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THE CONFIRMATION OF THE FORMATION OF CLATHRATE-LIKE HYDRATES OF POLY(TETRABUTYLAMMONIUM ETHENESULFONATE) AND OF POLY(TETRAISOPENTYLAMMONIUM ETHENESULFONATE)

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A thermal method using differential scanning calorimeter has been applied to aqueous solutions of a series of poly(tetraalkylammonium ethenesulfonates) (R_4NPES). It was found that only the salts with $R = n\text{–}C_4H_9$ and $R = i\text{–}C_5H_{11}$ could form stable hydrates having large hydration numbers. The melting point and hydration numbers of these two hydrates were 12.0°C and 30±1 for the $(n\text{–}C_4H_9)_4NPES$ hydrate and 16.0°C and 53±2 for the $(i\text{–}C_5H_{11})_4NPES$ hydrate, respectively. It was concluded that these hydrates were clathrate-like essentially similar to such hydrates as $(n\text{–}C_4H_9)_4NF{\cdot}30H_2O$ and $(i\text{–}C_5H_{11})_4NF{\cdot}40H_2O$.

Keywords: clathrate-like hydrates, DSC

Introduction

Various tetrabutylammonium and tetraisopentylammonium salts can form unusual hydrates which have large hydration numbers as well as fairly high melting points between 0°C and room temperature [1–4]. A single-crystal X-ray examination by Jeffrey and his coworkers [2, 3, 5] on these hydrates showed that these hydrates were clathrate-like similar to the so-called gas hydrates [6].

Several years ago, one of the authors first found that tetrabutyl(or tetraisopentyl)ammonium polyacrylate could form a similar type of hydrate [7]. The formation of a hydrate of such polymeric salts had never been known before. In this study, from experimental facts that various tetrabutyl(or tetraisopentyl) ammonium alkanesulfonates and alkanedisulfonates can form hydrates having large

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hydration numbers and fairly high melting points [8, 9], we anticipated the possibility of the formation of hydrates of poly(tetrabutyl(or tetraisopentyl)ammonium ethenesulfonate) and tried to know whether it is true or not applying thermal method.

Experimental

Aqueous solutions of poly(tetraalkylammonium ethenesulfonates) ($R_4NO_3S(CHCH_2)_n$; R = CH_3, C_2H_5, n–C_3H_7, n–C_4H_9, n–C_5H_{11}, and i–C_5H_{11}), which are abbreviated to R_4NPES hereafter, were obtained by the neutralization of an aqueous solution of poly(ethenesulfonic acid) with aqueous solutions of the corresponding tetraalkylammonium hydroxide. The aqueous solution of poly(ethenesulfonic acid) was obtained by passing a poly(sodium ethenesulfonate) solution through a column of cation-exchange resin (Amberlite IR-120B) converted, in advance, into the acid form. The poly(sodium ethenesulfonate) was obtained by polymerization of sodium ethenesulfonate and was purified by similar procedures reported by Breslow *et al.* [10]. The molecular weight of the poly(sodium ethenesulfonate) was estimated to be about 6000 from viscosity measurements in 0.5 mol·dm^{-3} NaCl solution at 25°C using an equation proposed by Dialer and Kerber [11].

The differential scanning calorimeter used was model DSC-10 with an SSC-580 thermal controller, manufactured by Seiko Instruments and Electronics Ltd. Each sample solution (about 15 mg) was sealed in a 15 μl aluminum pan was either cooled or heated at a rate of 0.5 deg·min^{-1}. An empty pan was used as a reference.

Results and discussion

Thermal behaviour of aqueous solutions of poly(tetraalkylammonium ethenesulfonates)

The cooling and heating curves in the differential scanning calorimetry for aqueous solutions of R_4NPES (R = CH_3–n–C_5H_{11}, and i–C_5H_{11}) as well as NaPES are shown in Fig. 1 as a function of temperature. The mole fractions, based on the monomeric units, are equal to 0.015 for all the solutions. It is obvious that in the cooling process steep exothermic peaks around –20°C indicate the solidification of supercooled water, and in the heating process endothermic peaks in the –10–0°C range are attributable to the melting of the ice phase. However, the thermal behaviour of $(n\text{–}C_4H_9)_4NPES$ and $(i\text{–}C_5H_{11})_4NPES$ solutions differs markedly from that of the other five solutions; except for the peaks due to ice phase, there is an exothermic peak around –5°C and an endothermic peak around 10°C in the $(n\text{–}C_4H_9)_4NPES$ solution and an exothermic peak around –3°C and an endothermic peak around 15°C in the $(i\text{–}C_5H_{11})_4NPES$ solution. This behaviour clearly indicates that another solid phase but not ice is formed in these two solutions and furthermore this phase contains some amounts of water, i.e., a hydrate, since, in these two solutions, the enthalpy changes due to melting of ice phase become fairly small compared with those in the other five solutions. The presence of the $(n\text{–}C_4H_9)_4NPES$ and $(i\text{–}C_5H_{11})_4NPES$ hydrates has not been known before. Further details of these hydrates will be discussed in the following sections.

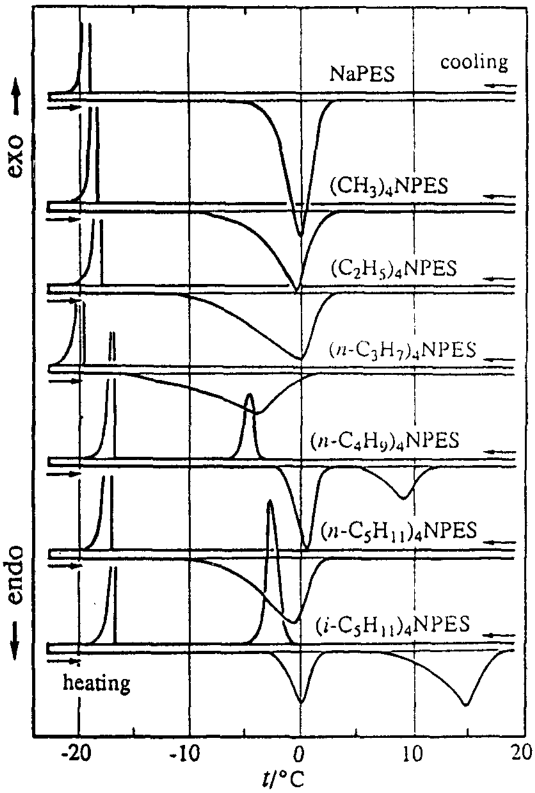

Fig. 1 DSC signals, expressed in arbitrary units, for aqueous solutions of poly(sodiumethenesulfonate) and a series of poly(tetraalkylammonium ethenesulfonates); R_4NPES. The mole fraction is equal to 0.015 for all the solutions

Poly(tetrabutylammonium ethenesulfonate) hydrate

The DSC signals for aqueous solutions of $(n\text{-}C_4H_9)_4NPES$ in various concentrations are shown in Fig. 2 as a function of temperature. X is the mole fraction based on the monomeric units. As mentioned above, the most important characteristic is the occurrence of peaks which are attributable to the formation of a hydrate. An enthalpy change (ΔH_1) due to the melting of ice phase decreases with increasing concentration and becomes very small when $X = 0.032$, i.e., the hydration numbers, m, are around 30. The hydration numbers can approximately be calculated by the following relation [7]:

$$m = \{n_o - \Delta H_1 / (6.01 \times 10^3)\} / n_1$$

where n_o and n_1 are the total number of moles of water and of $(n\text{-}C_4H_9)_4NPES$ (based on the monomeric units) contained in a sample solution. The hydration

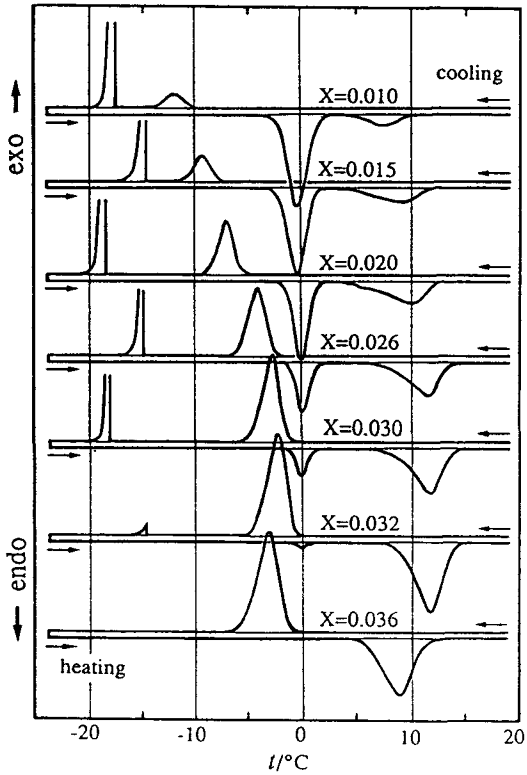

Fig. 2 DSC signals for aqueous solution of poly(tetraalkylammonium ethenesulfonate) in various concentrations

numbers calculated for the solutions with $X = 0.020\text{-}0.032$ are equal to 30±1, in good agreement with the value estimated above. The melting point of the $(n\text{-}C_4H_9)_4$NPES hydrate is determined to be 12.0°C by assuming that it is approximately equal to the temperature which corresponds to a maximum of the endothermic peak due to the melting of hydrate in the $X = 0.032$ solution.

From the facts that the hydration numbers are around 30 and the melting point is fairly high, this hydrate seems to have clathrate-like structure similar to such hydrate as $(n\text{-}C_4H_9)_4NF{\cdot}30H_2O$ and $(n\text{-}C_4H_9)_4NCl{\cdot}30H_2O$ [2].

Poly(tetraisopentylammonium ethenesulfonate) hydrate

The cooling and heating curves for aqueous solutions of $(i\text{-}C_5H_{11})_4$NPES are shown in Fig. 3 in a similar manner as in Fig. 2. The behaviour of these curves resembles that of the $(n\text{-}C_4H_9)_4$NPES solutions, suggesting the formation of a clathrate-like hydrate of $(i\text{-}C_5H_{11})_4$NPES. Thus, these curves can be analyzed in

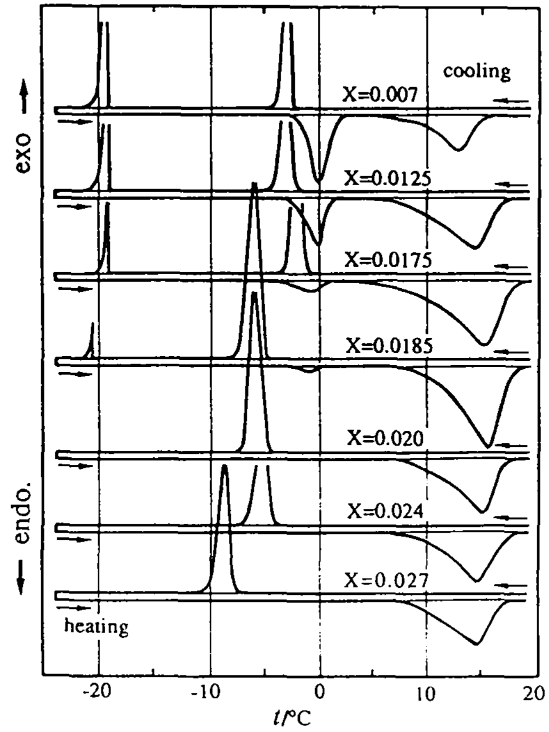

Fig. 3 DSC signals for aqueous solution of poly(tetraisopentylammonium ethenesulfonate) in various concentrations

the same way as in the $(n\text{-}C_4H_9)_4NPES\text{-}H_2O$ system, giving each peak the same physical meaning as mentioned before. The result that the ΔH_1 value becomes extremely small in the $X = 0.0185$ solution indicates the congruent composition of the hydrate is very close to $X = 0.0185$, i.e., hydration numbers are around 53. The hydration numbers calculated from the relation mentioned above are also 53±2 for solutions of X = 0.0125-0.0185. The melting point of the $(i\text{-}C_5H_{11})_4NPES$ hydrate is estimated to be 16.0°C. Although the hydration numbers of this hydrate are fairly different from those of a typical tetraisopentylammonium salt hydrate such as $(i\text{-}C_5H_{11})_4NF{\cdot}40H_2O$ [3], this hydrate could also be regarded as a clathrate-like hydrate since it has large hydration numbers and fairly high melting point.

Conclusion

The differential scanning calorimetry clearly revealed that poly(tetrabutylammonium ethenesulfonate) and poly(tetraisopentylammonium ethenesulfonate) can form unusual hydrates which have large hydration numbers and fairly high melting points. These hydrates have similar properties as those of tetrabutyl (or tetraisopentylammonium polyacrylate hydrates which were found several years ago [7]. Although there is no information about the crystal structure of these hydrates, they are considered to be a clathrate-like hydrate in which the poly(ethenesulfate) chain penetrates through associated, vacant polyhedra forming a hydrogen-bonded anionic host structure with water.

References

1 D. L. Fowler, W. V. Loebenstein, D. B. Pall and C. A. Kraus, J. Amer. Chem. Soc., 62 (1940) 1140.
2 R. K. McMullan, M. Bonamico and G. A. Jeffrey, J. Chem. Phys., 39 (1963) 3295.
3 D. Feil and G. A. Jeffrey, J. Chem. Phys., 35 (1961) 1863.
4 H. Nakayama, Bull. Chem. Soc. Jpn., 56 (1983) 877.
5 M. Bonamico, G. A. Jeffrey and R. K. McMullan, J. Chem. Phys., 37 (1962) 2219.
6 M. von Stackelberg and H. R. Muller, J. Chem. Phys., 19 (1951) 1319.
7 H. Nakayama, Bull. Chem. Soc. Jpn., 60 (1987) 2319.
8 H. Nakayama and H. Usui, Bull. Chem. Soc. Jpn., 59 (1986) 833.
9 H. Nakayama, M. Yamanobe and K. Baba, Bull. Chem. Soc. Jpn., 64 (1991) 3023.
10 D. S. Breslow and A. Kutner, J. Polym. Sci., 27 (1958) 295; W. Kern, V. V. Kale and B. Scherhag, Makromol. Chem., 32 (1959) 37.
11 K. Dialer and R. Kerber, Makromol. Chem., 17 (1956) 56.

Zusammenfassung — Unter Einsatz eines Differential-Scanning-Kalorimeters wurde eine thermoanalytische Methode an wäßrigen Lösungen einer Reihe von Poly(tetraalkylammoniumethensulfonat)-en (R_4NPES) angewendet. Man fand, daß nur die Salze mit R=n-C_4H_9 und R=i-C_5H_{11}

stabile Hydrate mit hoher Hydratationszahl bilden können. Der Schmelzpunkt und die Hydratationszahl für diese beiden Hydrate beträgt 12.0°C und 30±1 für $(n\text{-}C_4H_9)_4NPES$ Hydrat und 16.0°C und 53±2 für $(i\text{-}C_5H_{11})_4NPES$ Hydrat. Man zog die Schlußfolgerung, daß diese Hydrate klathratähnliche Verbindungen, ähnlich wie solche Hydrate wie $(n\text{-}C_4H_9)_4NF30H_2O$ und $(n\text{-}C_5H_{11})_4NF{\cdot}40H_2O$ sind.