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Thermodynamic Study on Aqueous Solutions of $(NH_4)_2SeO_4$ and K_2SeO_4 at 298.15 K

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Summary. The isopiestic method has been used to determine the osmotic coefficients of binary solutions of $(NH_4)_2SeO_4$ (from 2.739 to 5.502 $mol \cdot kg^{-1}$) and K_2SeO_4 (from 1.086 to 4.742 $mol \cdot kg^{-1}$) in H_2O at 298.15 K. The *Pitzer* ion-interaction model has been employed for the thermodynamic analysis of the results. The optimum values of the binary parameters of ionic interaction have been calculated, and important thermodynamic characteristics of $(NH_4)_2SeO_4$ and K_2SeO_4 have been determined.

Keywords. Ammonium selenate; Potassium selenate; Isopiestic method; Thermodynamic functions; *Pitzer* model.

Thermodynamische Untersuchungen an wäßrigen Lösungen von $(NH_4)_2SeO_4$ und K_2SeO_4 bei 298.15 K

Zusammenfassung. Die isopiestische Methode wurde zur Bestimmung der osmotischen Koeffizienten binärer Lösungen von $(NH_4)_2SeO_4$ (2.739–5.502 $mol \cdot kg^{-1}$) und K_2SeO_4 (1.086–4.742 $mol \cdot kg^{-1}$) in H_2O bei 298.15 K benutzt. Die Ergebnisse wurden mit Hilfe des *Pitzer*-Modells thermodynamisch analysiert. Optimale Werte der binären Parameter der interionischen Wechselwirkung wurden berechnet, und wichtige thermodynamische Charakteristiken von $(NH_4)_2SeO_4$ und K_2SeO_4 wurden bestimmt.

Introduction

Ternary and multicomponent systems involving alkali selenates have been the subject of many experimental investigations [1–12]. The data available in the literature on the thermodynamic characteristics of these salts are, however, incomplete. There are, *e.g.*, no initial isopiestic data on the dependence of the activity of water, osmotic coefficients, or activity coefficients on the molalities of binary aqueous solutions of $(NH_4)_2SeO_4$, Rb_2SeO_4, and Cs_2SeO_4. Therefore, complete thermodynamic analysis of the experimental data concerning the solubilities in the corresponding multicomponent solutions is impossible.

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Kumok and *Batireva* [12] have used the isopiestic method for the determination of thermodynamic characteristics of potassium selenate. However, the authors have obtained only 3 values for osmotic coefficients of highly-concentrated unsaturated solutions and 2 values for supersaturated K_2SeO_4 solutions. The same authors have used a quite simplified method for calculating the activity coefficients. For those reasons, they have obtained $\Delta_f G^\circ_m = -1013.7\,kJ \cdot mol^{-1}$ for the standard molar *Gibbs* energy of formation of potassium selenate, which differs very much from the value proposed by *Wagman et al.* [13] ($-1002.8\,kJ \cdot mol^{-1}$).

The present paper deals with $(NH_4)_2SeO_{4(aq)}$ and $K_2SeO_{4(aq)}$ at $T = 298.15\,K$. The isopiestic method has been used to determine the osmotic coefficients of the solutions. The *Pitzer* ion-interaction model has been employed for the thermodynamic analysis of the results. The binary parameters of ionic interaction have been optimized, and some important thermodynamic characteristics (the thermodynamic solubility product and the standard molar *Gibbs* energy of formation) of $(NH_4)_2SeO_4$ and K_2SeO_4 have been calculated.

Results and Discussion

Thermodynamic analysis of the experimental results was performed on the basis of the *Pitzer* ion-interaction model [16, 17] which allows the determination of the activity coefficients in unsaturated and saturated electrolyte solutions with an accuracy of ±2–6% [18]. It has been proved that the *Pitzer* equations are applicable to a sufficiently precise description of the properties of binary [2, 3] and multicomponent [17] solutions in which phases with a constant composition (simple and double salts) [2, 3] and solid solutions [14] crystallize.

The simulation of $(NH_4)_2SeO_{4(aq)}$ and $K_2SeO_{4(aq)}$ has been performed on the basis of the data obtained in the present study on the concentration dependence of the osmotic coefficient (Tables 1 and 2). The *Pitzer* parameters are presented in Table 3. Using these parameters for $M_2SeO_{4(aq)}$, we have calculated the concentration dependence of the osmotic coefficients up to saturation of the solutions. The results obtained are presented, together with the experimental data of Tables 1 and 2, in Figs. 1 and 2. The results of the calculation are in good agreement with the experimental data. The molalities b(sat) of saturated $M_2SO_{4(aq)}$ solutions have been reported in a series of papers [5–12]. The values obtained by the different authors are close and vary within relatively narrow limits: from 6.71 (Ref. [12]) to 6.715 (Refs. [8–10]) $mol \cdot kg^{-1}$ for $(NH_4)_2SeO_{4(aq)}$ and from 5.13 (Refs. [5–8]) to 5.16

Table 1. Isopiestic molalities b of aqueous solutions of $(NH_4)_2SeO_4$, molalities b of NaCl reference solutions, and osmotic coefficients ϕ of $(NH_4)_2SeO_4$ at 298.15 K

$b(NaCl)/mol \cdot kg^{-1}$	$b((NH_4)_2SeO_4)/mol \cdot kg^{-1}$	$\phi((NH_4)_2SeO_4)$
2.791	2.739	0.697
3.444	3.312	0.746
4.014	3.854	0.769
5.148	4.748	0.869
6.064	5.502	0.941

Table 2. Isopiestic molalities b of aqueous solutions of K_2SeO_4, molalities b of NaCl reference solutions, and osmotic coefficients ϕ of K_2SeO_4 at 298.15 K

b(NaCl)/mol · kg^{-1}	$b(K_2SeO_4)$/mol · kg^{-1}	$\phi(K_2SeO_4)$
1.2604	1.086	0.731
2.7000	2.246	0.822
3.8705	3.2325	0.883
5.0395	4.175	0.959
5.8697	4.742	1.040

Table 3. *Pitzer* binary parameters for $(NH_4)_2SeO_{4(aq)}$ and $K_2SeO_{4(aq)}$ at 298.15 K (σ: standard deviation of the osmotic coefficients)

System	$\beta^{(0)}$	$\beta^{(1)}$	C^{φ}	σ
$(NH_4)_2SeO_4$-H_2O	0.04155	0.77095	0.00312	0.00351
K_2SeO_4-H_2O	0.10911	0.71354	−0.00325	0.00698

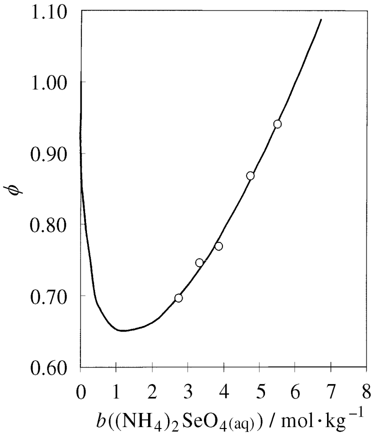

Fig. 1. Plot of the osmotic coefficients ϕ of $(NH_4)_2SeO_4$ against the molality b of $(NH_4)_2SeO_{4(aq)}$: o, experimental data (Table 1); —, calculated values using the parameters in Table 3

(Ref. [11]) mol · kg^{-1} for $K_2SeO_{4(aq)}$. In the literature there is no contradiction with respect to the solid phases crystallizing at $T = 298.15$ K from the saturated solutions. All papers mentioned [4–12] report crystallization of nonaqueous ammonium and potassium selenates.

On the basis of the binary parameter values optimized an on the molality of the saturated binary solutions proposed by *Vojtishek* and *Ebert* [5–10] (b(sat) = 6.715 mol · kg^{-1} for $(NH_4)_2SeO_{4(aq)}$ and 5.13 mol · kg^{-1} for $K_2SeO_{4(aq)}$) we have calculated the logarithms of the thermodynamic solubility product $\ln K^{\circ}_{sp}$ for $(NH_4)_2SeO_4$ and K_2SeO_4 (Table 4). On this basis and using initial thermodynamic data of *Wagman et al.* [13] we have determined the standard molar *Gibbs* energy $\Delta_f G^{\circ}_m$ of formation of ammonium and potassium selenates (Table 4). The value of

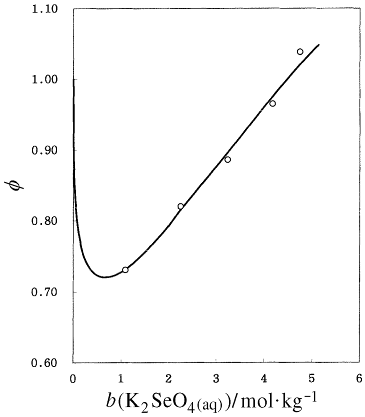

Fig. 2. Plot of the osmotic coefficients ϕ of K_2SeO_4 against the molality b of $K_2SeO_{4(aq)}$: o, experimental data (Table 2); —, calculated values using the parameters in Table 3

Table 4. Logarithms of the thermodynamic solubility product $\ln K^\circ_{sp}$ and standard molar *Gibbs* energy of formation $\Delta_f G^\circ_m$; b(sat): molality of the saturated binary solutions

Species	b(sat)/mol · kg^{-1}	$\ln K^\circ_{sp}$	$\Delta_f G^\circ_m$/kJ · mol^{-1}
$(NH_4)_2SeO_4$	6.715	2.118	−594.7
K_2SeO_4	5.13	2.077	−1002.7

$\Delta_f G^\circ_m$ obtained in this paper for K_2SeO_4 is very close to that proposed by *Wagman et al.* [13] (−1002.8 kJ · mol^{-1}).

Experimental

The metal selenates $(NH_4)_2SeO_4$ and K_2SeO_4 were prepared by reaction of the corresponding metal carbonates and selenic acid [1–3]. Merck reagents (A.R.) were used. The selenate solutions were filtered, concentrated, and cooled to room temperature to allow crystal formation. The salts obtained were recrystallized twice from distilled water at room temperature in a desiccator above concentrated sulfuric acid and dried in air.

The osmotic coefficients of the solutions were determined by the isopiestic method described by *Christov et al.* [2], *Ojkova et al.* [3], and *Stoilova et al.* [14]. The salts were weighed with an accuracy of up to 0.00001 g giving, after the addition of 3 cm^3 water, solutions of the desired concentration. The samples were placed in a copper vacuum desiccator which, after evacuation, was placed in a thermostat whose temperature was maintained at 298.15 K. Sodium chloride solutions were used as isopiestic reference standards. After equilibration, the samples were weighed again, and the concentrations of the isopiestic solutions obtained were calculated. Tables 1 and 2 show the isopiestic equilibrium molalities of $(NH_4)_2SeO_4$ and K_2SeO_4(aq), respectively, together with those of NaCl reference solutions. The reported molalities are the average of duplicate determinations. We found that an equilibrium period of 20 days yielded results with a good agreement of molalities for duplicate samples of the same electrolyte. The concentrations in Tables 1 and 2 are accurate to within ±0.2% or better. The osmotic coefficients ϕ of $(NH_4)_2SeO_{4(aq)}$ and $K_2SeO_{4(aq)}$ were calculated from equation (1) where b is the molality of $M_2SeO_{4(aq)}$, b^* is the molality of the reference solution $NaCl_{(aq)}$ in isopiestic equilibrium with the test solution, ϕ^* is the osmotic coefficient of the isopiestic reference standard, and ν and ν^* are the stoichiometric ionization numbers of M_2SeO_4 and the reference standard, respectively ($\nu = 3$ for M_2SeO_4, and $\nu^* = 2$ for NaCl). The values ϕ^* for NaCl were taken from *Hamer* and *Wu* [15].

$$\phi = \nu^* b^* \phi^* / \nu b \tag{1}$$

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