Thermodynamic parameters of polyacrylamides in water

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The heats of dilution of polyacrylamide and its *N*-methyl derivatives have been measured calorimetrically. Their apparent partial specific volumes have also been determined. For the unsubstituted polymer, χ_h was endothermic whereas for both the *N*-substituted polymers χ_h was exothermic. From a comparison with similar data on small amides it was thought likely that the endothermic heat of dilution arose from the energy required to separate the amide dipoles. The difference between the exothermic and endothermic heats of dilution may arise from the different mutual orientations of the substituted and unsubstituted amide groups. Osmotic pressure data indicates that water is a poor solvent for polyacrylamide.

INTRODUCTION

The heats of dilution or solution of many polar compounds[1,2] such as alcohols, ketones and certain amides in excess water are generally exothermic, as a result of hydrogen bond formation between water and the polar entity. The favourable heat term is often accompanied by an unfavourable entropy of dilution, and this entropy–enthalpy compensation has recently been discussed by Lumry[3]. Exceptions to this exothermic heat of solution include the amides on which the nitrogen group has no alkyl group substituted, such as formamide[4] or acetamide[5], where the heats of solution are endothermic. This may be a result of the different mutual alignments that the amide dipoles can adopt. The lack of an alkyl substituent on the nitrogen may allow the amide dipoles to align more closely or in a more opposing direction, requiring greater energy for their separation than in the case where their association is influenced by an intervening alkyl group. Where the amide group is incorporated into a polymer, though similar considerations would apply, it is possible that the orientation and alignments of the amide groups would be sufficiently influenced through being attached to a common backbone, that substituents on the nitrogen would not have the same effect as in the case of small molecules. From light scattering and viscosity data, Silberberg *et al.*[6] calculated that the heats of dilution for polyacrylamide, poly(methacrylamide) and poly(acyrlic acid) were endothermic whereas that of poly(methacrylic acid) was exothermic. In this work, some solution properties including heats of dilution measured calorimetrically, or polyacrylamides and related substituted polymers have been measured to determine whether the trends observed for small amides were also noticed in polymers.

EXPERIMENTAL

Polyacrylamide (PAAm) was polymerized using ammonium persulphate/sodium metabisulphite as initiator and propan-2-ol as a terminating agent. The polymer was precipitated with methanol, dialysed against water, freeze dried and stored over P_2O_5. For osmotic pressure measurements a PAAm with a narrow molecular weight distribution was obtained from Polysciences Inc. USA. *N*-methyl and *N*-dimethyl acrylamide monomers were prepared by reacting the appropriate amine with acryloyl chloride; n.m.r. and i.r. analysis indicated ~98% purity of the monomers. The polymers were prepared as for PAAm. Their molecular weights determined from viscosity and g.p.c. were: poly(*N*-*N* dimethyl acrylamide), PDMAm 100000 and poly(*N*-methyl acrylamide), PNMAm 80000. Heats of dilution were measured on an LKB 10700-2 Batch Microcalorimeter as described previously[7]. The total volume of the solution plus solvent was kept constant, thus minimizing vapour phase effects. Partial specific volumes of the polymers were measured with an Anton Paar Digital Density Measuring Apparatus, the temperature as measured by a Hewlett–Packard Quartz Thermometer, being controlled to ±0.005 K. The osmotic pressures were measured using a Knauer membrane osmometer and duplex membranes as supplied by the manufacturer. All results are at 298 K unless otherwise indicated.

RESULTS

The heats of dilution have been treated according to the normal method of Tompa[8], where the heat of dilution, ΔH_d in diluting from a polymer phase volume φ_2 to φ_1 by adding Δn moles of solvent is given by $\Delta H_d = RT\varphi_1\varphi_2\Delta n\chi_h$, where χ_h is the enthalpy parameter for the interaction between polymer segments and solvent. χ_h is often found to be concentration dependent and its value at infinite dilution, χ°_h can be taken as the net heat involved in the formation of the bond between polymer segments and solvent molecules. The values of χ_h for PAAm, PNMAm and PDMAm are shown in *Figure 1* as a function of $\frac{1}{2}(\varphi_1+\varphi_2)$. The values of χ°_h are:

(i) PAAm, $\chi^\circ_h = 0.08 \pm 0.008$;
(ii) PNAm, $\chi^\circ_h = -0.06 \pm 0.01$;

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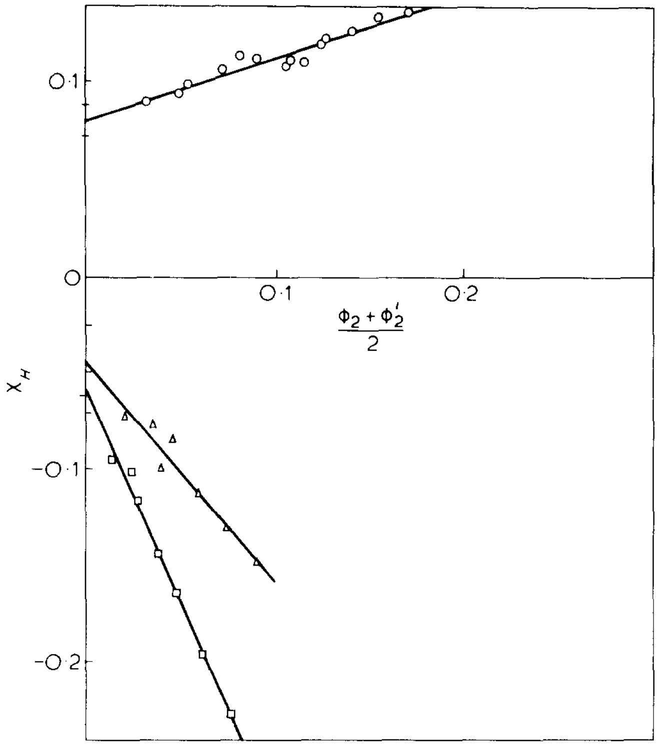

Figure 1 Heats of dilution χ_h of polyacrylamides as a function of average volume fraction ½($\phi_1 + \phi_2$). (○), polyacrylamide; (△), poly(*N*-dimethyl acrylamide); (□), poly(*N*-methyl acrylamide)

and

(iii) PDMAm, $\chi'_h = -0.044 \pm 0.018$

The partial specific volumes ($\bar{v}_2$) of each of the three polymers are shown in *Figure 2*. The data show no significant variation with concentration within the range 0–3%. The values of $\bar{v}_2$, extrapolated to zero concentration are:

(i) PAAm, 0.693 ± 0.002 cm^3 g^{-1} in reasonable agreement with the value of 0.716 cm^3 g^{-1} determined previously[9];

(ii) PNMAm, 0.783 ± 0.003 cm^3 g^{-1}

and

(iii) PDMAAm, 0.846 ± 0.003 cm^3 g^{-1}

The osmotic pressure of polyacrylamide could only be measured reliably using the relatively monodisperse sample from Polysciences, as with the more polydisperse preparations, some leakage of polymer across the membrane caused too great an uncertainty in the measurements. The osmotic pressure π (cms H_2O) is expressed as a function of PAAm concentration in *Figure 3*. The intercept gives the molecular weight of the polymer as 107 000, in agreement with a value of 100 000 as given by the supplier. The free energy parameter of the polymer solvent interaction, χ, was calculated from the slopes of the line in *Figure 3*, using the standard relationship[10]:

$$\frac{\pi}{C} = \frac{RT}{M_2} + RT(\tfrac{1}{2} - \chi)\frac{\bar{v}_2^2 \rho_1 C}{M_1} \qquad (1)$$

where C is the concentration of the polymer, M_2 its molecular weight and $\bar{v}_2$ its partial specific volume; ρ_1 is the density of water and M_1 its molecular weight. The value of χ for PAAm at 298 K was 0.495, giving χ_s, the entropy parameter, a value of 0.415. The second virial coefficient, B was 1.4×10^{-4} cm g^{-2}.

The value of χ'_h for PAAm (0.22) determined by Silberberg *et al.*[6] is much larger than that found here whereas the free energy parameter χ is smaller (0.44) than found here (0.495) by osmotic pressure. Another determination[11] of χ for several fractions of PAAm also made by osmotic pressure gave values between 0.487 and 0.495.

DISCUSSION

In understanding the heats of dilution of these polyacrylamides it is helpful to consider the heats of dilution or solution of related small amides. As shown by several workers[2,4,5,12] the heat of transferring *N*-substituted amides from the pure liquid state to solution in water is exothermic, and at 298 K, is only slightly dependent on the chain length of the substituents. The heats of solution range[2,5] from about −13 kJ mol^{-1} for *N*-methyl acetamide to −15.03 kJ mol^{-1} for *N*-methyl

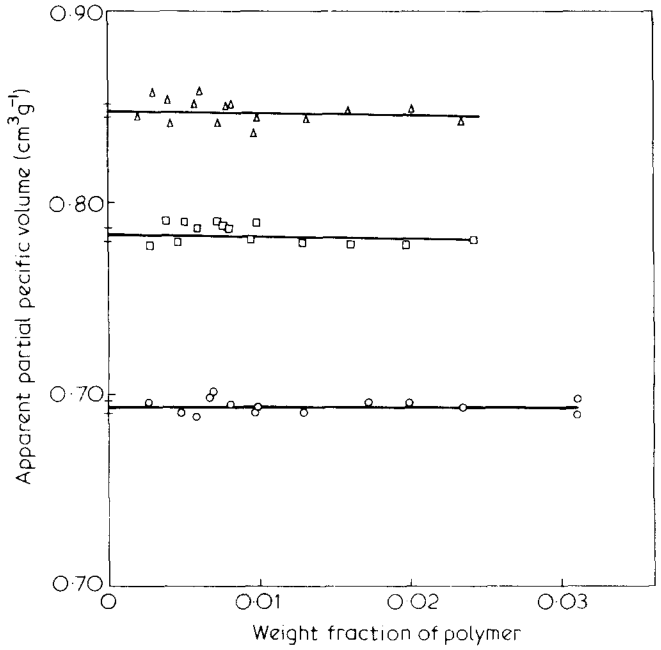

Figure 2 Apparent partial specific volume (cm^3 g^{-1}) as a function of weight fraction of polymer. (○), polyacrylamide; (□), poly(*N*-methyl acrylamide); (△), poly(*N*-dimethyl acrylamide)

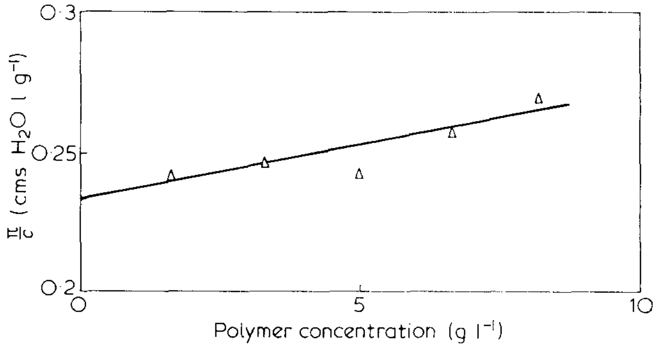

Figure 3 Reduced osmotic pressure of polyacrylamide (cms H_2O l g^{-1}) as a function of polymer concentration g l^{-1}

butyramide, indicating that the main part of this exothermic heat arises as a net result of breaking inter-amide hydrogen bonds and reforming amide–water hydrogen bonds. This conclusion is supported by data[13,14] on the transfer of *N*-substituted amides from non-polar solvents such as CCl_4 to H_2O. However, for formamide and acetamide, where the nitrogen has no alkyl chain substituent, the heats of solution into H_2O are endothermic[5]. This may well arise from the energy needed to separate the amide dipoles exceeding the heat, possibly exothermic, of breaking hydrogen bonds. This may result from the dipoles of the unsubstituted amides being able to align closely in opposing directions, whereas with the *N*-substituted amides, the alkyl group reduces this alignment and consequently alters the energy required to separate the dipoles. The energy of interaction (W) between two dipoles, of moments M_1 and M_2 is

$$W=\frac{M_1M_2}{r^3}(\cos\varphi-3\cos\theta_1\cos\theta_2)$$

where r is the distance between dipoles, θ_1 and θ_2 are the angles between the respective dipoles and r, and φ is the angle the dipoles make with each other. Taking values of the amide dipoles[15] of 3.8×10^{-18} esu, a dipole separation of 0.3 nm and the dipoles being oriented in parallel but opposing directions W is about 40 kJ mol^{-1}. For dipoles oriented perpendicular to each other, W is zero. Although each amide system will have a distribution of orientations, it is clear that the different average dipole orientations can produce heats of interaction, sufficiently large to account for the various heats of solution observed with small amides in water.

When the amide segments are incorporated into a polymer chain similar results to the small amide case are obtained, with PAAm having an endothermic heat of dilution whereas for PNMAm and PDMAm it is exothermic. It is possible that the aligned amide groups would be dehydrated when in contact, allowing hydrogen bonding directly between polymer segments. However, the specific volume data indicates that this is probably not the case. The partial molar volume[16] of n-propionamide is 71 cm^3 mol^{-1} and that expected for PAAm may be estimated from the fact that cyclization[16] of a molecule causes approximately a 15 cm^3 mol^{-1} decrease. Alternatively a CH_2 group has a partial molar volume about 10 cm^3 mol^{-1} smaller than a CH_3 group[17]. Thus PAAm might be expected to have a partial molar volume between 50–55 cm^3 mol^{-1}, close to that measured of 49.2 cm^3 mol^{-1}. Such a low value indicates that the amide groups of the polymer are hydrated to a similar extent as that of small amides. The increase in the apparent partial molar volume (34.8 cm^3 mol^{-1}) caused by the addition of two methyl groups to the polymer is also similar to that obtained for small amides e.g. 33.9 cm^3 mol^{-1} difference between acetamide and dimethylacetamide.

When comparing the *N*-methylated polymers with polyacrylamide the extra methyl groups must be considered in addition to the influence of the dipolar interaction. The heats of solution of small hydrocarbon groups are difficult to determine accurately, though they are probably slightly exothermic[1] at 25°C. Thus part of the exothermic χ_h^0 of PNMAm (compared to PAAm) is due to the addition of the methyl group though addition of the second methyl produces less change. Also the χ_h^0 found by Silberberg *et al.*[6] for polymethacrylamide, isomeric with PNMAm, was zero rather than exothermic. Thus part of the contribution to χ_h^0 changing from endothermic to exothermic is due to the hydrophobic nature of the methyl group, though this alone is unlikely to explain the data.

The value of the second virial coefficient is lower than that obtained by Silberberg *et al.*[6] and suggests that water is not a good solvent for PAAm as would be expected from a system where the heat of dilution is endothermic and any entropy of hydration is likely to be negative. If segment–segment contact occurred directly, i.e. the amide groups were dehydrated during contact, then the net entropy of dilution estimated from the data for other polar materials, is probably negative. This arises from a balance between the orienting effect of the dipoles on the water molecules (negative entropy) and the volume expansion term (positive entropy). If the heat of dilution were endothermic and the entropy of dilution were negative, polyacrylamide would not be expected to mix in all concentrations with water. However, if segment–segment contacts occur through water molecules, only the volume term applies. This would require that amides and water do not have random contacts but form discrete complexes. Assarsson and Eirich[18] using viscosity and specific volume data, demonstrated that this is indeed the case, indicating that polyacrylamide segments prefer contact with water to contact with other polymer segments. Bovey and Tiers n.m.r. data[19] also indicated that direct intramolecular hydrogen bonding between the amide groups did not occur extensively.

It is difficult to know to what extent the solution parameters measured here are determined by the unusual properties of water. It requires considerable energy to disturb water's three-dimensional hydrogen-bonded structure, giving rise to the well known hydrophobic interactions[20]. In addition, hydrophilic hydration can give rise to forces between surfaces separated by 2–3 nm[21,22]. At present no measurements have been made of comparable forces in non-aqueous systems, though they may exist in other strongly hydrogen-bonded systems. The salting-out of polymers[23] is a result of the negative adsorption of ions from the polymer and this may be a result of incompatible water structures surrounding the ion and polymer. In the case of PAAm even 0.5 mol dm^{-3} Na_2SO_4 has a negligible effect on the intrinsic viscosity of PAAm. Thus, contact between PAM and these ions is essentially random and any interaction between them is very weak.

CONCLUSIONS

The heats of dilution of polyacrylamide and two substituted polyacrylamides have been measured calorimetrically. That of PAAm was endothermic whereas both the substituted polymers had exothermic heats of dilution. It is proposed that this difference arises as a result of the different orientations of the amide dipoles when polymer segments are in contact. The partial specific volume and heat data suggest that the amide dipoles are separated by solvent, rather than being in direct contact.

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