Microcalorimetric investigation on interaction between poly(acrylic acid) and oxyethylene oligomers in water

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The interaction between poly(acrylic acid) (PAA) and oxyethylene oligomers (PEG) was investigated by solution microcalorimetry in water at 25°C. The enthalpy of interaction is endothermic, and, in the case of PEG-400 in large excess, the enthalpic parameter increases sharply with PEG/PAA ratio. No such behaviour was found for PEG-1000 and for dimethylated PEG-400. The apparent monomolar heat capacity of the binary solute was also determined, and the corresponding excess quantity is negative at any PEG/PAA ratio. The two series of microcalorimetric results indicate that PAA and oxyethylene oligomers interact noticeably in water and that a long PAA chain may be regarded as a linear adsorption surface for short PEG chains.

(Keywords: calorimetry; poly(acrylic acid); enthalpy)

INTRODUCTION

The complex formation through hydrogen bonding between polyoxyethylene (POE) or poly(ethylene glycol) (PEG) and poly(acrylic acid) (PAA) has been largely investigated using different experimental techniques[1,2]. The molar mass of PEG plays an important role in the degree of complexation between the two polymers; its lowest limit has been found close to 6000[3]. More recently[4], the fluorescence technique has shown the existence of increasing interaction between PEG-4800 and PAA of molar masses ranging from 1850 to 890000. Oyama *et al.*[4] came to the conclusion that the interaction between an ether oxygen and a carboxylic group is so small in water that a cooperative interaction between many of the two species is necessary in order to form a stable complex.

In the present work, measurements of enthalpy of interaction between low-molar-mass oligomers of oxyethylene and a high-molar-mass PAA sample were made in order to estimate the magnitude of this interaction. Some measurements of heat capacities on two of these systems are also reported. The effect of hydroxyl end-groups on the specific interaction between PEG and PAA was studied by making some measurements of enthalpy of interaction using a dimethylated oxyethylene oligomer.

EXPERIMENTAL

Materials

The PAA sample was obtained from Polysciences Inc. in the form of an aqueous solution, which was freeze-dried. Its viscosity-average molar mass was 150000. The low-molar-mass PEG-400 sample was obtained from Matheson, Coleman and Bell, and the PEG-1000 sample from The Dow Chemicals Co. Both samples were used as received. The poly(ethylene glycol dimethyl ether) (PEG-DME) was also obtained from Polysciences Inc. and the reported molar mass was between 380 and 420. The commercial sample contained an excess of methyl iodide and also some iodine, which were almost completely eliminated by a thorough purification. The sample (25 g) was first dissolved in water (500 ml) and the solution was evaporated under vacuum (8–12 mmHg) at 80°C in a Büchi Rotavapor. The resulting residue was then treated under high vacuum ($\sim$0.1 mmHg) at 50°C for 48 h. At that stage, the original dark red-brown colour turned to dark yellow. Further purification to remove iodine was done by extraction in the following way. The sample was dissolved in chloroform and the solution was vigorously stirred with a 20 wt% aqueous solution of sodium thiosulphate, saturated with sodium chloride in order to avoid the dissolution of the oligomer in the aqueous phase. The organic- to aqueous-phase ratio was 5:1. The operation was repeated three times. The resulting organic solution was dried over magnesium sulphate and filtered through a fine porous glass filter. Finally, chloroform was evaporated and the purified oligomer had a slight yellowish colour due to the presence of traces of iodine.

Glass-distilled deionized water was used as solvent and solutions were prepared gravimetrically.

Microcalorimetry

Enthalpy-of-dilution measurements were made by mixing equal volumes (about 10 ml) of solution and solvent in a Tian–Calvet differential microcalorimeter at 25°C. The experimental technique is described elsewhere[5]. The observed absolute heat effects ranged from 0.03 up to 8 J. Enthalpy-of-interaction measurements between PAA and PEG were done by mixing equal volumes (about 8–10 ml) of solutions of each species.

Measurements of volumetric heat capacities were done with a Picker model CP-D flow microcalorimeter. They were converted to specific heat capacities by dividing

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them by the densities of solutions measured with a Picker model 03D flow densimeter. The experimental technique is also described elsewhere[5].

Viscometry

Viscosity measurements were done with an Ubbelohde capillary viscometer at 25°C.

RESULTS

When a solution containing n_2 monomoles of polymer 2 and x g of solvent 1 is mixed with a solution containing n_3 monomoles of polymer 3 and y g of solvent 1, the following process takes place:

$$(x+n_2)+(y+n_3)\rightarrow(x+y+n_2+n_3)+\Delta h_{\mathrm{m}} \qquad (1)$$

The observed enthalpy of mixing (Δh_{m}) for this process is made up of three contributions: (a) the interaction between the two solutes, (b) the dilution of solution of polymer 2 from x to $(x+y)$ g of solvent, and (c) the dilution of solution of polymer 3 from y to $(x+y)$ g of solvent. Keeping the mixing ratio and the dilution ratio of solution always close to the same value (1:1 in the present case), the excess enthalpy of mixing solutions of polymer 2 at initial monomolality m_2 and of polymer 3 at initial monomolality m_3 in the same solvent can be defined by:

$$\Delta H_{\mathrm{E}}=\Delta H_{\mathrm{m}}-\Delta H_{\mathrm{d2}}-\Delta H_{\mathrm{d3}} \qquad (2)$$

expressed in J kg^{-1}. In this equation, ΔH_{m} is the enthalpy of mixing the two polymer solutions, expressed in J kg^{-1} of solvent in the final solution, and ΔH_{d2} and ΔH_{d3} are the intermediate enthalpies of dilution of the solution of each species with the pure solvent, also in J kg^{-1} of solvent in the final solution. In the Bragg–Williams approximation, ΔH_{E} can be defined by:

$$\Delta H_{\mathrm{E}}=Bx_2x_3(m'_2+m'_3) \qquad (3)$$

$$=Bm'_2m'_3/(m'_2+m'_3) \qquad (4)$$

where B is the enthalpic interaction parameter, expressed in J mol^{-1}, assumed to be independent of the composition of the system[6]. The quantities x_2 and x_3 are monomole fractions of each polymer in the binary solute excluding the solvent, and m'_2 and m'_3 are final monomolalities of the two polymers in the ternary system. In these calculations, it is assumed that the presence of polymer 3 does not affect the interaction between solvent and polymer 2 and vice versa.

The intermediate enthalpies of dilution ΔH_{d} have been determined first for each solute, and the results are shown in *Figure 1*. Values of ΔH_{d} are very similar for PEG-DME and PEG-1000 but are more exothermic for PEG-400. The enthalpies of mixing ΔH_{m} have been determined for initial monomolalities ranging from 0.4 to 2.6 for solutions of PEG samples (polymer 2) and from 0.04 to 1.7 for solutions of PAA (polymer 3). It is not possible to show graphically the variation of ΔH_{m} with polymer concentration since both ΔH_{d2} and ΔH_{d3} are not linear functions of average monomolalities $\bar{m}_2$ and $\bar{m}_3$. However, the parameter B can be readily calculated from equation (4) and its variation with x_2 is shown in *Figure 2* for the three binary polymer systems. The immediate observations are that ΔH_{E} is endothermic over the entire concentration range and that B is concentration-dependent. In the case of PEG-400, results show a rapidly increasing endothermic interaction with PAA at high concentration of the former ($x_2>0.9$). Interactions between PEG-DME or PEG-1000 and PAA are notably less endothermic in the same concentration range, but the general shape of the function $B(x_2)$ is the same for the three PEG samples with a maximum at x_2 close to 0.64 (or OE/AA ~ 2:1).

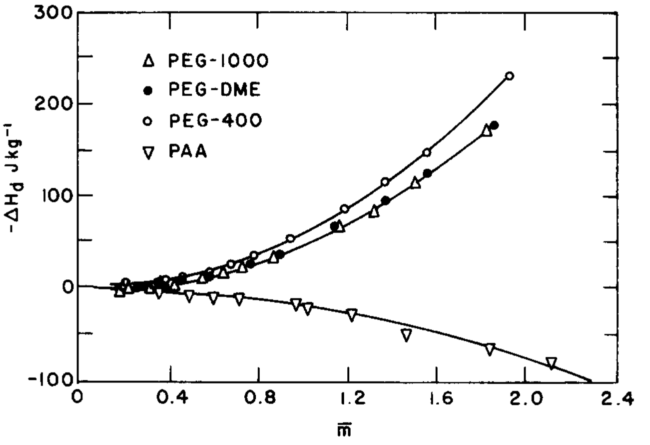

Figure 1 Intermediate heats of dilution as a function of mean monomolality in water at 25°C

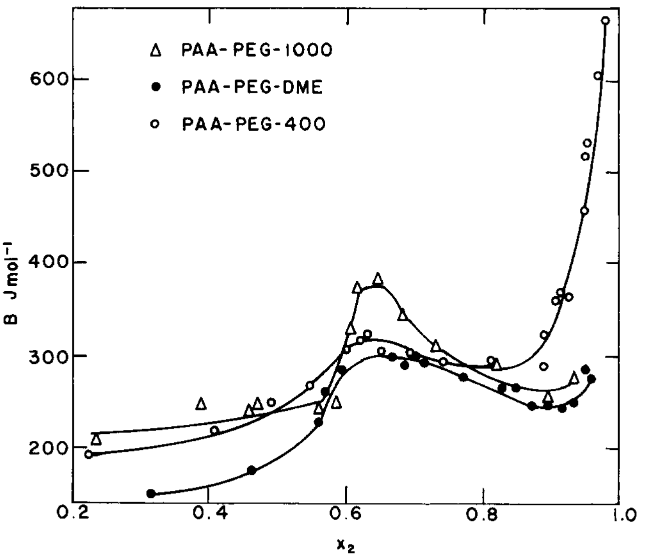

Figure 2 Dependence of enthalpic interaction parameter on binary solute composition in water at 25°C

The variation of the apparent monomolar heat capacity at constant pressure, $C_{p,\phi}$, with the monomolality is shown in *Figure 3* for PEG-400, PEG-1000 and PAA. Results for PEG-1000 are very similar to those obtained previously[7]. Those for PAA differ appreciably from those already published[8]; it has been found that a systematic error in the calculation of polymer concentration was then introduced. When corrected, previous results are almost identical to those shown here.

Two series of heat-capacity measurements have been made on PEG-400/PAA and PEG-1000/PAA pairs. First, the concentration of PEG was kept constant and that of PAA was varied; and in the second series, the concentration of PAA was kept constant and that of PEG was varied. *Figure 4* shows the variation of the apparent monomolar heat capacity at constant pressure of the binary solute, $C_{p,\phi,23}$, with the monomole fraction of PEG in this solute. The experimental values are

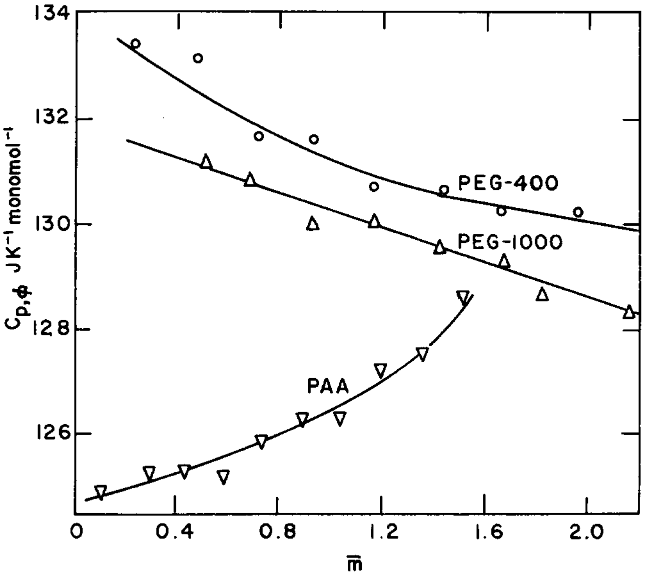

Figure 3 Concentration dependence of apparent monomolar heat capacity at constant pressure in water at 25°C

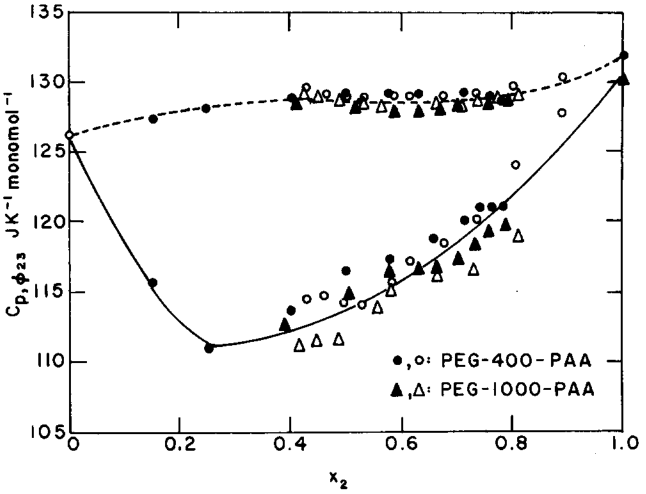

Figure 4 Dependence of apparent monomolar heat capacity at constant pressure on binary solute composition in water at 25°C: (– – –) from equation (5); (○, △) $m_3=0.8764$; (●, ▲) $m_2=1.1947$

compared with those calculated from the additivity law:

$$C_{p,\phi,23}=x_2C_{p,\phi,2}+x_3C_{p,\phi,3} \qquad (5)$$

where $C_{p,\phi,2}$ and $C_{p,\phi,3}$ are estimated from curves on *Figure 3*, corresponding to the molality of each polymer in the ternary system.

DISCUSSION

The simplest mechanism for complex formation between PAA and PEG in water is that, for a hydrogen bond to be formed between a carboxylic group and an ether oxygen atom, one hydrogen bond between a water molecule and each of the two implied species should be broken. But, the water molecules set free by the association between the two polymers will return to the bulk water and form hydrogen bonds with other water molecules. So, it seems rather difficult even to predict the sign of the change in enthalpy upon association of the two polymers. However, this quantity can be estimated to be 3.7 kJ mol^{-1} from enthalpies of activation of the association–dissociation processes between PAA and PEG-20000 in dilute solution in 1 M NaCl aqueous media with a PEG/PAA monomolar ratio of 10, the dissociation being activated by a change in pH (2.7 to 3.85)[9]. In the present work, the association occurs in much more concentrated media in the absence of salt and at pH values close to 3.05 after mixing both polymer solutions.

Based on literature[10], no noticeable association should be expected between PAA and any of the three oligomers investigated in the present work. Furthermore, values of the reduced specific viscosity of PAA in dilute solutions do not vary much when water is replaced by a 5 wt% aqueous solution of PEG-400 as solvent, as shown in *Figure 5*. These results indicate that the overall hydrodynamic volume of the PAA chain is not appreciably affected by the presence of PEG-400 for $x_2<0.4$. Complex formation between the two polymers being a cooperative process, a large number of interpolymer bonds must be formed to ensure the stability of the complex[9].

Let us assume that intimate contacts between PAA and any of the three oxyethylene oligomers studied in the present work do occur and that the value of B for a 1:1 complex is 7.4 kJ mol^{-1}. It now becomes possible to estimate the degree of association between the two species as a function of x_2 from data taken from *Figure 2*. At $x_2\sim0.3$ (great excess of PAA), the degree of association is low, about 2% in the case of PEG-DME and close to 3% in cases of PEG-400 and PEG-1000. As x_2 increases, the degree of association has a tendency to be somewhat higher in the case of PEG-1000, being close to 5% at $x_2\sim0.65$. Above this figure, the degree of association decreases slightly below 4% for the three oligomers. However, at $x_2>0.9$, the increasing value of B in the case of PEG-400 is rather interesting. First of all, the difference in behaviour between PEG-400 and PEG-DME seems to indicate that the terminal OH groups on each PEG-400 chain play an important role in the association process between PEG and PAA. The PAA chain can be assumed to be a linear surface on which short PEG-400 chains are adsorbed in a whisker-like fashion by one of the two terminal OH groups, which are more active in the formation of hydrogen bonds with

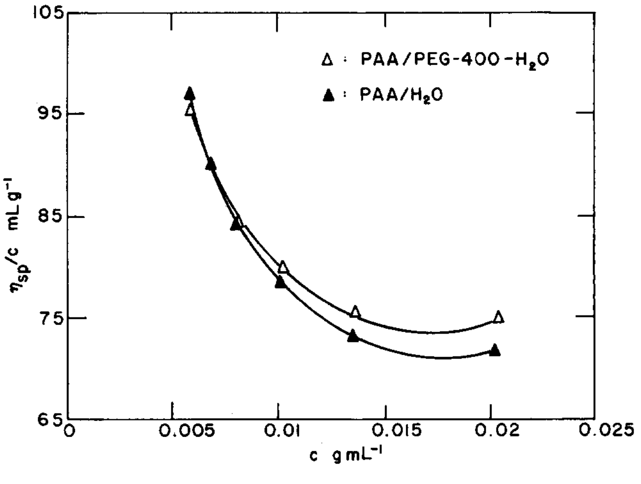

Figure 5 Concentration dependence of reduced specific viscosity of PAA at 25°C

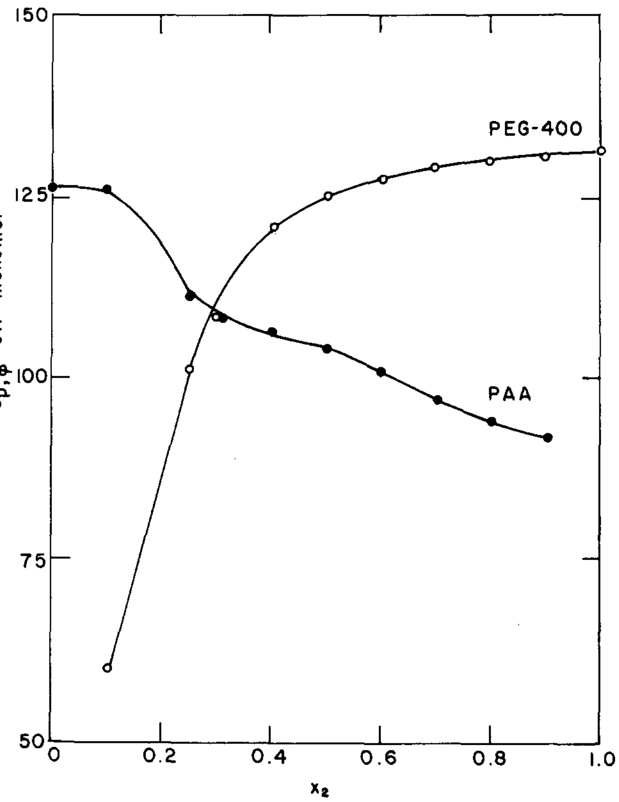

Figure 6 Dependence of partial apparent monomolar heat capacity at constant pressure for each solute on binary solute composition in water at 25°C

PAA than any of the ether oxygen atoms of the PEG chain. As for PEG-1000, the diameter of its equivalent sphere is only about 1.5 times that of PEG-400; this means that the conformation of the longer PEG chain is that of a flexible coil inside which terminal OH groups are more or less exposed in order to form hydrogen bonds with PAA. This might be the explanation why PEG-1000 behaves similarly to PEG-DME as far as the enthalpy of interaction with PAA is concerned.

Finally, *Figure 4* shows that the excess apparent heat capacity of the binary solute is negative. This indicates that the apparent monomolar heat capacity of each component is reduced due to specific interactions between PAA and oxyethylene oligomers. Partial apparent monomolar heat capacities for each component for the PAA/PEG-400 system as a function of x_2 have been estimated from the smoothed curve of *Figure 4* using the method of intercepts developed for binary systems. Here, $C_{p,\phi,2}$ and $C_{p,\phi,3}$ are concentration-dependent in the 'ideal' ternary system but, as shown in *Figure 4*, the relation between $C_{p,\phi,23}$ and x_2 (or x_3) as calculated using equation (5) is not far from a straight line, as in the case of an ideal binary system. As shown in *Figure 6*, the mobility of PEG-400 chains in the presence of an excess of PAA is affected more than that of PAA chains in the presence of an excess of PEG-400. Similar behaviour for the PAA/PEG-1000 pair can be predicted from the trend of results shown in *Figure 4*. From both series of results on heat-capacity measurements, it can be concluded that PAA chains may be seen as mobile linear adsorption surfaces for short PEG chains, as discussed earlier.

ACKNOWLEDGEMENTS

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