Journal of Thermal Analysis, Vol. 45 (1995) 7-12

ENTHALPY OF ADSORPTION AND ADSORPTION ISOTHERMS OF POLYACRYLAMIDE ON SEA SAND

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Abstract

The enthalpy of dilution of polyacrylamide 3530s (*HPAM*) solution, the enthalpy of adsorption of the polymer on sea sand, and the adsorption isotherms, were determined at 298.15 K. The effect of NaCl on these properties were also determined. From the experimental results and certain assumptions, it was deduced that, for an adsorbed *HPAM* molecule, a large number of segments are in contact with the surface of the solid, some of them forming hydrogen-bonds, most of them belonging to Van der Waals interactions, which are much weaker than hydrogen-bonds, and the *HPAM* molecules adsorbed on the surface of the solid are spread out.

Keywords: adsorption isotherm, enthalpy of adsorption, polyacrylamide, sea sand

Introduction

The adsorption of polymers on solids has been studied extensively [1–7]. The behavior of polymers at solid–liquid interfaces is closely related with many industrial processes, such as enhanced oil recovery, flocculation and coating, etc. Calorimetry is one of the useful techniques for investigating the interactions between adsorbates and adsorbents at solid–liquid interfaces. However, study of the adsorption enthalpy of a polymer on a solid has been very limited [6, 7], especially for polymers of high molecular weights because the measurements are difficult. In the present paper, the enthalpy of dilution of polyacrylamide (3530s) solution, the enthalpy of adsorption of the polymer on sea sand, and the adsorption isotherm at 298.15 K are reported and discussed.

Experimental

Materials

The polyacrylamide 3530s (*HPAM*) was supplied by Pfizer Inc. with a mean molecular weight of 15 million. It was partially hydrolysed (25%). The NaCl

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0368–4466/95/ $ 4.00

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used was of analytical grade, and the water was distilled. The diameter of the sea sand was in the range from 0.11 to 0.22 mm, with a specific surface area of 0.39 m^2/g, determined by calorimetry [8]. The composition of the sea sand, which was determined by X-ray fluorescence analysis, is given in Table 1. It was dried for 4 h at 403.15 K before use.

Table 1 Composition of sea sand (wt%)

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3
0.07	0.08	5.06	92.80	0.01	0.34	0.07	0.06	0.01	0.03

Apparatus

The enthalpy of dilution of the polyacrylamide solution and the enthalpy of adsorption of the polymer on sea sand (i.e. the enthalpy of displacement of water adsorbed on the solid by the polymer) were measured with an LKB-8700 titration calorimeter. The concentrations of the *HPAM* solutions were determined with a UV-spectrometer manufactured by The Shanghai Second Optical Instrument Factory.

Procedures

Enthalpy of dilutions: 40.000 g of distilled water was placed in the reaction vessel of the calorimeter. After thermal equilibrium had been reached, the desired amount of the polymer solution of 2000 ppm was titrated into the reaction vessel. The procedure for determining the enthalpy of dilution of the polymer solution with 500 ppm NaCl was nearly the same as when the water in the reaction vessel contained 500 ppm NaCl.

Enthalpy of adsorption: 7.000 g sea sand and 40.000 g water was first placed in the reaction vessel of the calorimeter. The specified amount of 2000 ppm polymer solution was titrated into the reaction vessel, using the LKB injection pump, after thermal equilibrium had been reached. The concentration of NaCl was 500 ppm both in the water and in the polymer solution to be titrated, when the enthalpy of adsorption of the polymer from 500 ppm NaCl solution was determined. The reaction time was 50 min, long enough for equilibrium to be reached.

Adsorption isotherms: A static method was used to determine the adsorption isotherms. Briefly, weighed amounts of adsorbents were placed in a series of test-tubes and known amounts of the solution of desired concentration were added to each of them. The system was stirred at constant temperature. The test-tubes were centrifuged after the adsorption equilibrium had been reached. Experiments showed that adsorption of the polymer on the solid was quite rapid, only about 1 h being required for equilibrium to be reached. However, the equilibrium time was usually about 12 h in this work. The concentrations of the solutions in equilibrium with the solid were analysed by a method described in the literature [9].

Results and discussion

Figure 1 gives the integral enthalpies of dilution (Δ*H*) of the polymer solutions with and without NaCl at 298.15 K. In Fig. 1 *Ce* stands for the concentration of the polymer after dilution. Δ*H* is the enthalpy change for the titration of a 2000 ppm solution to 1 g of water until the concentration of the solution is *Ce*. Figure 1 reveals that Δ*H* is negative (exothermic) in the concentration range studied. For the solution without NaCl, –Δ*H* is higher than that for the solution with NaCl when *Ce* is less than about 500 ppm. –Δ*H* increases until *Ce* is about 1000 ppm without NaCl. However, –Δ*H* becomes constant when *Ce* is higher than about 700 ppm in the presence of NaCl. The –Δ*H* *vs.* *Ce* curves can be explained qualitatively as follows.

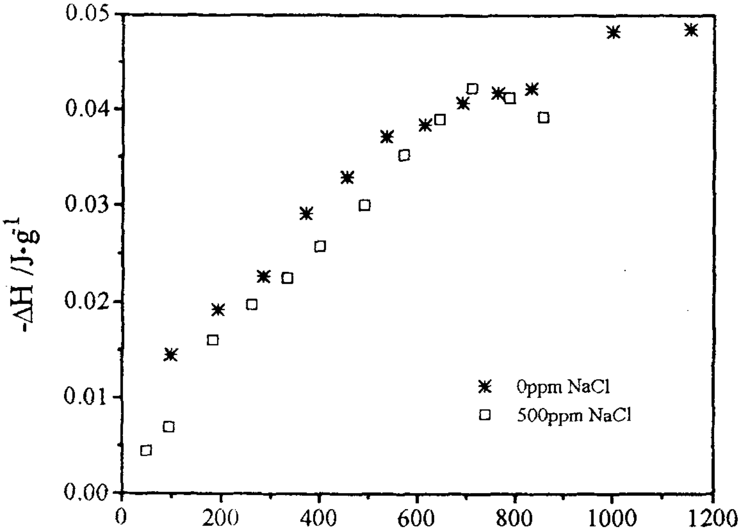

Fig. 1 Integral enthalpy of dilution of *HPAM* solution

The polymer is partially hydrolysed. In dilute solution, the negatively charged groups $-COO^-$ repel each other. Thus, the polymers spread out in solution. In the higher concentration range, however, negative charges are neutralized or shielded by ions in solution to some degree, and some of the polymers become coils. The concentration of the spread-out polymers becomes nearly constant when the total concentration of the polymer is high enough, and an increase in *Ce* causes an increase in the polymer coils, whose conformation is the same as that in the polymer solution to be titrated. Thus, a plateau appears in the $-\Delta H$ *vs.* *Ce* curve. From this, it seems that the conformation change is the main reason for the enthalpy change in the experimental concentration range. In the presence of NaCl, the ionic strength in the solution is increased. Thus, the plateau of the $-\Delta H$ *vs.* *Ce* curve appears at lower *Ce*.

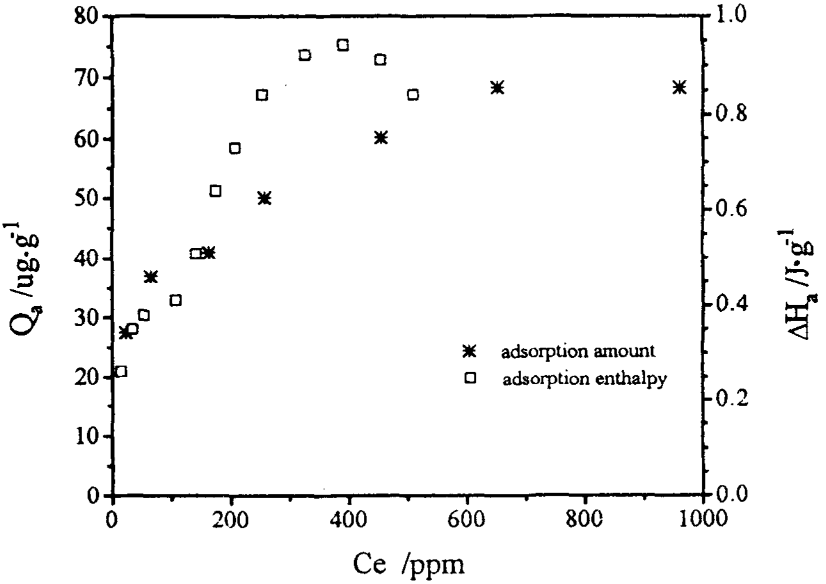

Fig. 2 Enthalpy of adsorption and adsorption amount of *HPAM* on sea sand without NaCl

Figures 2 and 3 show the adsorption isotherms and enthalpies of adsorption (ΔH_a) of the polymer on the solid with and without NaCl, respectively. The enthalpies of dilution of the corresponding polymer solutions have been considered for the results in Figs 2 and 3, where *Ce* is the equilibrium concentration, Q_a is the amount of *HPAM* adsorbed per g of solid, and ΔH_a denotes the enthalpy of adsorption of *HPAM* on the surface of 1 g of solid, i.e. the enthalpy of displacement of the water adsorbed on the solid by *HPAM*.

The data in Fig. 2 show that the adsorption of *HPAM* (Q_a) increases with the equilibrium concentration (*Ce*) when *Ce* is less than about 600 ppm. Q_a is independent of *Ce* when *Ce* is higher than about 600 ppm. A comparison of the results in Figs 2 and 3 reveals that the effect of NaCl on the adsorption isotherm is not significant.

From the data in Fig. 2, it can seen that in the absence of NaCl the enthalpy of adsorption ΔH_a is positive (endothermic), and increases with *Ce* (or Q_a) until *Ce* reaches about 400 ppm. Figure 3 shows that in the presence of NaCl ΔH_a is

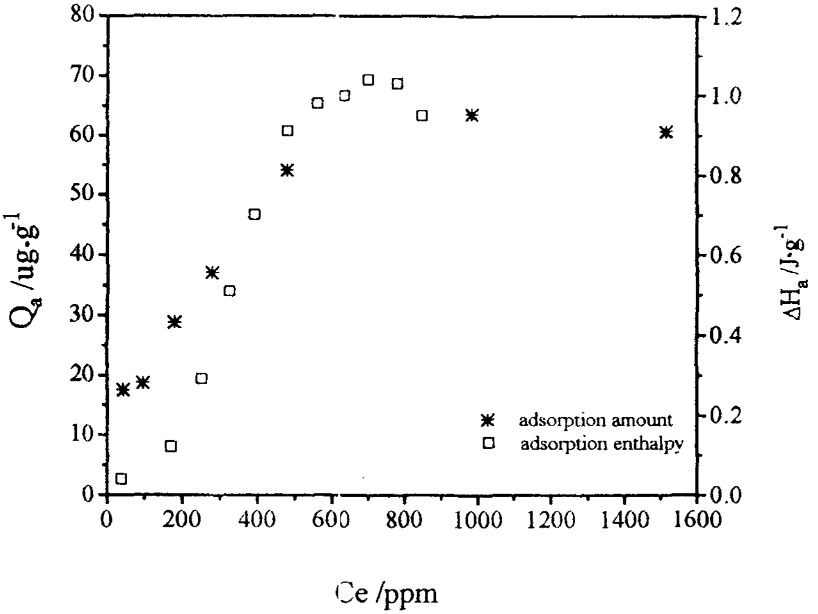

Fig. 3 Enthalpy of adsorption and adsorption amount of *HPAM* on sea sand in the presence of 500 ppm NaCl

also positive, and increases with *Ce* when *Ce* is lower than about 600 ppm. As mentioned above, ΔH_a is the enthalpy of displacement of water adsorbed on the solid by *HPAM*. For this process, a number of thermodynamic interactions should be taken into account when describing the adsorption of *HPAM* on solid surfaces, such as hydrogen-bonds, hydrophobic effect. Van der Waals interactions, conformational changes, electrostatic interactions, etc. All of these interactions affect the value of ΔH_a. However, one of the reasons for the positive enthalpy of adsorption may be that, for an adsorbed *HPAM* molecule, a large number of segments are in contact with the surface of the solid, some of them forming hydrogen-bonds, and most of them involving Van der Waals interactions, which are much weaker than hydrogen-bonds.

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Zusammenfassung — Bei 298.15 K wurde die Verdünnungsenthalpie von Polyacrylamid 353s (*HPAM*), die Enthalpie für die Adsorption des Polymers auf Meeressand und die Adsorptionsisothermen ermittelt. Der Einfluß von NaCl auf diese Eigenschaften wurde ebenfalls bestimmt. Anhand der experimentellen Ergebnisse und sicherer Annahmen schloß man darauf, daß bei einem adsorbierten *HPAM*-Molekül eine große Anzahl von Segmenten mit der Feststoffoberfläche in Kontakt steht, einige davon bilden Wasserstoffbindungen, die meisten sind an Van der Waals'schen Wechselwirkungen beteiligt, die wesentlich schwächer sind als Wasserstoffbindungen. Die an der Oberfläche adsorbierten *HPAM*-Moleküle sind gespreitet.