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Enthalpy of Solution of Potassium Tetrafluoroborate in Water and in Aqueous Sodium Fluoride. Thermodynamic Properties of the Aqueous Tetrafluoroborate Anion and Potassium Tetrafluoroborate

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An adiabatic calorimeter was used to measure the enthalpy of solution of potassium tetrafluoroborate ($0.01\ \mathrm{mol{\cdot}kg^{-1}}$ to $0.02\ \mathrm{mol{\cdot}kg^{-1}}$) in water and in aqueous sodium fluoride of different ionic strengths ($0.2\ \mathrm{mol{\cdot}kg^{-1}}$ and $0.5\ \mathrm{mol{\cdot}kg^{-1}}$) at 298 K and 313 K. The present results yield the standard-state enthalpy and heat capacity for the solution process and, when combined with literature values for solubilities, yield the standard-state entropy of the solution process. From these properties, and previous measurements involving potassium tetrafluoroborate, we provide a new analysis of thermodynamic properties of the aqueous tetrafluoroborate ion and compare these new properties to previous tabulations and explain the sources of discrepancies in the literature.

Introduction

Materials known as “ionic liquids” have attracted considerable interest recently as replacements for volatile organic solvents in which synthesis reactions are conducted. These ionic liquids are essentially salts in which one or more of the ions is a fairly large organic ion. Several ionic liquids consist of a large organic cation combined with an inorganic anion. These materials indeed show large differences, one compared to another, in several of their properties, including their aqueous solubility and hygroscopy. Generally, for a given large organic cation, the aqueous solubilities of the ionic liquids formed with a halide are much greater than those formed with a less well hydrated anion (e.g., tetrafluoroborate or hexafluorophosphate ions). We have begun examinations of the aqueous thermodynamics of ionic liquids. We intend to make use of the additivity of standard-state properties of aqueous ions. For thermodynamic reasons, we initiate our studies with moderately soluble ionic liquids. This group is composed largely of ionic liquids that contain either the hexafluorophosphate ion or the tetrafluoroborate ion. However, there are some questions as to how well known are the thermodynamic properties of these aqueous anions. Large uncertainties in the thermodynamic properties of the inorganic anions would limit the ability to extract the standard-state properties of the aqueous cations from measured thermodynamic properties. As an example of the level of uncertainty of the thermodynamic properties of these anions, we cite literature values. The NBS Tables[1] gave the enthalpy of formation of the aqueous tetrafluoroborate anion as $-1574.9\ \mathrm{kJ{\cdot}mol^{-1}}$, whereas Devina et al.[2] gave $(-1581.31 \pm 3.00)\ \mathrm{kJ{\cdot}mol^{-1}}$ as the enthalpy of formation value. Literature sources also disagree about values of the standard-state entropy and the heat capacity of the aqueous tetrafluoroborate ion. Entropy values of $180\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and $193.3\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ are given in the NBS Tables and by Devina et al., respectively. For the standard-state heat capacity of the ion, there is disagreement even on the sign of the property. Devina et al. gave $(25 \pm 5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, whereas Shock and Helgeson[3] estimated the value to be $-23\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Considering also the differences between the two references[1,2] for the formation properties of crystalline $NaBF_4$ and KBF_4, fairly large differences are observed in thermodynamic properties calculated for real processes. For example, the enthalpies of solution calculated from the NBS Tables for $NaBF_4$ and KBF_4 are $(29.7\ \text{and}\ 54.8)\ \mathrm{kJ{\cdot}mol^{-1}}$, respectively, and are $(22.8\ \text{and}\ 57.2)\ \mathrm{kJ{\cdot}mol^{-1}}$, respectively, from Devina et al. It seemed that some improvement could be made. To this end, we report here new measurements of the enthalpy of solution of potassium tetrafluoroborate in water and in aqueous sodium fluoride.

Experimental Section

Chemicals. Potassium tetrafluoroborate (99.99+%) was obtained from Aldrich. The manufacturer’s purity analysis used inductively coupled plasma spectroscopy, which identified 11 metal impurities; the largest impurity was present at a concentration of less than 10 ppm. The manufacturer’s atomic absorption analysis identified alkali metal impurities; in addition to potassium, the largest alkali metal impurities were rubidium and sodium, both present at less than 9 ppm. A titration with sodium hydroxide was performed by the manufacturer to confirm BF_4 anion content. The value obtained for BF_4 was in excess of that expected theoretically, which is consistent with an assessment indicating that the material does not have a significant amount of any hydrolysis products. The 99.99+% purity was thus based on the trace metals analysis. The sample of KBF_4 was stored in a glovebox, the recirculating atmosphere of which contained less than 1 ppm of water. Sodium fluoride (99%) was also obtained from Aldrich. Sodium fluoride solutions were prepared by weight. The

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purity of sodium fluoride was not very critical because its role was to provide a fluoride-containing medium that was capable of suppressing the potential hydrolysis of the tetrafluoroborate ion. Water was distilled and deionized. All weighings were corrected for buoyancy.

Apparatus and Procedures. The adiabatic solution calorimeter was that described previously.[4] The high accuracy of the calorimeter was demonstrated in ref 4. The calorimeter's thermometer was calibrated on the International Temperature Scale of 1990 at NIST. All other measurement instruments had calibrations that were performed at NIST or were traceable to NIST. Electrical calibrations of the calorimeter and its contents were made both before and after each mixing experiment. At the onset of mixing in the calorimeter, a controlled amount of electrical energy was introduced into the calorimeter through the calibration heater. The observed temperature change in the calorimeter during the mixing measurement resulted from the known input of electrical energy, the change of enthalpy from the mixing, and some much smaller sources such as the vaporization of water into the free space in the sample cell, shield imbalance at the onset of the mixing process, and changes in vapor pressure due to changes in the temperature of the calorimeter during the electrical calibrations and the mixing experiment.[4] The individual values of the enthalpy change for the dissolution process were calculated from the observed temperature changes, which were converted to enthalpy values through the electrical calibrations of the calorimeter, combined with the individual known amounts of electrical energy converted to heat in the calorimeter during the early part of the mixing process, and they were corrected for the additional small energy effects.

The initial mass of the solute used in the enthalpy of solution measurements ranged from 0.4 g to 0.7 g. The initial mass of the solute was determined with an uncertainty of ±0.0002 g. The mass of the solvent, either water or NaF(aq), was approximately 300 g and was determined with an uncertainty of ±0.1 g. These values can be used to estimate the uncertainty of the molality of KBF_4 in the solution. The mass of NaF(cr) used for the preparation of NaF(aq) was determined with an uncertainty of ±0.0002 g, and the uncertainty of the mass of the approximate kilogram of water used was ±0.1 g. These values can be used to estimate the uncertainty of the molality of the NaF(aq) solutions. Because of the extended equilibrium periods that varied from measurement to measurement and the fact that the conditions of the measurements (i.e., temperature and composition) varied from measurement to measurement, it is not mathematically practical to estimate well the uncertainty of each individual enthalpy of solution measurement. Rather, the standard deviation of the measurements was estimated to be $\pm 0.15\ kJ\cdot mol^{-1}$, which was obtained by applying a model described below to the measurements. This standard deviation value must contain any model bias that might exist and so is not directly a measure of the standard deviation of the measurements but rather provides the upper bound for that estimated value.

Results

Measured Enthalpies of Solution. The dissolution of potassium tetrafluoroborate was fairly slow at 298 K, occurring over a few hours in the calorimeter. However, the time at which dissolution was complete was obvious from an examination of the time derivative of the temperature of the calorimeter. An example of some of the temperature drift values for one of the measurements is shown in Figure 1. Each point in the Figure is a calorimeter drift rate calculated from a first-order representation of 300 temperatures obtained at a $1\text{-}s^{-1}$ sampling rate. Drift rates prior to and following the first electrical calibration are shown, as are drift rates following the mixing experiment. As can be seen, the return to the normal drift characteristics of the calorimeter is quite obvious, and for that particular measurement, complete dissolution required more than 10 000 s at 298.17 K. Dissolution was faster either at higher temperature or with sodium fluoride present. At 313 K, in water, dissolution was completed within 1 to 2 h.

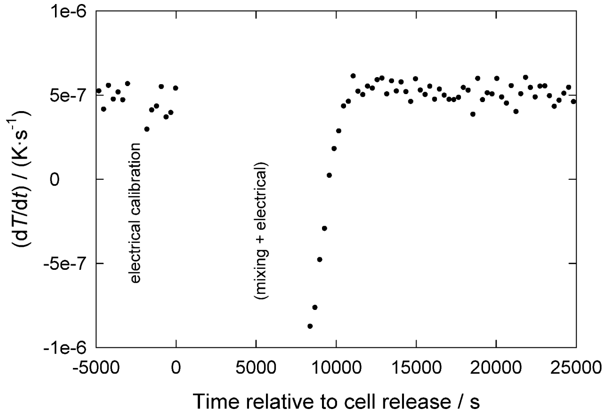

Figure 1. Values of dT/dt for the calorimeter during the progress of one of the measurements.

The pH values of the solutions formed in the calorimeter were determined after disassembly of the calorimeter vessel. For dissolutions of KBF_4 into water, the pH values were acidic; for example, at 313 K, pH values fell between 4.5 and 5.5. For dissolution into aqueous sodium fluoride, the pH values were weakly basic, approximately pH 8. The acidic pH values resulted from the slow hydrolysis of the fluoroborate anion:

$$BF_4^-(aq) + H_2O(l) = BF_3OH^-(aq) + HF(aq) \quad (1)$$

The equilibrium constant for reaction 1, in dilute solution, can be approximated from Wamser's[5] measurements for the reaction

$$HBF_4(aq) + H_2O(l) = HBF_3OH(aq) + HF(aq) \quad (2)$$

Wamser found, at equilibrium and 298.15 K, that 13.7% hydrolysis occurred for reaction 2. Additional hydrolysis reactions follow the first step of reaction 1:

$$BF_3OH^-(aq) + H_2O(l) = BF_2(OH)_2^-(aq) + HF(aq) \quad (3)$$

$$BF_2(OH)_2^-(aq) + H_2O(l) = BF(OH)_3^-(aq) + HF(aq) \quad (4)$$

$$BF(OH)_3^-(aq) = B(OH)_3(aq) + F^-(aq) \quad (5)$$

Mesmer et al.[6] quantified equilibrium quotients for the subsequent hydrolysis reactions (eqs 3–5). Platford[7] examined the effect of aging of aqueous solutions of sodium tetrafluoroborate and potassium tetrafluoroborate. Platford[7] advised that the half-life for the hydrolysis of $0.01\ mol\cdot kg^{-1}$ $NaBF_4$ and KBF_4 is 250 h at 298.15 K. We extrapolated the observed drift temperatures, after dissolution was complete, to the time at which the cell was opened. This practice should eliminate enthalpy effects from the slow hydrolysis reactions. The experimental values of the enthalpy of solution determinations for potassium tetrafluoroborate, the temperatures of the mixing process, and the final solution compositions are given in Table 1.

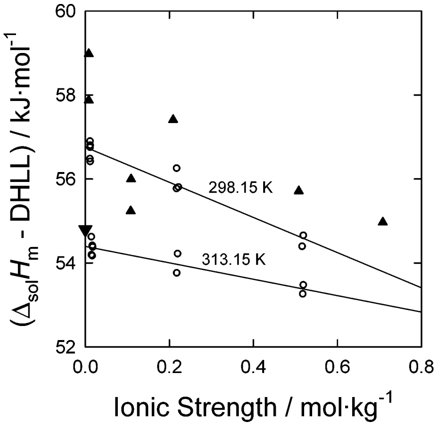

Figure 2. Values of the enthalpy of solution, less a Debye–Hückel contribution to the enthalpy, against the ionic strength of the final solution for 298.15 K: ○, present measurements; ▲, measured values tabulated by Devina et al.;[2] ▼, value for the standard state from Wagman et al.[1]

Table 1. Enthalpy of Solution of KBF_4(cr) in Water and in Aqueous Sodium Fluoride

T(ITS-90)	$m(KBF_4)$	m(NaF)	$\Delta_{sol}H_m$(obs)
K	mol·kg^{-1}	mol·kg^{-1}	J·mol^{-1}
298.1552	0.011596	0	57.00
298.1691	0.011112	0	57.10
298.1781	0.010950	0	56.68
298.1643	0.011470	0	56.62
298.1547	0.011287	0	56.96
298.1739	0.012647	0.2047	56.99
298.1703	0.012264	0.2047	56.51
298.1686	0.016843	0.2047	56.55
298.1426	0.013942	0.5020	55.43
298.1465	0.019197	0.4995	55.69
298.1648	0.016503	0.5020	54.92[a]
313.1441	0.014267	0	54.90
313.1491	0.014414	0	54.48
313.1654	0.017430	0	54.69
313.1614	0.016244	0	54.47
313.1446	0.016682	0	54.72
313.1487	0.015950	0.2015	54.69
313.1578	0.018019	0.2015	55.16
313.1672	0.015307	0.5020	54.56
313.1699	0.019174	0.4995	54.78

[a] This measurement was excluded from the statistical calculations.

Figure 2 shows values of $\Delta_{sol}H_m - \{\nu|z_Mz_X|A_H \ln[1 + bI^{1/2}]/2b\}$ from the present results for the nominal temperatures of 298 K and 313 K against ionic strength, where the second term in the quantity is a Debye–Hückel limiting term for the relative apparent molar enthalpy. The following symbols are used: ν is the number of particles into which the solute dissociates ($\nu = 2$); z_M and z_X are the charges of the cation and the anion, respectively; b is a constant, chosen to be 1.2 kg$^{1/2}$·mol$^{-1/2}$; I is the ionic strength; A_H is the Debye–Hückel coefficient for the apparent molar enthalpy, and $m°$ is 1 mol·kg^{-1}. The Debye–Hückel coefficients used in the present work were calculated from the equation of state for water from Hill[8] and the dielectric-constant equation from Archer and Wang.[9] Also shown for comparative purposes in Figure 2 are values calculated from the individual measurements reported by Devina et al.[2] for 298.15 K. The much better precision of the present values is readily apparent. The Figure also shows a value of $\Delta_{sol}H_m°(T = 298.15\ \mathrm{K})$ calculated from the NBS Tables.[1]

Standard-State Properties of Solution. The standard-state enthalpy and heat capacity of solution were extracted from the measured enthalpies of solution. Complete dissociation of potassium tetrafluoroborate and sodium fluoride was assumed. The following function was fit to the measured enthalpies of solution:

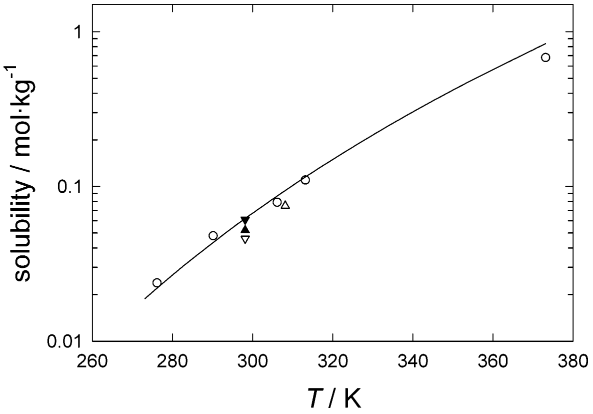

Figure 3. Values of the solubility against temperature: ▲, gravimetric results from Crooks et al.;[10] ▼,ICP results from Crooks et al.;[10] ○, De Boer and van Liempt;[11] ▽, Ray and Mitra;[12] △, Ray and Mitra.[13] The solid line was calculated from the standard-state properties for the solution process given here and a Debye–Hückel limiting law for calculated values of the solute activity coefficient.

Table 2. Thermodynamic Properties of the Aqueous Solution Process for Potassium Tetrafluoroborate and of the Aqueous Tetrafluoroborate Ion at 298.15 K

$\Delta_{sol}H°$	(56.76 ± 0.20) kJ·mol^{-1}
$\Delta_{sol}C_p°$	(−158 ± 18) J·K^{-1}·mol^{-1}
dB/dT	−4.191 ± 0.74
d^2B/dT^2	0.1493 ± 0.070
derived from solubility and the above results	
$\Delta_{sol}G°$	(15.08 ± 0.40) kJ·mol^{-1}
$\Delta_{sol}S°$	(139.8 ± 1.5) J·K^{-1}·mol^{-1}
entropy and heat capacity of the aqueous tetrafluoroborate ion	
$S°(BF_4^-$(aq))	(196.3 ± 1.5) J·K^{-1}·mol^{-1}
$C_p°(BF_4^-$(aq))	(−50 ± 18) J·K^{-1}·mol^{-1}

$$\Delta_{sol}H_m - \frac{\nu|z_Mz_X|A_H\ln(1 + bI^{1/2})}{2b} = \Delta_{sol}H_m°(T_r) + \Delta_{sol}C_p°(T_r)(T - T_r) + \frac{T°[(\mathrm{d}B/\mathrm{d}T) + (\mathrm{d}^2B/\mathrm{d}T^2)(T - T_r)]IH°}{m°} \tag{6}$$

where $\Delta_{sol}H_m$ is the observed enthalpy of solution, $T°$ is 1 K, and $H°$ is 1 J·mol^{-1}. $\Delta_{sol}H_m°(T_r)$ and $\Delta_{sol}C_p°(T_r)$ are the standard-state enthalpy and heat capacity at a temperature T_r, which was chosen to be 298.15 K. dB/dT and d^2B/dT^2 are coefficients of an ionic strength term. The fitted parameters, and their 95% confidence intervals within this model, are given in Table 2. We have not used the ion-interaction model because sufficient ion-interaction terms to model the process are not available and the present data are not sufficient to determine all, or even most, of the ion-interaction terms required.

Figure 3 shows values of the solubility of potassium tetrafluoroborate in water against temperature. The most recent value, which was determined by Crooks et al.[10] with inductively coupled plasma spectroscopy (ICP), agrees well with earlier work by de Boer and van Liempt.[11] A second value determined by Crooks et al., using a gravimetric method, was somewhat lower. From the ICP result and the study by de Boer and van Liempt, the solubility at 298.15 K is 0.062 mol·kg^{-1}. The activity coefficient of the solute is required to calculate the Gibbs energy of solution from the solubility value. Because of the low solubility of KBF_4 at 298.15 K, the types of data usually used for determining ion-interaction parameters are not available. Because of the absence of direct data, we attempted to extract ion-interaction parameters from solubility measurements of KBF_4 in a mixed electrolyte system. Crooks et al. determined the solubility of KBF_4 in the aqueous $NaBF_4 + KBF_4$ system for $NaBF_4$(aq) compositions ranging from 0 to 2.5 $mol\cdot kg^{-1}$. In principle, one might extract the ion-interaction parameters for the binary KBF_4(aq) from the solubility of KBF_4(cr) against the concentration of $NaBF_4$(aq) if the ion-interaction parameters for $NaBF_4$(aq) are available. Our attempt at this calculation is described next.

In the Pitzer formalism,[14] the activity coefficient of an electrolyte, MX, in a mixture containing just two symmetrical electrolytes with charge z and with a common anion X is

$$\ln \gamma_{MX} =$$

$$z^2 f^\gamma + m\Big\{B_{MX} + (1-y)B^\phi_{MX} + yB^\phi_{NX} + m\Big[\Big(\frac{3}{2} - y\Big)C^\phi_{MX} + yC^\phi_{NX}\Big] + y\Big[\Phi_{MN} + \Big(1 - \frac{y}{2}\Big)m\psi_{MNX} + (1-y)I\Phi'_{MN}\Big]\Big\} \quad (7)$$

where f^γ is a function of ionic strength,

$$f^\gamma = -A_\phi\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \left(\frac{2}{b}\right)\ln(1 + bI^{1/2})\right] \quad (8)$$

B_{MX} and B^ϕ_{MX} are functions of ionic strength, and they contain the ion interaction terms for pair interactions of the binary MX electrolyte

$$B^\phi_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX}\exp(-\alpha I^{1/2}) \quad (9)$$

$$B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} g(-\alpha I^{1/2}) \quad (10)$$

where

$$g(x) = \frac{2\left[1 - \left(1 + x + \frac{x^2}{2}\right)\exp(-x)\right]}{x^2} \quad (11)$$

and $\beta^{(0)}_{MX}$ and $\beta^{(1)}_{MX}$ are ion-interaction parameters for pair interactions of solute in the binary MX(aq) system and α is a somewhat arbitrary parameter, which is generally set at $\alpha = 2\ (kg\cdot mol)^{-1/2}$ for many aqueous electrolytes. C^ϕ_{MX} is the ion-interaction term for triplet interactions in the binary MX(aq) system. Φ_{MN}, ψ_{MNX}, and Φ'_{MN} represent contributions from additional ion interactions that occur in the ternary solution. The fraction of total solute that is NX is designated by y. The ion-interaction parameters for $NaBF_4$(aq) were taken from the tabulation in the reference by Pitzer.[14] The mean ionic activity coefficient of KBF_4(aq), γ_{MX}, was obtained from $(K_{sp}/Q_{sp})^{1/2}$, where Q_{sp} is the reaction quotient for the solubility product from Crooks et al.[10] (i.e., $Q_{sp} = m(K^+(aq))\ m(BF_4^-(aq))/(m^{\circ 2})$) and K_{sp} is the thermodynamic equilibrium constant for the solubility. These calculated activity coefficients were fitted with the model of eq 7. The data were capable of supporting the determination of only $\beta^{(0)}_{MX}$ at a 95% confidence interval. We note that using statistics of parameters to determine the validity of inclusion of the parameter in the model is problematic. The validity of the statistical measures of least-squares parameters depends on the assumption of correctness of the model. Reducing the numbers of parameters in a model from those expected on a theoretical or experiential basis can give erroneously small uncertainties of the retained parameters. Fortunately, in the ion-interaction model there is not a high covariance of the ion-interaction parameters.[15] The least-squares calculation returned $\beta^{(0)}_{MX} = -0.12 \pm 0.07$. This value for KBF_4(aq) is about 0.1 smaller (more negative) than $\beta^{(0)}_{MX}$ for $NaBF_4$(aq). This difference falls within the limits of differences of other ion-interaction parameters for sodium versus potassium salts with a common anion.

The activity coefficient of KBF_4(aq) for the 298.15 K solubility, 0.062 $mol\cdot kg^{-1}$, was calculated from the ion-interaction equation using the above determined $\beta^{(0)}_{MX} = -0.12$, giving $\gamma_\pm = 0.771$. The standard-state Gibbs energy for the solution process at 298.15 K was calculated from those two values and is $\Delta_{sol}G^\circ = (15.08 \pm 0.4)\ kJ\cdot mol^{-1}$. The uncertainty in the Gibbs energy of solution was calculated to be twice the value calculated from an assumption of $\pm 0.02\ mol\cdot kg^{-1}$ in the solubility determination. The combination of that value of the standard-state Gibbs energy of solution with the standard-state enthalpy of solution for 298.15 K, $\Delta_{sol}H^\circ = (56.76 \pm 0.2)\ kJ\cdot mol^{-1}$, was used to obtain a value for the standard-state entropy of the solution process, $\Delta_{sol}S^\circ = (139.8 \pm 1.5)\ J\cdot K^{-1}\cdot mol^{-1}$.

If we take the heat capacity and entropy of KBF_4(cr) from the adiabatic calorimetric measurements described in Gorbunov et al.[16] ($S^\circ(cr) = (157.7 \pm 0.3)\ J\cdot K^{-1}\cdot mol^{-1}$ and $C_p^\circ(cr) = (114.7 \pm 0.2)\ J\cdot K^{-1}\cdot mol^{-1}$, both for 298.15 K), then the standard-state apparent molar heat capacity and standard-state entropy of fully dissociated KBF_4(aq) at 298.15 K are $C_{p,\phi}^\circ = (-43 \pm 18)\ J\cdot K^{-1}\cdot mol^{-1}$ and $S^\circ = (297.5 \pm 1.5)\ J\cdot K^{-1}\cdot mol^{-1}$, respectively. The uncertainty calculations are rough because Gorbunov et al. did not describe the basis of their uncertainty values. We included them in the calculation as though they were 95% confidence intervals, even though this level of certainty would be unlikely.

The combination of the above calculated entropy value for KBF_4(aq) with the standard-state entropy of K^+(aq) from the CODATA Key Values[17] ($S^\circ(K^+(aq)) = (101.2 \pm 0.2)\ J\cdot K^{-1}\cdot mol^{-1}$) leads to the standard-state entropy of the BF_4^-(aq) anion, $S^\circ(BF_4^-(aq)) = (196.3 \pm 1.5)\ J\cdot K^{-1}\cdot mol^{-1}$. The basis of the uncertainties in the CODATA Key Values is unclear to me.

The combination of the above-calculated heat capacity value for KBF_4(aq) with the standard-state heat capacity of the aqueous potassium ion, which can be obtained from Archer's standard-state heat capacity value for aqueous potassium chloride[18] and Holmes et al.'s value of $C_{p,\phi}^\circ$ for aqueous hydrochloric acid,[19] $C_{p,\phi}^\circ(K^+(aq)) = (6.5 \pm 4)\ J\cdot K^{-1}\cdot mol^{-1}$, leads to the standard-state heat capacity of the aqueous tetrafluoroborate ion, $C_p^\circ(BF_4^-(aq)) = (-50 \pm 18)\ J\cdot K^{-1}\cdot mol^{-1}$.

Solubilities calculated from the standard-state properties calculated here and reported in Table 2 are shown against temperature in Figure 3. For this calculation, we used a Debye–Hückel calculation of the solute activity coefficient but did not include the ion-interaction parameters in the calculation because we do not have the temperature dependence of the β parameter and because the slopes of the curves in Figure 2 suggest that the temperature dependence of this parameter might not be negligible. Regardless, the calculated solubilities are in good agreement with the reported values.

Discussion

We have reduced the uncertainty of $\Delta_{sol}H_m^\circ(T_r)$ from the $\pm 1.5\ kJ\cdot mol^{-1}$ reported by Devina et al.[2] for their results (the uncertainty is on an unreported basis) to an uncertainty of $\pm 0.2\ kJ\cdot mol^{-1}$ (95% confidence interval) for the present results. Our value of the heat capacity of the solution reaction, (-158 ± 18) J·K^{-1}·mol^{-1}, is about twice as large as the value stated by Devina et al., (-75.6 ± 5) J·K^{-1}·mol^{-1}. We demonstrated earlier the accuracy capable with the present instrument in determining the heat capacity of the solution process. Although the concentrations here are smaller and the equilibration times are longer than those in ref 4 and hence the uncertainty of the enthalpy of solution and heat capacity of solution are somewhat larger, there is no expectation that the uncertainty of the heat capacity value extracted from the present measurements is significantly larger than the ±18 J·K^{-1}·mol^{-1} that was obtained from the present representation. Thus, we attribute the difference between our heat capacity of solution and that from Devina et al. to systematic errors in the measurements made by Devina et al. We note that very different 95% confidence intervals can be calculated for $\Delta_{sol}H_m°(T_r)$ from the Devina et al. measurements, depending upon the model applied. Our fitting of their measurements using different combinations of parameters from eq 6 also did not support the uncertainty that Devina et al. assigned to their value of $\Delta_{sol}C_p°(T_r)$, namely, ±5 J·K^{-1}·mol^{-1}. The uncertainties stated by Devina et al. for their enthalpies of solution, when used in a propagation of error equation, yielded a minimum uncertainty of ±55 J·K^{-1}·mol^{-1} for $\Delta_{sol}C_p°(T_r)$.

We consider next the agreement of the present values for the entropy and heat capacity of BF_4^-(aq) with those reported elsewhere. As noted above, Shock and Helgeson[3] gave $C_p°(BF_4^-(aq)) = -23$ J·K^{-1}·mol^{-1}. Their value was obtained from a correlation of heat capacity values for monovalent aqueous oxyanions against the entropies of those ions. Shock and Helgeson then assumed that correlation would give a reasonable value for the BF_4^-(aq) ion. In their correlation for the oxyanions, some individual values showed discrepancies of up to 10 cal·K^{-1}·mol^{-1} (40 J·K^{-1}·mol^{-1}) or more. For their calculation for the BF_4^-(aq) ion, they took the entropy of BF_4^-(aq) from the NBS Tables, $S°(BF_4^-(aq)) = 180$ J·K^{-1}·mol^{-1}, which is about 16 J·K^{-1}·mol^{-1} different than the value we obtained here. If one substitutes the present entropy for BF_4^-(aq) into Shock and Helgeson's correlation, then the value $C_p°(BF_4^-(aq)) = -2$ J·K^{-1}·mol^{-1} would be obtained from the estimation method. (Shock and Helgeson did not cite Devina et al. in their analysis.) All things considered, a rather hefty uncertainty must be considered to be attached to the $C_p°(BF_4^-(aq))$ value from Shock and Helgeson. However, we note that their value is indeed negative, which is in accord with the observation that most small inorganic aqueous anions have negative heat capacities on the conventional hydrogen-based scale. Devina et al., however, obtained $C_p°(BF_4^-(aq)) = 25$ J·K^{-1}·mol^{-1}; that positive value is not in accord with the usual observations of negative heat capacities for small inorganic aqueous anions. Neither of those values[2,3] is in good agreement with the present value, $C_p°(BF_4^-(aq)) = (-50 \pm 18)$ J·K^{-1}·mol^{-1}. We attribute the differences to the weakness of the correlation method in Shock and Helgeson and to the aforementioned systematic biases of the measurements made by Devina et al.

In the above analysis, we took thermodynamic properties of KBF_4(cr) from Gorbunov et al.[16] Callanan et al.[20] also measured the low-temperature heat capacity of KBF_4(cr) and gave values of the entropy and heat capacity at 298.15 K. Callanan et al.'s value for the 298.15 K heat capacity is about 1% greater than that from Gorbunov et al. This difference, although significantly greater than the accuracy usually attributed to adiabatic calorimetry, is not significant compared to the uncertainty in the standard-state heat capacity of the solution process. The entropy and heat capacity for KBF_4(cr) given in Wagman et al. for 298.15 K are 152.3 J·K^{-1}·mol^{-1} and 110.6 J·K^{-1}·mol^{-1}, respectively. These values, somewhat smaller than those from either Gorbunov et al. or Callanan et al., arose from personal communications that attributed those values to the adiabatic calorimetry facility of W. H. Johnson. To the best of our knowledge, those measurements were never published.

Literature Cited

(1) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(2) Devina, O. A.; Kuyunko, N. S.; Efimov, M. E.; Medvedev, V. A.; Khodakovsky, I. L. Thermodynamic Properties of BF_4^- and Boron Hydroxyfluoride Complexes in Aqueous Solution within 25−300° C Temperature Range. *Geokhimiya* **1983**, 1150−1159.

(3) Shock, E. L.; Helgeson, H. C. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Predictions to 5 kb and 1000°C. *Geochim. Cosmochim. Acta* **1988**, *52*, 2009−2036.

(4) Archer, D. G.; Kirklin, D. R. Enthalpies of Solution of Sodium Chloride and Potassium Sulfate in Water. Thermodynamic Properties of the Potassium Sulfate + Water System. *J. Chem. Eng. Data* **2002**, *47*, 33−46.

(5) Wamser, C. A. Hydrolysis of Fluoboric Acid in Aqueous Solution. *J. Am. Chem. Soc.* **1948**, *70*, 1209−1215.

(6) Mesmer, R. E.; Palen, K. M.; Baes, C. F. Fluoroborate Equilibria in Aqueous Solutions. *Inorg. Chem.* **1973**, *12*, 89−95.

(7) Platford, R. F. Osmotic and Activity Coefficients of Some Simple Borate Solutions at the Freezing Point. *Can. J. Chem.* **1971**, *49*, 709−711.

(8) Hill, P. G. A Unified Fundamental Equation for the Thermodynamic Properties of H_2O. *J. Phys. Chem. Ref. Data* **1990**, *19*, 1233−1274.

(9) Archer, D. G.; Wang, P. The Dielectric Constant of Water and Debye−Hückel Limiting Law Slopes. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371−411.

(10) Crooks, W. J.; Rhodes, W. D.; Christian, J. D. *Use of Modeling for the Prevention of Solids Formation during Canyon Processing of Legacy Nuclear Fuels.* Report No. WSRC-TR-2002-00462; National Technical Information Service: Springfield, VA, 2003

(11) De Boer, J. H.; Van Liempt, J. A. M. The Thermal Dissociation of the Alkaliborofluorides. *Recl. Trav. Chim.* **1927**, *46*, 124−132.

(12) Ray, R. C.; Mitra, H. C. The Ternary System Potassium Perchlorate − Potassium Fluoborate − Water at 25°. *Trans. Faraday Soc.* **1934**, *30*, 1161−1163. Also Ray, R. C.; Chattterji, K. K. The Ternary System Potassium Permanganate − Potassium Fluoborate − Water. *J. Chem. Soc.* **1932**, 384−386.

(13) Ray, R. C.; Mitra, H. C.; The Ternary System Potassium Fluoborate − Potassium Periodate − Water at 35°. *Trans. Faraday Soc.* **1935**, *31*, 1312−1314.

(14) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991.

(15) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268−177.

(16) Gorbunov, V. E.; Gavrichev, K. S.; Golushina, L. N.; Totrova, G. A.; Plakhotnik, V. N.; Tul'chinskii, V. B.; Kovtun, Yu. V. Low-Temperature Specific Heat of Potassium Tetraborate. *Russ. J. Phys. Chem.* **1993**, *67*, 550−553.

(17) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1989.

(18) Archer, D. G. Thermodynamic Properties of the KCl + H_2O System. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1−17.

(19) Holmes, H. F.; Busey, R. H.; Simonson, J. M.; Mesmer, R. E.; Archer, D. G.; Wood, R. H. The Enthalpy of Dilution of HCl(aq) to 648 K and 40 MPa. Thermodynamic Properties. *J. Chem. Thermodyn.* **1987**, *19*, 863−890.

(20) Callanan, J. E.; Granville, N. W.; Green, N. H.; Staveley, L. A. K.; Weir, R. D.; White, M. A. A Study of Cationic Disorder in Nitrosyl Tetrafluoroborate, by Comparison of the Heat Capacity of This Salt with That of Potassium Tetrafluoroborate from 9 to 304 K. *J. Chem. Phys.* **1981**, *74*, 1911−1915.

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