

HEAT OF DILUTION IN POTASSIUM BICHROMATE-WATER SYSTEM AT 25°C

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Received February 13th, 1978

The values of the heat of dilution in the potassium bichromate-water system at 25°C, derived from the empirical concentration dependence of the integral and differential heats of dissolution, are compared with the Debye-Hückel limiting relation. Some features of these dependences are discussed.

In our preceding work¹ we presented the results of measurement of integral dissolution heat of potassium bichromate in water at 25°C. These data were fitted with a maximum relative error of 1% by the polynomial

$$\Delta H_m = 83.881 - 102.202m^{1/2} + 347.577m - 587.751m^{3/2} + 346.737m^2, \quad (1)$$

where m denotes molal concentration (mol/kg) and ΔH_m is expressed in kJ/mol of the solute. This concentration dependence was also substantiated by several measured values of the heat of dilution¹. The integral heat of dilution, V_m , is given as

$$V_m(m) = \lim_{m \rightarrow 0} \Delta H_m(m) - \Delta H_m(m). \quad (2)$$

By combining Eqs (1) and (2) we obtain

$$V_m = 102.202m^{1/2} - 347.577m + 587.751m^{3/2} - 346.737m^2. \quad (3)$$

The integral heat of dilution is according to the Debye-Hückel theory of diluted electrolytes given in the form²

$$V_m = -K(\sum v_i z_i^2)^{3/2} \left(1 + \frac{d \ln \epsilon}{d \ln T} + \frac{T}{3V} \left(\frac{\partial V}{\partial T} \right)_p \right) \sqrt{c}, \quad (4)$$

where v_i denotes stoichiometric coefficient, z_i valency of i -th ion, T temperature, ϵ dielectric constant, V volume of solution, K constant independent of the solute,

c molar concentration, and P pressure. At very low concentrations the difference between the molar and molal concentrations can be neglected (the density of 1% $K_2Cr_2O_7$ is 1.005 g/cm^3). It follows from Eq. (4) that all electrolytes of the same valency type should have a common initial value of the quotient $dV_m/d\sqrt{c}$. For completely dissociated electrolytes, an extensive comparison of the experimentally found dependences $V_m = V_m(m)$ was given by Lange², who showed that for selected salts of the 1-1, 1-2, 1-3, and 1-4 valency types the initial value of the slope $dV_m/d\sqrt{c}$ is close to the theoretical following from Eq. (4). In contrast, for salts of the 2-2, 2-3, 2-4, and 3-3 valency types the theoretical and experimental values of this slope differ much from each other and no explanation of this disagreement is not available so far.

A comparison of the concentration dependence of the integral heat of dilution for potassium bichromate calculated from Eq. (3) with the theoretical initial slope from Eq. (4) is shown in Fig. 1. For completeness, the function $V_m = V_m(m)$ is shown in the whole concentration region of unsaturated solutions. Also shown are the concentration dependences of the integral heats of dilution of ammonium bichromate and potassium chromate (based on several data from the literature^{3,4}; they are less founded than the dependence after Eq. (3)) along with other simple electrolytes of the same valency type.

It is seen from this comparison that the initial value of the mentioned slope is surprisingly larger by the factor of 10 than the theoretical in the case of $K_2Cr_2O_7$ and by the factor of 3.5 in the case of ammonium bichromate. The dependence for K_2CrO_4 shows similar properties as with other common electrolytes illustrated in Fig. 1. Similarly, a positive deviation of the initial slope from the theoretical value shows a number of salts², e.g., $CuSO_4$, $CdSO_4$, $ZnSO_4$, $Ca_2Fe(CN)_6$, $Sr_2Fe(CN)_6$,

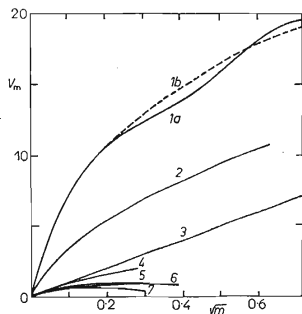


FIG. 1

Dependence of Integral Heat of Dilution V_m (kJ/mol) on Molality m

1 $K_2Cr_2O_7$, a integral data, Eq. (3), b differential data, Eq. (5); 2 $(NH_4)_2Cr_2O_7$, according to literature^{3,4}; 3 initial slope according to Eq. (4) (ref.²); 4 Li_2SO_4 , 5 K_2SO_4 , 6 K_2CrO_4 , 7 $Ba(NO_3)_2$; data for curves 4-7 were taken from the literature^{2,4}.

$\text{Mg}_2\text{Fe}(\text{CN})_6$, but among uni-divalent electrolytes the bichromates are interesting by their pronounced deviation which is not satisfactorily explained so far.

The high value of the initial slope $dV/d\sqrt{c}$ in the region of $m \leq 0.05$ is with potassium bichromate closely related to the extremely high absolute value of the initial slope of the concentration dependence of the integral heat of dilution, $d\Delta H_m/dm$, in the region of $m \leq 0.05$, described in our previous work¹. An interesting feature of the concentration dependence of the integral heats of dilution for both bichromates, shown in Fig. 1, is the approximate accord of the slope $dV_m/d\sqrt{c}$ with the initial theoretical value from the Debye-Hückel limiting equation in the region of moderately concentrated solutions (the theoretical value is justified only for very diluted solutions). In the region of more concentrated solutions, the concentration dependence of the heat of dilution of potassium bichromate is unusually undulated. Therefore, we included in Fig. 1 also the alternative dependence of $V_m(m)$ calculated from our measured differential heat of dissolution of potassium bichromate⁵ according to the equation

$$V_m = 29.04 \sqrt{m} - 13.84m + 5.50. \quad (5)$$

From a comparison of both dependences it can be concluded that the undulation of the concentration dependence derived from integral data is due to the polynomial approximation of the measured data (see discussion in refs^{1,5}). In this respect, we consider the dependences $V_m(m)$ obtained from differential data as more reliable. On the other hand, in the region of very diluted solutions it is better to start from the integral data.

In very diluted solutions, both dissociation and hydrolysis can take place. According to Muldrow and Hepler³, the heat of the hydrolysis

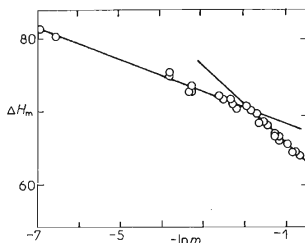


FIG. 2
Dependence of Integral Heat of Dissolution ΔH_m (kJ/mol) for Potassium Bichromate on Molality

is relatively small (-2.9 kJ/mol); they showed by an experiment in a medium suppressing the hydrolysis³ that eventual hydrolysis has in their concentration region (10^{-3} – 10^{-2} mol/kg) a negligible influence. We did not find enough data in the literature to estimate the influence of other hydrolytic or dissociation reactions.

The aim to elucidate processes connected with dissolution or dilution of electrolytes leads to attempts to find a causal explanation of the empirically found dependence of the heats of dilution and dissolution on concentration. Shmagin and Shidlovskii⁶ found a break on the dependence of $V_m(\ln m)$ in their unique experimental study of the heats of dilution and dissolution of potassium bichromate in the region of both under- and supersaturated solutions. This break was without a deeper theoretical or experimental evidence attributed to structural changes, which take place according to these authors during the transition from under- to supersaturated solutions.

The integral heats of dissolution measured in the preceding work¹ have an interesting property: the function $\Delta H_m(m)$ can be linearized to $\Delta H_m(q)$, where $q = \ln(m/C_1 - C_2m)$. For example, with $C_1 = 0.65$ and $C_2 = 1$ we obtain an almost linear dependence in the whole concentration interval. Similarly as in the cited work⁶, the our data of ΔH_m plotted against $\ln m$ give a curve that can be interpreted as a linear dependence with a break (Fig. 2). Therefore, we do not think that we have to deal with a result of some structural changes. The reason is rather an incomplete hydration, since the limit of complete hydration for potassium bichromate lies close to the saturated solution. A more detailed discussion is prevented by the uncertainty in the solvation numbers of both ions under consideration and insufficient experimental evidence for breaks of the described type. It is not certain whether the break in the cited work⁶ is not due to the mathematical treatment of the data, namely transformation of the independent variable into its logarithm.

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Translated by K. Micka.