THERMODYNAMIC STUDY OF $Na_2Cr_2O_7$(aq) AT 25 °C

Christomir CHRISTOV[a,*,+], Snejana VELIKOVA[b], Kalina IVANOVA[b] and Stefan TANEV[b]

[a] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; e-mail: christov@scichem.c.chiba-u.ac.jp*

[b] *Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 8000 Bourgas, Bulgaria*

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The isopiestic method was used to determine osmotic coefficients of binary $Na_2Cr_2O_7$(aq) solutions of concentrations 0.6777–3.8792 mol kg^{-1} at 25 °C. The concentration of a saturated binary solution $Na_2Cr_2O_7$(aq) at 25 °C was determined. The Pitzer ion-interaction model has been used for thermodynamic analysis of the results obtained. Optimum values of the binary parameters of interionic interaction have been calculated and important thermodynamic characteristics of $Na_2Cr_2O_7 \cdot 2\,H_2O$ determined.

Key words: Sodium dichromate; Isopiestic method; Solubility; Pitzer model.

Investigations on solubilities in binary, ternary and multicomponent solutions containing dichromate salts are of special practical interest. The production of $M_2Cr_2O_7$ (M = Na, K, NH_4) and $MgCr_2O_7$ salts is based on the conversion in four-component water–salt systems[1–3]. For that reason, ternary and multicomponent $M_2Cr_2P_7$ systems have been the subject of many experimental works[1–6]. However, the data available in the literature on thermodynamic characteristics of dichromate salts are incomplete. For instance, there are no isopiestic data on the dependence of activity of water, a_w, osmotic coefficients, ϕ, or activity coefficients, γ, on molalities, m, of binary dichromate solutions, which does not permit performing complete thermodynamic analysis of experimental data on solubilities in multicomponent solutions.

+ Present address: Chiba University, Dept. of Chemistry, Faculty of Sci., 1-33, Yayoi-Cho, Inage-Ku, Chiba-city, 263 Japan.

The present paper deals with the binary solutions $Na_2Cr_2O_7$(aq) at 25 °C. The isopiestic method was used to determine the osmotic coefficients of the solutions. The molality, m^s, of the saturated binary solution has been determined. The Pitzer ion-interaction model has been applied to thermodynamic analysis of the results obtained. Optimum values of binary parameters of interionic interaction have been determined and some important thermodynamic characteristics (thermodynamic solubility product, $\ln K^0_{sp}$, and standard molar Gibbs energy of formation, $\Delta G^0_{f,m}$) of $Na_2Cr_2O_7 \cdot 2\,H_2O$ crystallizing from a saturated solution have been calculated.

EXPERIMENTAL

The sodium dichromate dihydrate of analytical grade was twice recrystallized. Osmotic coefficients of the $Na_2Cr_2O_7$(aq) binary solutions were determined by the isopiestic method described by Christov *et al.*[7], Ojkova *et al.*[8] and Stoilova *et al.*[9]. The solutions used were prepared by the gravimetric method. The salts were weighed with an accuracy of up to 0.00001 g in amounts giving, after the addition of 3 ml water, a solution with the desired concentration. The solutions were placed in a copper vacuum desiccator which, after evacuation, was placed in an ultra-thermostat maintaining a temperature of 25 ± 0.1 °C. Sodium chloride solutions were used as isopiestic reference standards. After attaining equilibrium, the solutions were weighed again and the concentrations of the isopiestic solutions obtained were calculated. Table I shows the isopiestic equilibrium molalities of $Na_2Cr_2O_7$(aq) with NaCl(aq) reference solutions. The reported molalities are averages of duplicate determinations. We have found that an equilibrium period of 30 days gave results showing good agreement of molalities for duplicate samples of the same electrolyte. This relatively long

TABLE I
Isopiestic molalities m of aqueous $Na_2Cr_2O_7$, the molalities m of NaCl reference solutions and osmotic coefficients of $Na_2Cr_2O_7$, ϕ, at 25 °C

m (NaCl)	m ($Na_2Cr_2O_7$)	ϕ ($Na_2Cr_2O_7$)
0.7442	0.6777	0.6792
1.2860	0.9767	0.8319
2.2813	1.5248	1.0054
3.6863	2.2707	1.1820
4.7785	2.9657	1.2611
5.6781	3.5996	1.3095
6.0621	3.8792	1.3276

time needed to obtain equilibrium can be attributed to the fact that we have not shaken the desiccator with solutions investigated. The concentrations in Table I are accurate to ±0.2% or better. The osmotic coefficients ϕ of $Na_2Cr_2O_7$(aq) have been calculated from Eq. (*1*) (ref.[7]):

$$\phi = (\nu^* m^* \phi^*)/(\nu m) , \qquad (1)$$

where m is the molality of $Na_2Cr_2O_7$(aq), m^* is the molality of the reference NaCl(aq) solution 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 $Na_2Cr_2O_7$ and the reference standard, respectively (ν = 3 for $Na_2Cr_2O_7$, and ν^* = 2 for NaCl). The values ϕ^* for NaCl have been taken from Hammer and Wu[10]. Table I contains the derived values of ϕ for the $Na_2Cr_2O_7$(aq) solutions.

To obtain a saturated $Na_2Cr_2O_7$(aq) solution at 25 °C we used the method of isothermal decrease of the supersaturation[11,12]. Equilibrium was attained by continuous stirring for 48 h. The dichromate ions were determined by iodometric titration[2,13].

The data reported in the literature on the concentration of the saturated binary solution $Na_2Cr_2O_7$(aq) at 25 °C are summarized in Table II. In all cases, crystallization of $Na_2Cr_2O_7 \cdot 2\,H_2O$ has been established.

In the present work, we have established a sodium dichromate solubility of 65.05 wt.% (7.106 mol kg^{-1}) at 25 °C. This value is the average of three parallel determinations, the differences between them not exceeding 0.1 wt.%.

THERMODYNAMIC PITZER SIMULATION

Thermodynamic analysis of the experimental results obtained has been performed on the basis of the Pitzer ion-interaction model[14,15] which allows

TABLE II
Reference data on the solubility of $Na_2Cr_2O_7$ at 25 °C

Liquid phase		Solid phase	Reference
wt.%	molality		
64.53	7.055	$Na_2Cr_2O_7 \cdot 2\,H_2O$	3
65.00	7.089	$Na_2Cr_2O_7 \cdot 2\,H_2O$	23
65.01	7.092	$Na_2Cr_2O_7 \cdot 2\,H_2O$	24
65.06	7.108	$Na_2Cr_2O_7 \cdot 2\,H_2O$	2
65.10	7.120	$Na_2Cr_2O_7 \cdot 2\,H_2O$	4
65.50	7.246	$Na_2Cr_2O_7 \cdot 2\,H_2O$	6

the determination of activity coefficients in unsaturated and saturated electrolyte solutions with an accuracy of 2 to 6% (ref.[16]). It has been proved that the Pitzer equations are applicable to a sufficiently precise description of properties of binary[14] and multicomponent[15–18] solutions in which phases with a constant composition[7,8,11,12] (simple and double salts) and solid solutions[9,19] crystallize.

Pitzer simulation of $Na_2Cr_2O_7$(aq) has been performed on the basis of the data obtained in the present study on the concentration dependence of the osmotic coefficient (Table I). Various approaches, the applicability of which was proved by simulation of other binary and multicomponent solutions, have been used, for instance: (i) three-parameter ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) approach, using $\alpha = 2$ (ref.[14]), which is standard for electrolytes of the type 1–2; (ii) four-parameter approach (involving also $\beta^{(2)}$ using $\alpha_1 = 2$ and $\alpha_2 = 1$ (refs[12,20]); (iii) four-parameter approach, with $\alpha_1 = 2$ and $\alpha_2 = -1$ (refs[8,12,17,18]); (iv) four-parameter approach for simulation of 2–2 electrolytes, with $\alpha_1 = 1.4$ and $\alpha_2 = 12$ (ref.[21]); and (v), three-parameter approach ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}), using $\alpha = 1.4$ (refs[9,19]). When utilizing approach (ii), we calculated parameters ($\beta^{(0)} = 0.13513$, $\beta^{(1)} = -8.94435$, $\beta^{(2)} = 2.03150$ and $C^{\phi} = -0.00495$) with a much lower standard deviation σ of osmotic coefficients ($\sigma = 0.00268$). Using these parameters for $Na_2Cr_2O_7$(aq), we calculated the concentration dependence of osmotic coefficients up to saturation of the solution. The results obtained are presented, together with the experimental data of Table I, in Fig. 1. The results of the calculation are in good agreement with the experimental data.

On the basis of the binary parameter values chosen and of the experimentally determined molality of saturated binary solutions ($m^s = 7.106$ mol kg^{-1}), we

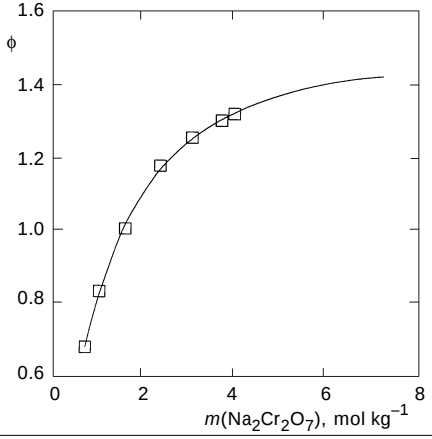

FIG. 1
Plot of osmotic coefficients ϕ of $Na_2Cr_2O_7$ against the molality m of $Na_2Cr_2O_7$(aq): ❐ experimental data (Table I); — calculated values

have calculated the logarithm of the thermodynamic solubility product $\ln K_{sp}^0$ for sodium dichromate dihydrate. The value $\ln K_{sp}^0 = 2.42$ has been obtained. On its basis and using initial thermodynamic data of Wagman *et al.*[22], we have calculated the standard molar Gibbs energy $\Delta G_{f,m}^0$ of formation of $Na_2Cr_2O_7 \cdot 2\,H_2O$ ($\Delta G_{f,m}^0 = -2\,293.2$ kJ mol^{-1}).

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