THE HEAT OF DEHYDRATION OF CONCENTRATED SODIUM CHLORIDE AND POTASSIUM CHLORIDE SOLUTIONS

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ABSTRACT

The molar heats of dehydration, $\Delta\bar{H}_{dehyd.}$, of concentrated sodium chloride and potassium chloride solutions were measured with a differential scanning calorimeter in the scanning and isothermal modes. The overall $\Delta\bar{H}_{dehyd.}$ was found to be 44.5 and 44.3 kJ mole^{-1} H$_2$O for NaCl and KCl solutions respectively. There is an astonishing difference between concentrated NaCl and KCl solutions in the way water is lost. The number of fractions of heat dehydration were 2 for NaCl and 3 for KCl. The excess $\Delta\bar{H}_{dehyd.}$ was about 10 kJ mole^{-1} H$_2$O for fraction II of NaCl, and 17 and 55 kJ mole^{-1} H$_2$O for fractions II and III, respectively, of KCl.

INTRODUCTION

The motivation for following the heat of dehydration of highly concentrated solutions of sodium chloride and potassium chloride came from studies of the behaviour of the above-mentioned ions in halophilic bacteria [1]. Recently, we followed the heat of dehydration of this very system [2]. Halophilic bacteria show a remarkable degree of selectivity between K$^+$ and Na$^+$ ions, which has been postulated to be due to strong interactions of water with the proteins within the bacteria [3,4]. Due to the fact that the bacterial system is relatively dry, it seems that there is not enough water to complete the hydration shells around the biopolymers, as well as around all the ions. This is the same situation that Stokes and Robinson [5] and later Braunstein [6] described for very concentrated electrolyte solutions, where water becomes distributed among ions and biopolymers so that some ions and/or biopolymers bind to water, some have incomplete hydration shells, some have complete hydration shells and some may have multiple layers of water molecules.

As Stokes and Robinson [5] have pointed out, such a model corresponds to multilayer adsorption (e.g. the BET adsorption equation describes such situations). A useful parameter of the BET treatment is C, the ratio of partition fractions of adsorbed molecules in the first and second (or higher)

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layers, given by $g_1/g_2 \exp[-(H-H_L)/RT]$. $(H-H_L)$ is the difference between the heats of adsorption and that of liquefaction, and the assumption usually made that this difference is zero for adsorption in all layers beyond the first is not necessarily true in all cases.

There are several important papers describing the adsorption of water by Na^+ and K^+ chloride crystals [7] and in particular, measurements of the heat of adsorption as a function of surface coverage. There are discrepancies between these data, which are very likely due to differences in experimental conditions and procedure. Heats of adsorption up to 150 kJ mole^{-1} [8] were reported for the NaCl crystal, even though in other cases the numbers are much smaller. Walter [9] reports on values up to 80 kJ mole^{-1} for isoteric heat of adsorption of water vapours on coarse powders of NaCl and KCl. For KCl, Hall and Tomkins [10] found heats of adsorption of 12.7 kJ mole^{-1} and 48 kJ mole^{-1}, depending on the temperature used.

In the following we describe measurements of the heat of dehydration of concentrated solutions of KCl and NaCl (>3 M) carried out in a differential scanning calorimeter (Perkin-Elmer DSC-2). We show a large difference in the way the heat of dehydration is distributed within solutions of KCl and NaCl.

METHODS

Solutions were prepared from Analar grade NaCl and KCl. Double-distilled water from a glass still was used throughout. The Perkin-Elmer differential scanning calorimeter, model DSC-2, was used to determine the heat of dehydration or evaporation of the solution. A sample was placed inside an aluminium pan, which was completely sealed except for a pinhole of 0.3 mm diameter drilled in the cover of the pan. This pinhole retarded the loss of water vapour without causing any appreciable build-up of pressure inside the closed pan; this conclusion can be drawn from the observation that the boiling point of pure water in the pan did not exceed 373 K by more than 0.5—1°C. (The boiling point is obtained by extrapolating back from the ascending curve of the thermogram, according to McNaughton and Mortimer [11].) The pan was weighed first empty, then after sealing, and finally after heating in the calorimeter; the difference between the two latter weights was taken as the weight of water evaporated or desorbed.

The pan was placed in the calorimeter, which was closed. The machine was continuously flushed with N_2 gas; heating was started a few minutes later. In the scanning mode a recording was made of the heat needed to maintain a constant rate of increase in temperature. The calorimeter response of DSC-2 can be assumed to be constant over the entire temperature range [11]. After completion of the heating-run, the sample was cooled and reheated over the same temperature range, care being taken not to change the position of the pan inside the calorimeter. The purpose of this second run, done with dry salt, was to obtain a baseline without recourse to any arbitrary calculations; the problem of defining the baseline is not trivial

for quantitative measurements of enthalpy [11,12]. The enthalpy of water desorption was defined as the area between the curves obtained from the first and second runs. The area is almost closed (e.g. Figs. 1—3; [12]).

For the isotherm mode, at zero time the initial heating rate is very fast (80—160°C min^{-1}), and thus an apparent given temperature of the measured pan is achieved in a relatively short time, and is kept at the given temperature until no water remains in the pan.

The area of the power—time curve (thermogram) was measured with an Albritt planimeter. Each area was measured two to three times so as to ensure a reproducibility of 1%. Most areas were between 25 and 75 cm^2. The accuracy of the planimeter area measurement itself was checked by measuring known areas of 25 and 50 cm^2 at least 10 times. The S.D. was less than 1% of the average.

The output of DSC-2 was calibrated in two ways. (1) The endothermic peak of melting of a pure sample of indium, supplied by Perkin-Elmer, was measured in a sealed aluminium pan. This was done with two different amounts of indium (7.35 mg and 15.8 mg) at several sensitivities and rates of heating. (2) Known amounts of water (9.0 mg and 19.9 mg) were sealed into aluminium pans and heated over a wide temperature range. As the C_p of water is constant between 273 and 350 K, the enthalpy of heating water between 333 and 343 K could be calculated.

Samples of indium: 0.1892 ± 0.0012 cal cm^{-2} paper
                0.1853 ± 0.0011 cal cm^{-2} paper
Samples of water: 0.1916 ± 0.0014 cal cm^{-2} paper
                0.1895 ± 0.0010 cal cm^{-2} paper

The two methods of calibration agreed within 2%.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 depict thermograms of evaporation, or dehydration of pure water, NaCl solution and KCl solution, respectively. In Fig. 1, where evaporation of pure water is described we see a monotonic increase of power (dQ/dt) with increase of temperature (scanning mode) until a maximum is reached; the recorded trace then returns abruptly to the baseline, presumably because no water is left in the pan. Extrapolating back to baseline, we can obtain the boiling point of water which is, as expected, around 373 K. (This procedure is discussed in ref. 11.) In Fig. 2, where water is evaporated from concentrated NaCl solution (~3 M), we also observe a monotonic increase of dQ/dt with the increase of temperature. In Fig. 2b there may be a discontinuity, though this is not certain. Extrapolating back to baseline, we obtain an apparent boiling point at 389 K. On the other hand, the dehydration of KCl solution (3 M) in Fig. 3 describes a very different course of events. We observe three peaks: the first is around 382 K, the second at 388 K and the third around 391 K. Thus the dehydration of water of concentrated KCl solution appears to be different from that of NaCl solution, or of pure water.

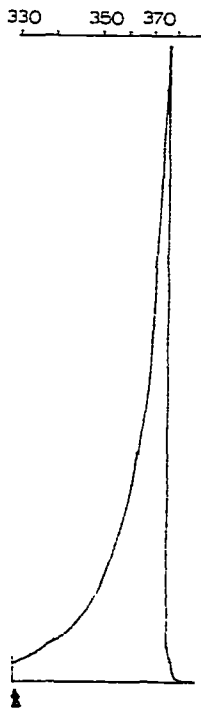In Figs. 4—6 we observe dehydration (or evaporation) of the same systems

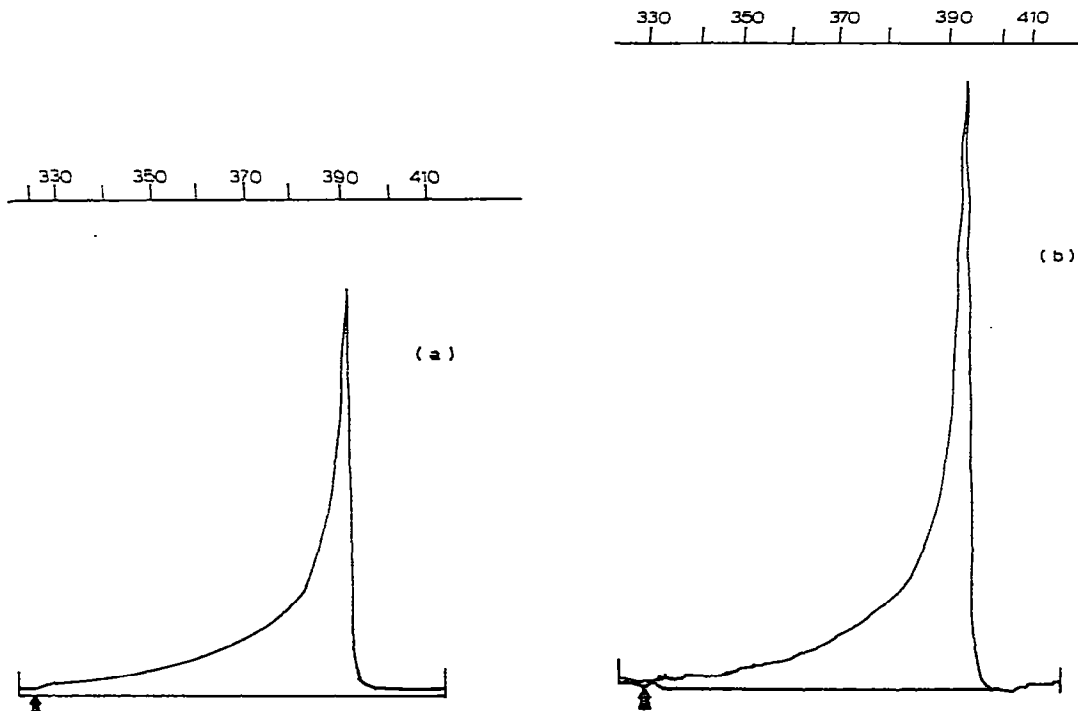Fig. 1. Thermogram of pure water evaporation. Scanning mode. 10°C min⁻¹; 10 mcal sec⁻¹. 2.21 mg H₂O.

Fig. 2. Thermogram of the dehydration of NaCl (3 M) solution. Scanning mode. 10°C min⁻¹; 10 mcal sec⁻¹. (a) 1.37 mg water; (b) 1.52 mg water.
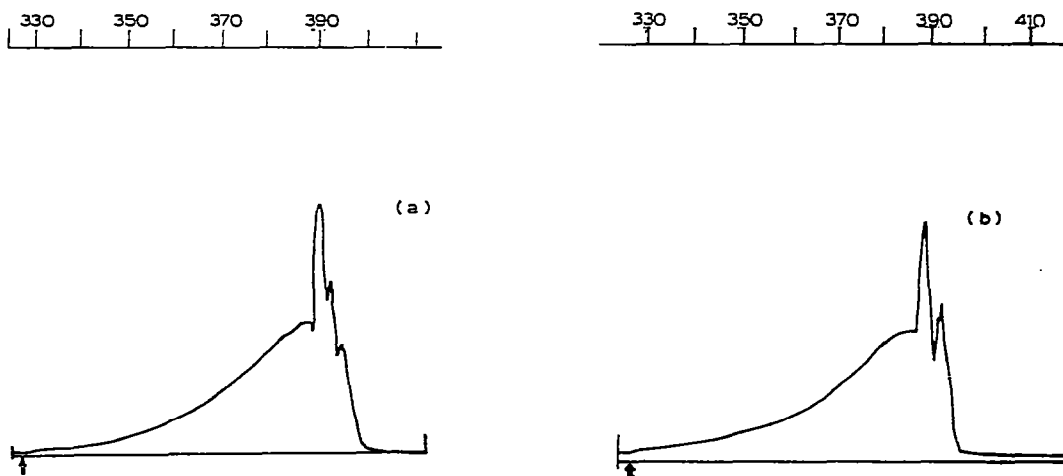
330   350   370   390   330   350   370   390   410

Fig. 3. Thermogram of the dehydration of KCl (3 M) solution. Scanning mode. 10°C min⁻¹; 10 mcal sec⁻¹. (a) 1.37 mg H_2O; (b) 1.04 mg water.

in the isothermal mode, rather than in the scanning mode.

Figure 4 describes evaporation from a pan which contains only pure water. We see that after a relatively short transient ("the dynamic period" using the term of Staub and Schnyder [13]) the trace of dQ/dt is kept constant ("stationary isothermal period") for a while and then returns abruptly to the baseline. This thermal event seems to be consistent with Fig. 1, where water evaporation in the scanning mode shows only one apparent population of water molecules.

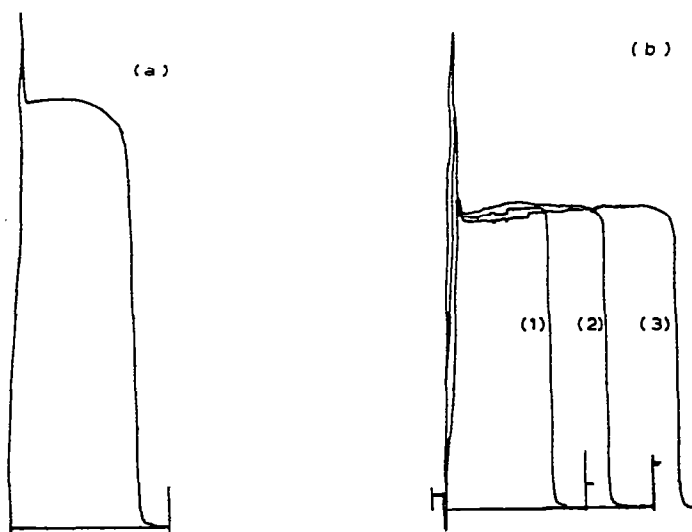In Fig. 5 we see the isothermal mode of dehydration of NaCl solution. In

Fig. 4. Thermogram of the evaporation of pure water. Isothermal mode. (a) 5.8 mg H_2O; (b) three separate measurements: (1) 3.2 mg H_2O; (2) 5.21 mg H_2O; (3) 7.13 mg H_2O/ 373 K.
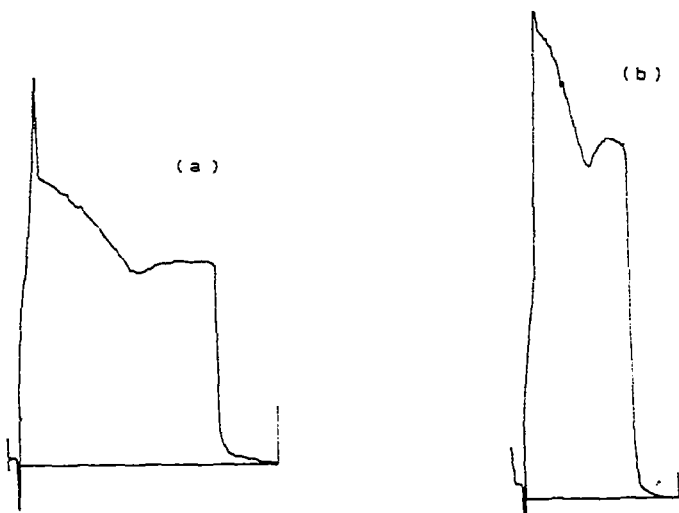
Fig. 5. Thermogram of the dehydration of NaCl (3 M) solution. Isothermal mode (a) 379 K; (b) 383 K.

contrast to Fig. 4, the form of the curve dQ/dt vs. time has a two-step form. In Fig. 6 where the dehydration of KCl solution is described there is a three-step curve. This is consistent with Fig. 3, where the scanning mode of dehydration of KCl solution is depicted. Figure 3 shows three peaks, which seem to correspond to the three steps of Fig. 6. Thus it appears from the two modes of operation of the DSC that there are different ways of escape of water into vapour from pure water, NaCl solution or KCl solution, respectively.
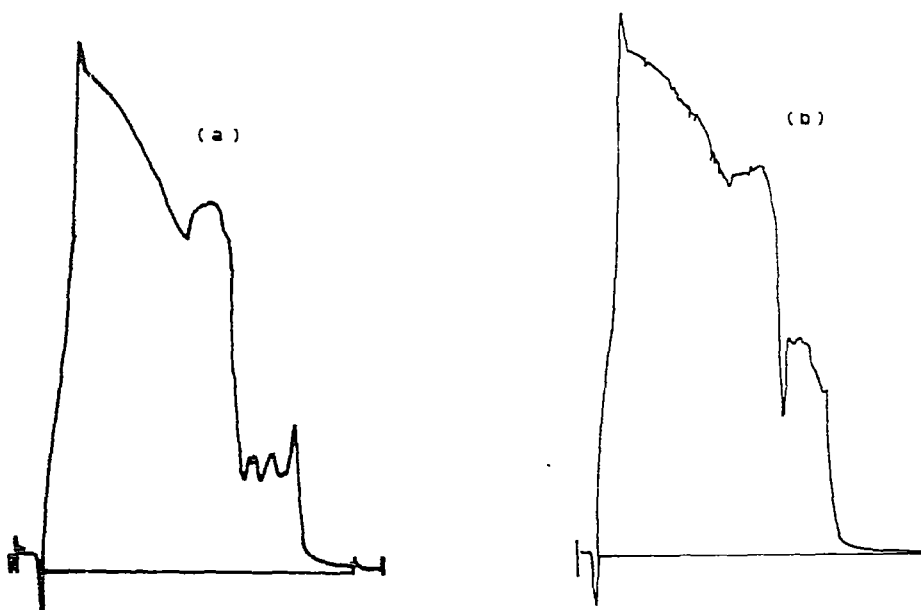

Fig. 6. Thermogram of the dehydration of KCl (3 M) solution. Isothermal mode. (a) 383 K; (b) 381 K.

TABLE 1

The heat of evaporation ($\Delta \bar{H}_{evap.}$) or dehydration ($\Delta \bar{H}_{dehyd.}$) (kJ mole^{-1}) of water from pure water, NaCl solution (~3 M) and KCl solution (~3 M) by DSC

	Isothermal mode	Scanning mode	Literature
Water	41.72 ± 0.97 (373 K)	41.05 ± 0.92 (323—373 K)	40.61 (373.16 K)
NaCl	44.53 ± 0.53	42.25 ± 0.42	
KCl	44.30 ± 0.35	43.10 ± 0.47	

In Table 1 the total molar enthalpy ($\Delta \bar{H}_{dehyd.}$) of dehydration in the two modes of measurement is given. It should be realized that in the isothermal mode a part of $\Delta \bar{H}$ comes from the "dynamic period," where fast changes of temperature occur. Thus as $\Delta \bar{H}_{dehyd.}$ falls slightly with increase of temperature (see ref. 13), the $\Delta \bar{H}_{evap.}$ at a given temperature is slightly overestimated. On the other hand, in the scanning mode the evaporation takes place throughout the temperature range from 323 K to the boiling point. Thus the $\Delta \bar{H}_{dehyd.}$ includes the heating of the liquid water and also $\Delta \bar{H}_{dehyd.}$ at different temperatures, which is a decreasing function with temperature increase. Yet in fact, as can be seen in Fig. 1, most of the thermal event quantitatively occurs at the higher temperature end, and indeed for pure water $\Delta \bar{H}_{dehyd.}$ in the two modes, is not very different from that found by other methods [14]. The values of $\Delta \bar{H}_{dehyd.}$ were obtained from the areas of the curves in Figs. 1—6. The baseline is that of the empty pan for pure water and of dried salt for the solution.

Thus, in Table 1 we see that for pure water there is a difference of 1.1% in $\Delta \bar{H}_{evap.}$ between the two modes. The values are a little higher than values in the literature.

In the case of the two salts there is about 3% difference in $\Delta \bar{H}_{dehyd.}$ between the two modes, the scanning mode being the lower.

The excess of $\Delta \bar{H}$ is 2.5 kJ mole^{-1} and 2.3 kJ mole^{-1} for NaCl solution and water and KCl solution and water, respectively. This is true if we treat all the water molecules in the solution as a uniform population. In Figs. 3, 5 and 6 we see that it is not justified to use this assumption: water in the concentrated solution of NaCl is apparently divided into two populations, while that of KCl consists of even three apparent populations (or fractions). We wish to find a way of assigning a molar heat of dehydration to each population. For that purpose, we have to find the weight of water for each fraction and its heat of dehydration.

Let us start with NaCl. In Table 2 we see that the heat of dehydration is divided into two fractions, the first fraction (fraction I) has about 66% of the total heat and the second one (fraction II) has 34%.

For calculating the amount of water in these two fractions, we will make the assumption that the water molecules in fraction I have no interaction with ions; therefore their heat of dehydration is near to that of pure water, i.e. 41.72 kJ mole^{-1}. From measurements, we know the total heat of dehydration, multiplying by 0.66 we obtain $\Delta H^I_{dehyd.}$ of the first fraction. By dividing $\Delta H^I_{dehyd.}$ by its molar heat of dehydration, we obtain the amount

TABLE 2

The heat of dehydration of water ($\Delta\bar{H}_{dehyd.}$) per gram of water of NaCl (3 M) and KCl (3 M)

	KCl (fraction)				NaCl (fraction)	
	I.	II and III	II	III	I	II
% Heat	68	32	25	7	66	34
$\Delta H_{dehyd.}$ calculated from I *	41.72	52.5			41.72	51.44
$\Delta H_{dehyd.}$ calculated from II *	41.72		57.16	96.17	41.72	53.85
No. of moles of water/mole of salt		5.48	4.80	0.68		6.03

* See text.

of water in this fraction. From the total amount of water, by subtraction, we obtain the amount of water in the second fraction and by subtraction we also obtain the amount of heat of dehydration of this fraction, whence we get the molar heat of dehydration for this fraction, which comes to be 51.44 kJ mole^{-1}.

Another way of calculating the molar heat of dehydration of the two fractions is from the ratio of the levels of the stationary isothermal mode (Fig. 5). Here again we have to assume a value for the first fraction and then we obtain the value for the second fraction, which is 53.85 kJ mole^{-1}. Thus we can consider that there is reasonable agreement between the two different methods of calculation of the molar heat of dehydration. From this calculation, we can also obtain the amount of water per mole of salt, which is roughly speaking the water of hydration and is 6 mole of H_2O per mole of NaCl. This is not too far from various estimates of hydration in dilute solution.

It is more difficult to make the first calculation for KCl solution, where three apparent populations have been found. We can calculate by the same methods a combined molar heat of dehydration for fractions II and III, which is 52.5 kJ mole^{-1}. From the ratio of the levels we obtain 57.2 kJ mole^{-1} for fraction II and 96.2 kJ mole^{-1} for fraction III.

To sum up, there is an astonishing difference in the way water is lost between concentrated solutions of NaCl and KCl. In NaCl only two fractions of water were found; the second must be equivalent to the water of hydration of the ions. Its excess of molar heat of dehydration above that of pure water is about 10 kJ mole^{-1}, and is about 6 moles of water per mole of NaCl. In contrast to this, in KCl there is an extra small fraction of water which has a much larger molar heat of evaporation, and consists of 0.68 mole H_2O per mole KCl. The difference between NaCl and KCl solutions was found at a temperature around 400 K, and must reflect a difference in the interaction of water with these two cations. This difference may be one of the features which leads to the known difference in behaviour of Na$^+$ and K$^+$ in many biological systems, and which is the basis of the most important biological processes.

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