl(aq)) was placed in the Dewar, and (0.1 to 2) g of solute (KCl, THAM, or $VOSO_4 \cdot 3.52H_2O(s)$) was placed in the sample cell. The inevitable heat transfer and heat generation owing to friction were compensated, and the corrected temperature change (the adiabatic temperature change) ΔT^* was obtained according to a conventional method (the equal area method). The enthalpies of solution were calculated from the equation

$$Q_s/\Delta T_s^* = Q_E/\Delta T_E^* \qquad (1)$$

where Q_s is the enthalpy of solution of the sample, ΔT_s^* is the adiabatic temperature change of the solution process, Q_E is the electric energy calibration, and ΔT_E^* is the adiabatic temperature change of the electric calibration.

We tested the performance and accuracy of the calorimetric system by measuring the molal enthalpy of solution of KCl in water and THAM in 0.1 $mol \cdot dm^{-3}$ HCl(aq) at 298.15 K. The results are listed in the Supporting Information. The mean molal

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Table 1. Values of Molal Solution Enthalpy of $VOSO_4 \cdot nH_2O$, $\Delta_{sol}H_m(n)$, with Different Molalities and Extrapolation Function, Y, at 298.15 K

$VOSO_4 \cdot nH_2O$	10^2m $mol \cdot kg^{-1}$	$-\Delta_{sol}H_m(n)$ $kJ \cdot mol^{-1}$	$-Y$ $kJ \cdot mol^{-1}$	$-\Delta_sH_m(anh)$ $kJ \cdot mol^{-1}$
$VOSO_4 \cdot 4.21H_2O$	8.562	11.64 ± 0.06	15.16	42.12
	7.959	11.89 ± 0.07	15.31	42.37
	7.388	12.21 ± 0.08	15.53	42.69
	6.854	12.44 ± 0.08	15.67	42.92
	6.353	12.76 ± 0.09	15.89	43.24
	5.809	13.11 ± 0.10	16.13	43.59
	5.288	13.46 ± 0.12	16.37	43.94
$VOSO_4 \cdot 3.90H_2O$	8.059	13.21 ± 0.05	16.65	41.45
	7.447	13.62 ± 0.06	16.95	41.86
	6.856	14.09 ± 0.07	17.32	42.33
	6.321	14.48 ± 0.08	17.61	42.72
	5.796	14.83 ± 0.10	17.85	43.07
$VOSO_4 \cdot 3.00H_2O$	9.176	19.04 ± 0.07	22.66	40.76
	8.595	19.37 ± 0.07	22.90	41.09
	8.013	19.74 ± 0.08	23.17	41.46
	7.449	20.14 ± 0.11	23.48	41.86
	6.884	20.51 ± 0.13	23.74	42.23
$VOSO_4 \cdot 2.63H_2O$	9.184	21.41 ± 0.07	25.03	40.45
	8.609	21.82 ± 0.08	25.35	40.86
	8.013	22.28 ± 0.09	25.71	41.32
	7.447	22.64 ± 0.10	25.97	41.68
	6.864	23.08 ± 0.12	26.31	42.12

enthalpies of solution are $\Delta_{sol}H_m = (17\,526 \pm 26)$ $J \cdot mol^{-1}$ for KCl (molal ratio: KCl/water 1/1110) and $(-29\,761 \pm 25)$ $J \cdot mol^{-1}$ for THAM (0.750 g of THAM dissolved in 0.150 L of 0.1 $mol \cdot dm^{-3}$ HCl(aq)), which are in good agreement with published data $(17\,536 \pm 9)$ $J \cdot mol^{-1}$ for KCl[13,14] and $(-29\,766 \pm 31.5)$ $J \cdot mol^{-1}$ for THAM.[14] These results verified the credibility of the isoperibol calorimeter. Then, the molal enthalpies of solution of $VOSO_4 \cdot nH_2O$ (n = 4.21, 3.90, 3.00, and 2.63) at different molalities were measured.

3. Results and Discussion

3.1. Molal Enthalpy of Solution of $VOSO_4 \cdot nH_2O(s)$. The values of the molal enthalpy of solution, $\Delta_{sol}H_m(n)$, for $VOSO_4 \cdot nH_2O(s)$ at different molalities and (298.15 ± 0.01) K are listed in Table 1. The molalities, m, were known to within 0.05 %. From Table 1, it is shown that the dissolving $VOSO4 \cdot nH_2O(s)$ in water is an exothermic process, and the values of $-\Delta_{sol}H_m(n)$ decrease with increasing molality.

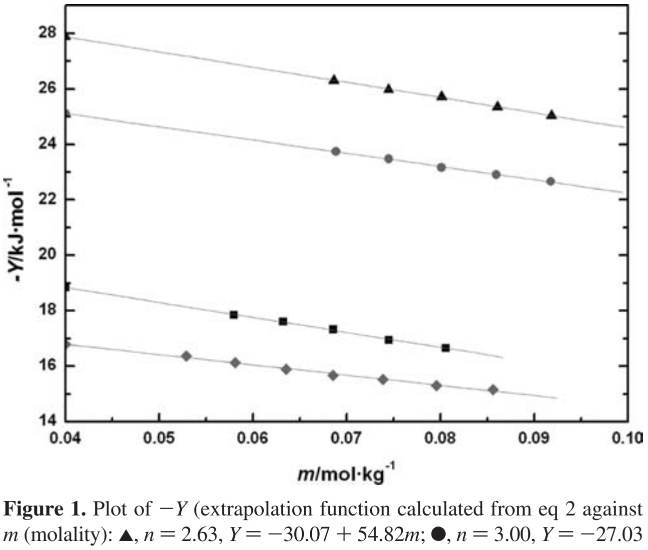

Figure 1. Plot of $-Y$ (extrapolation function calculated from eq 2 against m (molality): ▲, $n = 2.63$, $Y = -30.07 + 54.82m$; ●, $n = 3.00$, $Y = -27.03 + 47.81m$; ■, $n = 3.90$, $Y = -21.01 + 54.17m$; ◆, $n = 4.21$, $Y = -18.28 + 37.06m$.

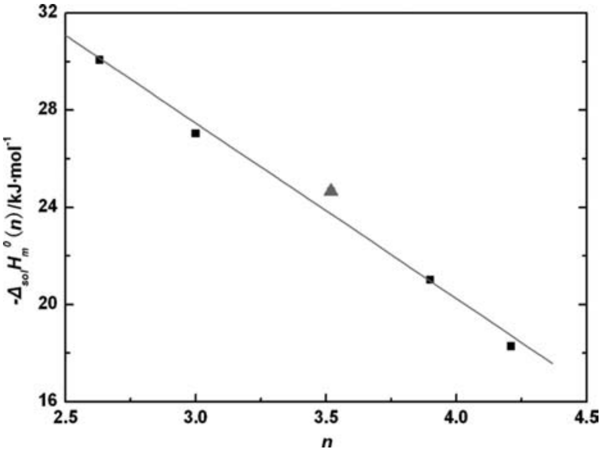

Figure 2. Plot of $-\Delta_{sol}H_m^0(n)$ for $VOSO_4 \cdot nH_2O(s)$ versus n. (The fitting equation is $\Delta_{sol}H_m^0(n) = -49.19 + 7.24n$ with the coefficients of determination, $r^2 > 0.99$, and standard deviation, $s = 0.65$ $kJ \cdot mol^{-1}$. The intercept −49.19 is the value of the standard molal solution enthalpy of anhydrous $VOSO_4$, $\Delta_{sol}H_m^0$. ▲ is the previous work by our laboratory.)

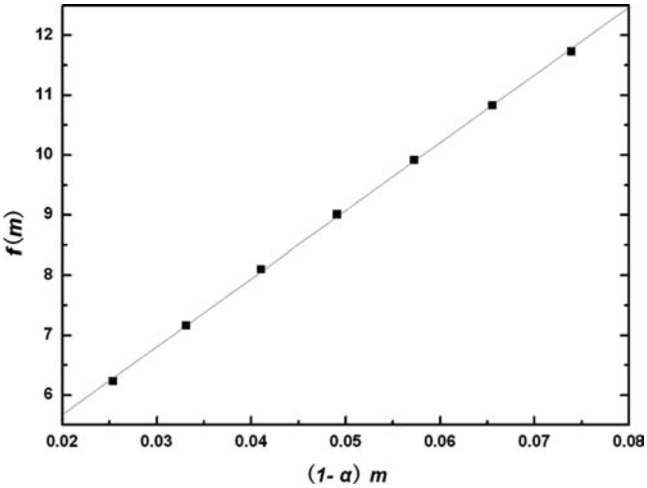

Figure 3. Plot of $f(m)$ versus $(1 - \alpha)m$. (The fitting equation is $f(m) = 3.4152 + 113.18(1 - \alpha)m$ with the coefficients of determination, $r^2 > 0.99$, and standard deviation, $s = 0.04$ $kJ \cdot mol^{-1}$. The intercept 3.42 $kJ \cdot mol^{-1}$ is the molal enthalpy of reaction for formation of the ion pair $[VOSO_4]^0$, $\Delta_{as}H_m^0$.)

3.2. Standard Molal Enthalpies of Solution, $\Delta_{sol}H_m^0(n)$, for $VOSO_4 \cdot nH_2O$. If the infinite dilution of aqueous $VOSO_4 \cdot nH_2O$ is selected as the reference state, then according to Archer's method,[9] the values of the standard molal enthalpy of solution of $VOSO_4 \cdot nH_2O$, $\Delta_{sol}H_m^0(n)$, can be obtained using the following equation

$$Y = \Delta_{sol}H_m(n) - (|z_+z_-|A_H/b)\ln(1 + bI^{1/2}) = \Delta_{sol}H_m^0(n) + \beta m \quad (2)$$

where z_+ and z_- are the charge numbers of the positive and negative ions, respectively, m is molality, I is ionic strength, b is a constant assigned to be 1.2,[15] A_H is the Debye−Hückel parameter for enthalpy (its value was taken from the literature),[15] β is an empirical constant, and Y is an extrapolation function that was calculated from experimental data. The values of $-Y$ against m for all $VOSO_4 \cdot nH_2O(s)$ were regressed according to eq 1, and good straight lines were obtained. (See Figure 1.) The coefficients of determination of the linear regression, r^2, were greater than 0.99. The values of $\Delta_{sol}H_m^0(n)$ and β obtained from the intercepts and slopes of these linear regressions are listed in Table 2. From Figure 1 and Table 2, it is clear that the values of $-\Delta_{\mathrm{sol}}H_{\mathrm{m}}{}^{0}(n)$ decrease with an increase of n in $\mathrm{VOSO_4 \cdot} n\mathrm{H_2O}$.

3.3. Standard Molal Enthalpy of Solution, $\Delta_{sol}H^0_m$, of Anhydrous $VOSO_4$. The values of $-\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(n)$ were plotted against n in $\mathrm{VOSO_4 \cdot} n\mathrm{H_2O}$, a straight line was obtained (Figure 2), and the coefficients of determination of the linear regression, r^2, are greater than 0.99 and the standard error is less than 0.65 kJ·mol^{-1}. The intercept of the line is the standard molal enthalpy of solution for anhydrous $\mathrm{VOSO_4(s)}$, $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}} = (-49.19 \pm 0.65)$ kJ·mol^{-1}. The relationship between $\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(n)$ and n is expressed in the following empirical equation

$$\Delta_{\mathrm{sol}}H^0_{\mathrm{m}}(n) = \Delta_{\mathrm{sol}}H^0_{\mathrm{m}} + an \tag{3}$$

where the empirical constant $a = 7.24$ kJ·mol^{-1} is the mean contribution per mole of water in $\mathrm{VOSO_4 \cdot} n\mathrm{H_2O}$ to the molal enthalpy of solution so that the molal enthalpy of solution of anhydrous $\mathrm{VOSO_4}$ at various concentrations, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{anh})$, can be calculated using the following equation

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{anh}) = \Delta_{\mathrm{sol}}H_{\mathrm{m}}(n) - na \tag{4}$$

The values calculated using eq 4 are listed in Table 1.

3.4. Estimation of the Enthalpy of Reaction for Formation of the Ion Pair $[VOSO_4]^0$. Some authors have pointed out that divalent metal sulfates can form ion pairs in aqueous solution.[15−17] For aqueous $\mathrm{VOSO_4}$ we have

$$\mathrm{VO^{2+} + SO_4^{2-} \rightarrow [VOSO_4]^0}$$

In the formation of the ion pair $[\mathrm{VOSO_4}]^0$, the observed apparent molal enthalpy, φ_{H}, can be considered to be made up of two components[16,17]

$$\varphi_{\mathrm{H}} = \alpha\varphi_{\mathrm{H}}(\mathrm{VO^{2+},SO_4^{2-}}) + (1-\alpha)\varphi_{\mathrm{H}}([\mathrm{VOSO_4}]^0) \tag{5}$$

where α is the fraction of the free ions ($\mathrm{VO^{2+}}$, $\mathrm{SO_4{}^{2-}}$), $\varphi_{\mathrm{H}}(\mathrm{VO^{2+}}, \mathrm{SO_4{}^{2-}})$ is the apparent molal enthalpy of the free ions, and $\varphi_{\mathrm{H}}([\mathrm{VOSO_4}]^0)$ is the apparent molal enthalpy of the ion pair. By using the definition of the relative apparent molal enthalpy, φ_{L}

$$\varphi_{\mathrm{L}} = \varphi_{\mathrm{H}} - \varphi^0_{\mathrm{H}} \tag{6}$$

where φ^0_{H} is the infinite dilution apparent molal enthalpy. Noting that the observed $\varphi H^0_{\mathrm{H}} = \varphi^0_{\mathrm{H}}(\mathrm{VO^{2+}}, \mathrm{SO_4{}^{2-}})$ at infinite dilution upon substituting into eq 5 and rearranging, we have for the observed φ_{L}

$$\varphi_{\mathrm{L}} = \alpha\varphi_{\mathrm{L}}(\mathrm{VO^{2+},SO_4^{2-}}) + (1-\alpha)\{\varphi_{\mathrm{L}}([\mathrm{VOSO_4}]^0) + \varphi^0_{\mathrm{H}}([\mathrm{VOSO_4}]^0 - \varphi^0_{\mathrm{H}}(\mathrm{VO^{2+},SO_4^{2-}})\} \tag{7}$$

According to thermodynamic relationships,[15] the observed φ_{L} can be obtained from the enthalpy of solution of anhydrous $\mathrm{VOSO_4}$ using the following equation

$$\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{anh}) = \varphi_{\mathrm{L}} + \Delta_{\mathrm{sol}}H^0_{\mathrm{m}} \tag{8}$$

The values of φ_{L} calculated using eq 8 are listed in Table 3.

Because the molal enthalpy of reaction for formation of the ion pair $[\mathrm{VOSO_4}]^0$, $\Delta_{\mathrm{as}}H^0_{\mathrm{m}}$, is given by

$$\Delta_{\mathrm{as}}H^0_{\mathrm{m}} = \varphi^0_{\mathrm{H}}([\mathrm{VOSO_4}]^0) - \varphi^0_{\mathrm{H}}(\mathrm{VO^{2+},SO_4^{2-}}) \tag{9}$$

we obtain upon substituting into eq 7

$$\varphi_{\mathrm{L}} = \alpha\varphi_{\mathrm{L}}(\mathrm{VO^{2+},SO_4^{2-}}) + (1-\alpha)\{\varphi_{\mathrm{L}}([\mathrm{VOSO_4}]^0) + \Delta_{\mathrm{as}}H^0_{\mathrm{m}}\} \tag{10}$$

From this equation it is possible to determine $\Delta_{\mathrm{as}}H^0_{\mathrm{m}}$, provided that one can estimate α, $\varphi_{\mathrm{L}}(\mathrm{VO^{2+}}, \mathrm{SO_4{}^{2-}})$, and $\varphi_{\mathrm{L}}([\mathrm{VOSO_4}]^0)$.

The value of $\varphi_{\mathrm{L}}(\mathrm{VO^{2+}}, \mathrm{SO_4{}^{2-}})$ for the free ions needed in the calculation of $\Delta_{\mathrm{as}}H^0_{\mathrm{m}}$ can be estimated by using the Debye−Hückel equation[16,17]

$$\varphi_{\mathrm{L}}(\mathrm{VO^{2+}, SO_4^{2-}}) = S_{\mathrm{H}}(4\alpha m)^{1/2}/[1 + B_{\mathrm{H}}a^0(4\alpha m)^{1/2}] \tag{11}$$

According to the literature,[16] $S_{\mathrm{H}} = 7.899$ kJ·mol$^{-1/2}$, $B_{\mathrm{H}} = 0.3291$ at 298.15 K, and $a^0 = 4$ is the ion size parameter for aqueous divalent metal sulfates. Considering the larger size of

Table 2. Values of Standard Molal Enthalpy of Solution for $\mathrm{VOSO_4 \cdot} n\mathrm{H_2O}$ at 298.15 K

N	$\Delta_{\mathrm{s}}H_{\mathrm{m}}{}^{0}(n)$ / kJ·mol^{-1}	β	r	SD	n	$\Delta_{\mathrm{s}}H_{\mathrm{m}}{}^{0}(n)$ / kJ·mol^{-1}	β	r	SD
4.21	−18.28	−37.06	0.99	0.05	3.00	−27.03	−47.81	0.99	0.02
3.90	−21.01	−54.17	0.99	0.03	2.63	−30.07	−54.82	0.99	0.02

Table 3. Values of Molal Solution Enthalpy of Anhydrous $\mathrm{VOSO_4}$, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{anh})$, with Different Molalities in Water

m / mol·kg^{-1}	$\Delta_{\mathrm{s}}H^0_{\mathrm{m}}(n)$ / kJ·mol^{-1}	φ_{L} / kJ·mol^{-1}	α	φ_{L} ($\mathrm{VO^{2+}}$, $\mathrm{SO_4{}^{2-}}$) / kJ·mol^{-1}	$f(m)$ / kJ·mol^{-1}
0.10	40.09	9.10	0.2612	1.67	11.73
0.09	40.86	8.33	0.2719	1.63	10.83
0.08	41.64	7.55	0.2842	1.59	9.92
0.07	42.41	6.78	0.2988	1.55	9.01
0.06	43.18	6.01	0.3163	1.50	8.10
0.05	43.96	5.23	0.3380	1.44	7.16
0.04	44.70	4.45	0.3659	1.37	6.23

Table 4. Standard Molal Enthalpy of Formation Reaction of Divalent Metal Sulfate Ion Pair $[MSO_4]^0$, $\Delta_{as}H_m^0$

	$[VOSO_4]^0$	$[MgSO_4]^0$	$[ZnSO_4]^0$	$[CdSO_4]^0$	$[CaSO_4]^0$	$[CuSO_4]^0$	$[NiSO_4]^0$
$\Delta_{as}H_m^0/kJ\cdot mol^{-1}$	3.42[a]	5.31[b]	5.69[b]	9.00[b]	6.28[b]	7.20[b]	6.36[b]

[a] This work. [b] Larson, J. W. *J. Phys. Chem.* **1970**, *74*, 3392.

VO^{2+}, $a^0 = 5$ for aqueous $VOSO_4$ was used in this work. The values of $\varphi_L(VO^{2+}, SO_4^{2-})$ calculated using eq 11 are listed in Table 3.

The values of the fraction of the free ions (VO^{2+}, SO_4^{2-}), α, at any concentration needed to calculate $\Delta_{as}H_m^0$ may be determined by successive approximations from the association constant of the ion pair, K_{as}

$$K_{as} = (1 - \alpha)/(\alpha^2 f_\pm^2 m) \tag{12}$$

where m is the molality and $f_\pm$ is the activity coefficient of the free ions. (The activity coefficient of $[VOSO_4]^0$ is assumed to be 1.0.) The values of $f_\pm$ in dilute solution (below 0.1 mol·kg^{-1}) can be estimated by using the Debye−Hückel equation

$$\log f_\pm = -A(4\alpha m)^{1/2}/[1 + Ba^0(4\alpha m)^{1/2}] \tag{13}$$

where A and B are Debye−Hückel parameters for activity coefficients at 298.15 K.[18] The value of K_{as} in eq 12 may be estimated by the Bjerrum theory

$$K_{as} = (4\pi N/1000)(|z_+z_-|e^2/DkT)^3 Q(b) \tag{14}$$

where N is Avogadro's number, e is the charge of the electron, k is the Boltzmann constant, D is the dielectric constant, $b = |z_+z_-|\, e^2/DkTa^0$, and $Q(b)$ is taken from the literature.[18] Using eq 14, we obtained $K_{as} = 178$, which is in reasonable agreement with $K_{as} = 213$ for the $[ZnSO_4]^0$ ion pair.[16]

The estimated values of the fraction of the free ions (VO^{2+}, SO_4^{2-}), α, using successive approximations are listed in Table 3.

By assuming that $\varphi_L([VOSO_4]^0)$ varies as a function of concentration by[16,17]

$$\varphi_L([VOSO_4]^0) = g(1 - \alpha)m \tag{15}$$

where g is an empirical parameter. It is possible to determine $\Delta_{as}H_m^0$ from the observed φ_L data using the following linear equation

$$\begin{aligned} f(m) &= [\varphi_L - \alpha\varphi_L(VO^{2+}, SO_4^{2-})]/(1 - \alpha) \\ &= \Delta_{as}H_m^0 + g(1 - \alpha)m \end{aligned} \tag{16}$$

On the left side of eq 16, $f(m)$, is an extrapolation function, and φ_L (VO^{2+}, SO_4^{2-}) has been calculated from eq 11. By plotting $f(m)$ versus $(1 - \alpha)m$, we obtained a good straight line (Figure 3), and the fitting equation is $f(m) = 3.4152 + 113.18(1 - \alpha)m$. The intercept of the line is $\Delta_{as}H_m^0 = (3.42 \pm 0.04)$ kJ·mol^{-1}, and the coefficient of determination of the fitting, r^2, is greater than 0.99.

To our knowledge, no measurement of the enthalpy of reaction for the formation of the ion pair $[VOSO_4]^0$ is presently available. To explain the rationality of the estimation, the value of $\Delta_{as}H_m^0$ estimated in this work is compared in Table 4 with the values of other divalent metal sulfate ion pairs $[MSO_4]^0$ determined by Larson.[16] As one might expect, the magnitude of $\Delta_{as}H_m^0 = (3.42 \pm 0.04)$ kJ·mol^{-1} is in good agreement with those of other divalent metal sulfate ion pairs. This result means that our estimation is credible.

Supporting Information Available:

Values of molar enthalpy of solution in water of KCl and enthalpy of the reaction of THAM in 0.1 mol·dm^{-3} of HCl(aq). This material is available free of charge via the Internet at http://pubs.acs.org.

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