

**PARTIAL MOLAR HEAT CAPACITY OF ADSORBED
WATER ON AN ION-EXCHANGER**

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ABSTRACT

Heat capacity of a polystyrene sulfonate ion-exchanger has been investigated with a TIAN-CALVET microcalorimeter as a function of the water content. Three ionic forms K^+ , Na^+ and Ba^{2+} were examined. The partial molar heat capacity of water has been then deduced. The observed variations may be explained by the presence of strong interactions between water and ion-exchanger. The hydration proceeds by way of two steps. The counter-ion charge density is the main factor.

INTRODUCTION

The great affinity of polystyrene sulfonate ion-exchangers for water allows to use them as drying agent. The easy regeneration of the adsorbent (about 80-100°C) lends additional interest. For the determination of the regeneration conditions it is necessary to know the corresponding heat capacity. Therefore we have measured, for three ionic forms : K^+ , Na^+ and Ba^{2+} , the heat capacity of this material as a function of water content.

MEASURING METHOD

We use a TIAN-CALVET microcalorimeter. The selected method necessitates the comparison of three curves when the system returns to equilibrium : one for an empty cell, another for a cell filled with benzoic acid and the last for a cell containing the ion-exchanger. Equation (1) gives the specific heat capacity of the sample :

$$C = \frac{S_2 - S_0}{S_1 - S_0} \cdot \frac{M_1}{M_2} \cdot C_e \quad (1)$$

where : S_0, S_1, S_2 : area under the curve for empty cell, benzoic acid and ion-exchanger
 M_1, M_2 : weight of benzoic acid and ion-exchanger
 C_e : benzoic acid specific heat capacity.

A better precision is obtained by producing the same joule effect in the sample cell and in a reference cell which is always empty. We estimate the error on the heat capacity being 5%.

RESULTS AND DISCUSSION

The working temperature is 30°C . We measure the heat capacity of the ion-exchanger for three ionic forms : K^+ , Na^+ and Ba^{2+} (heat capacity and water content are referred to the equivalent of dried adsorbent). The graph of C_p of the ion-exchanger versus the number n of adsorbed water moles has a slightly sigmoid form in all cases. Figure 1 illustrates the results we obtain with Na^+ as counter-ion.

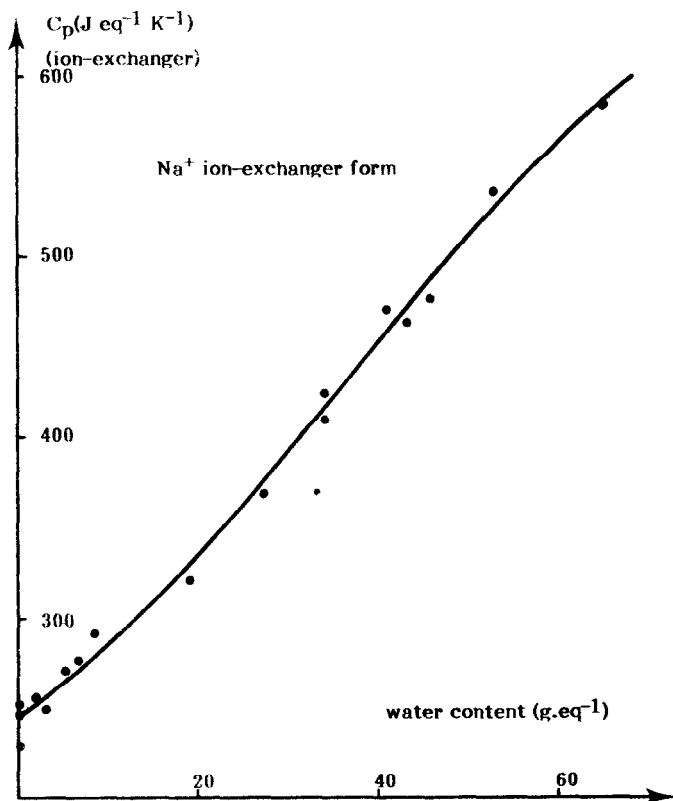


FIGURE 1

We correlate the experimental data with a third degree polynomial function. The use of a greater degree does not improve the estimated variance on the one hand and gives no significant variation for partial metal quantity on the other hand. The coefficient values are compiled in table 1.

The heat capacity being referred to the equivalent of dried ion-exchanger, partial molal heat capacity for adsorbed water is given by equation (2) :

$$\bar{C}_{p,e} = \left(\frac{\partial C_p}{\partial n} \right)_{T,P,n_j} = 3 An^2 + 2 Bn + C \quad (2)$$

TABLE 1

Counter ion	$C_p(\text{J eq}^{-1}\text{K}^{-1}) = An^3 + Bn^2 + Cn + D$ (n : adsorbed water mole eq ⁻¹)			
	A	B	C	D
K ⁺	- 3,84	22,21	55,46	246,3
Na ⁺	- 3,94	24,68	56,49	245,1
Ba ²⁺	- 2,36	18,36	44,23	296,7

This quantity, first lower than for pure water, rises to a maximum and then decreases. GARTNER and FUCHS (1) report a similar evolution for carboxylic ion-exchanger. LAL and DOUGLAS (2) have measured the volume for a polystyrene sulfonate ion-exchanger (H⁺ form) as a function of water content. The water partial molar volume thus obtained is also lower than for pure water.

This lower value observed for water partial molal heat capacity may be explained by the presence of an interaction between water and ion-exchanger. As suggested by ZUNDEL (3) in his study on polyelectrolyte membrane, the first water molecules that adsorb are hydrogen bonded with the anionic sites -SO₃⁻ on the one hand and are attached to cation by dipôle-dipôle interaction on the other hand. These interactions are not independant but mutually grow stronger for low humidity content by increasing dipôle moment of water molecules. This effect must increase the more so as the electrical charge density of the counter-ion. The lower values observed for Ba²⁺ than for K⁺ or Na⁺ fully agree with this idea.

We note that water partial molal heat capacity increases as the ion-exchanger water content. The diminution of the intensity of the electrical field of the counter-ion on each water molecules, which are more numerous, may be explanatory of this fact. As a result, the hydrogen bonds between water and sulfonate groups -SO₃⁻ are weakened.

The maximum value of partial molal heat capacity is observed for 1,93 - 2,08 and 2,59 mole of adsorbed water by equivalent of dried resin when corresponding counter-ion is K⁺, Na⁺ and Ba²⁺. These results compare favorably with the critical hydratation

number 2 indicated by ZUNDEL (3) and the value 2,6 given by ALEXANDER and coll (4) for the hydrogen form of the ion exchanger. This maximum would indicate the end of the first hydration step for the ion-exchanger. The hydration water molecules link the cations with the neighboring anions so that these water molecules each form two hydrogen bridges and more water molecules, depending on the electrical density charge of the cation, are bonded to this later by dipôle-dipôle interaction.

With increasing degrees of hydration, two and subsequently more "layers" of water molecules are found among the ion-exchanger sites. Being far from the cation, these supplementary water molecules are slightly bonded. So they will partly associate between them because the hydrogen bonds formed are stronger than dipole-dipole interactions with cation. This may be an explanation for the observed decrease of water partial molal heat capacity when water content on the ion exchanger is greater than about two moles eq^{-1} . The more the electrical charge density of cation is great, the more this second hydration step will appear late. This agree with our experimental results.

CONCLUSION

The measured heat capacity of a polystyrene sulfonate ion-exchanger as a function of its water content and the nature of the counter-ion, allowed us to determine partial molar heat capacity of adsorbed water. The observed results agree with the idea that the hydration of the ion-exchanger proceeds through two steps :

- anionic sites hydration by hydrogen bonds and hydration of the associated cation by dipôle-dipôle interaction,
- the building of a second hydration shell around cationic and anionic sites where water molecules are partly associated between themselves.

All this interaction are in mainly part dependent on the electrical charge density of the counter-ion.

The experimental results we have obtained are useful in the determination of better conditions for regenerating polystyrene sulfonate ion-exchangers.

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