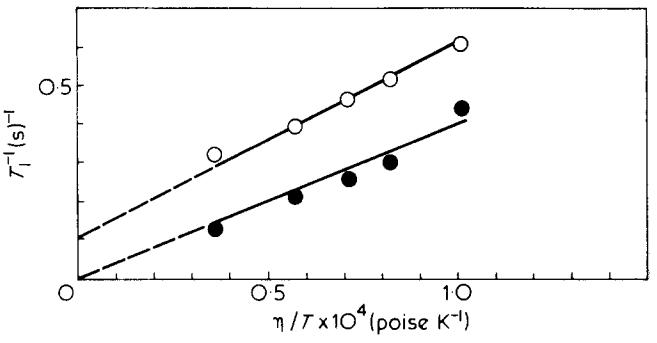

Figure 1 Dependence of proton T_1^{-1} of n–$C_{32}H_{66}$ as a function of η/T. Intramolecular-T_1 (○); intermolecular-T_1 (●)

PE, $E_a = 59.5$ kJ mol^{-1}. This means that the effect of entanglement on the molecular motion is smaller when compared with the case of molten PE.

According to equations (2a) and (2b), the rates of both translational and segmental motions are proportional to the η/T and the distance terms. In order to investigate the relationship between the molecular motions and the viscosity on molecular surroundings, the values of $1/T_1$ are plotted against η/T as shown in *Figure 1* where the values of η/T for n-$C_{32}H_{66}$ reported by Porter *et al.*[15] were used. The rates of both intra- and intermolecular T_1's increase linearly with increasing η/T. The positive sign of the slope of their straight lines comes from the increase in the distance between the protons in the same molecule or the protons in neighbouring molecules with increasing temperature. The value of intermolecular T_1^{-1} extrapolated to $\eta/T=0$ is zero and that of intramolecular T_1^{-1} extrapolated to $\eta/T=0$ deviates from zero. These values suggest that the intermolecular T_1 behaviour follows equation (2b), and the translational motion is isotropic and the effect of chain entangling can be neglected.

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Hydrogen ion equilibria in poly(methacrylic acid) and poly(ethacrylic acid) solutions

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INTRODUCTION

We described recently, results on hydrogen ion equilibria of weakly basic cationic polysoaps in their aqueous solution[1]. We have shown that the concept of hydrophobic interactions may be used effectively in the construction of feasible models to aid interpretation of experimental data obtained at different temperatures. Anomalous titration curves for poly(methacrylic acid), PMA, compared with poly(acrylic acid), PAA, in aqueous solution, have also been explained by invoking the hydrophobic effect[2–4], which results in the formation of a compact globular state for PMA at low degrees of ionization. Further support for this interpretation appears to be provided by a recent report concerning aqueous solutions of poly(ethacrylic acid), PEA[5].

In this work we determined the effect of temperature on the titration behaviour of the polyacids. Our primary aim has been to ascertain whether or not these materials are suitable for extending our previous work and conclusions concerned with the basicity of hydrophobic weak polyelectrolytes.

EXPERIMENTAL

Materials

The poly(acrylic acid) sample was obtained from Aldrich Chemical Co. (average molecular weight of 250 000). Poly(methacrylic acid) was prepared by polymerization of methacrylic acid in aqueious solution using benzoyl peroxide as initiator. The polymer was recovered from solution by precipitation with hydrochloric acid and by drying *in vacuo*. Ethacrylic acid was prepared according to the method of Böhme and Teltz[6]; it was polymerized in 5% aqueous solution using the intiator asobisisobutarymidine hydrochloride at about $\frac{1}{2}$% w/w of monomer. After approximately 12 h at 50–60°C a milky suspension was evident; the reaction mixture was kept in this temperature range for a further 2 days. Small molecular weight material was then removed by exhaustive dialysis against water.

Potentiometric titrations

An EIL Model 7050 pH meter (Electronics Instruments

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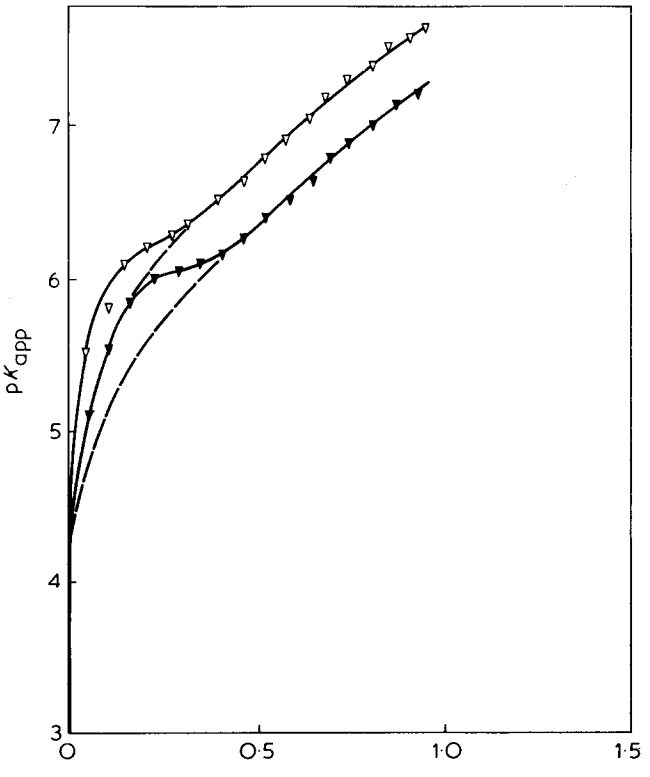

Figure 1 Potentiometric titration of poly(methacrylic acid) in salt-free aqueous solution. Filled and empty symbols refer to the temperatures of 25 and 80°C, respectively. Broken lines are extrapolated curves for 'b' state

Ltd., Surrey, England) coupled with a combination glass electrode (121 AP7, Titron Instruments Pty. Ltd., Braeside, Victoria) was used. The precision of the meter is 0.004 pH units. Two separate baths were maintained at 25.0 and 80.0°C. The meter-electrode systems were standardized with pH 4 and pH 9 buffers (to NBS specifications). Titrants were kept at ambient temperature and delivered either from an Agla micrometer syringe or from a Dosimat 10 cm^3 macropiston burette (Metrohm, AG, CH-9100, Herisau, Switzerland). All titrants were either 1 mol dm^{-3} or 0.1 mol dm^{-3} solutions of hydrochloric acid and sodium hydroxide.

Titrations were performed in closed cells at both temperatures under an atmosphere of nitrogen with 50 cm^3 of sample solution at a concentration calculated to require ~ 1 cm^3 of titrant for neutralization. Each titration consisted of a blank titration followed in quick succession by a solution titration.

RESULTS

Titration results are expressed in terms of the dependence of an apparent dissociation constant, k_{app} or pK_{app}, on the degree of dissociation, α, where $pK_{app} = pH + \log[(1-\alpha)/\alpha]$. Titration curves of this type have been used before to calculate the standard free energy change of transition, ΔG_t^0, from an uncharged compact form (the 'a' state) to an uncharged random coil form (the 'b' state) for polymers undergoing conformational transitions:

$$\Delta G_t^0 = 2.303\ RT \int_0^{\alpha} [pK_{app}(a) - pK_{app}(b)]d\alpha$$

The integral in this expression is the area bounded by the low α region of the 'a' state curve, the experimental data and the 'b' state curve. The extrapolation procedures of Leyte and Mandel[8] were used to calculate hypothetical values of $pK_{app}(b)$.

Results for PAA are not shown here. No evidence was found for a conformational transition from the pK_{app} vs. α curves at either of the two temperatures studied. Moreover, the two curves at 25 and at 80°C essentially coincided.

The titration curves for PMA are shown in *Figure 1*. We note that the curve corresponding to the back titration of sodium polymethacrylate with hydrochloric acid coincided with that of the forward titration. *Figure 1* also includes the hypothetical 'b' state curves. The acidity of PMA decreases with increasing temperature; at half-neutralization the apparent acid strength decreases by 0.43 pH units. The values of ΔG_t^0 obtained for PMA are shown in *Table 1*; it can be seen that the effect of increased temperature on ΔG_t^0 is marginal.

The sample of PEA prepared by us did not dissolve in water at $\alpha = 0$; on standing the polymer preparation separated into a very dilute solution of PEA in water and solid PEA. Temperature had no noticeable effect on the solubility characteristics. It is possible that the lack of solubility observed for our sample under these conditions is due to its relatively high molecular weight compared with that used by the previous workers[5].

When sodium hydroxide was added to suspensions of PEA, solutions were obtained at pH 8.5–9.0 and 7.5, at 25 and 80°C, respectively, and with further addition of NaOH sharp titration end points were observed. Back titration of the sodium polyethyacrylate solution was possible over the whole range of neutralization without any phase separation. Both titre values in such experiments were found to agree within experimental error. *Figure 2* shows the titration curves of PEA together with the extrapolated values of pK_{app} for the 'b' state Calculated values of ΔG_t^0 are given in *Table 1*.

DISCUSSION

The potentiometric titration results confirm the existence of conformational transitions in PMA and PEA solutions as functions of ionization. The values of ΔG_t^0 found for PMA are in satisfactory agreement with some previously reported values in aqueous solutions both with respect to magnitude and trend with temperature[4,9,10]. However, the ΔG_t^0 values for PEA are smaller by a factor of about three compared with the value previously reported[5]; this discrepancy could be attributed to the possibility that a phase transition from suspension to solution state may have occurred during the forward titration procedure of Fichtner and Schönert.

Dubin and Strauss[11] obtained the value of ~ 1600–1700 J mol^{-1} as the contribution of one methylene group in the side-chain of the polymer to hydrophobic bonding, $\Delta G_{CH_2}^0$, by comparing results on copolymers with butyl and hexyl side-chains. These authors pointed out that the shorter are the hydrophobic side-chains, the less efficient is the contact between them and, accordingly, $\Delta G_{CH_2}^0$ is expected to decrease significantly with decreasing length of the side-chain, In our case, compared with PMA the ΔG_t^0 values for PEA are ~ 1000 J mol^{-1} higher giving a $\Delta G_{CH_2}^0$ value which is, therefore, fully consistent with

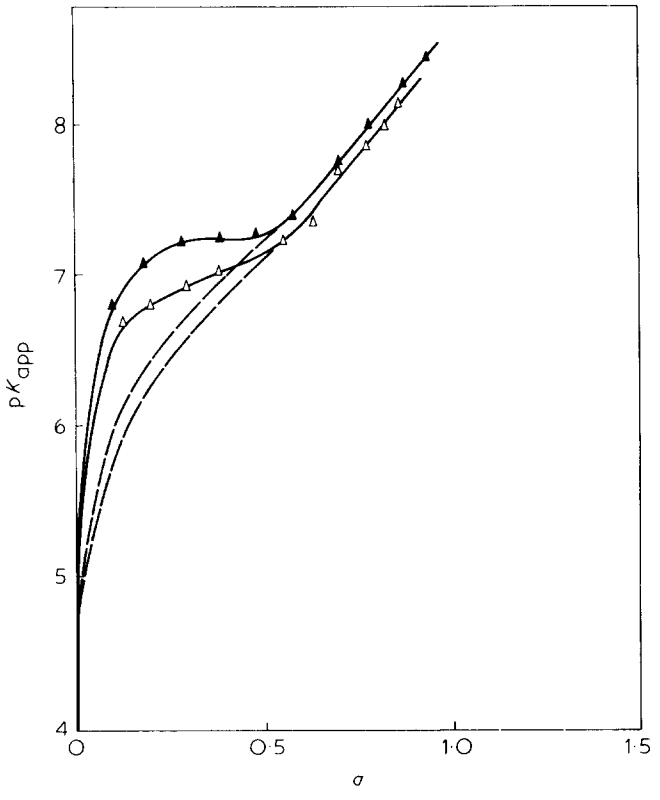

Figure 2 Potentiometric titration of poly(ethacrylic acid) in salt-free aqueous solution. Symbols the same as *Figure 1*

Table 1 Values of ΔG_t^0 (J mol^{-1}) in water

	T	
	298°	353°
PMA	585 ± 25	510 ± 25
PEA	1600 ± 150	1500 ± 150

expectation and which would seem to imply that the environment of the ethylene group in PEA is relatively polar, presumably a considerable portion of it being exposed to water. It has been remarked that PMA represents 'a limiting example for a hydrophobic polyelectrolyte'[3]; on the basis of our result a similar conclusion may apply to PEA and, consequently, it cannot be regarded as a very suitable material for the purposes of studying the hydrophobic effect in aqueous solutions of polymeric electrolytes.

A notable difference between PMA and PEA is the influence of temperature on the acidity of the polyacids. The acidity of PEA is somewhat higher at 80 than at 25°C; the effect is, however, very small (*Figure 2*). In contrast, as shown in *Figure 1*, the acid strength of PMA is markedly lower at the higher of the two temperatures; this is a real change in acid strength which is not related to the conformational transition. We believe that an explanation for these effects may be found by considering the possibility of hydrogen bonding between carboxylic acid groups in the polyacids. The presence of a hydrophobic polymer backbone is conducive to the formation of hydrogen bonds between carboxylic acid groups in PMA at low temperature. The reduced acid strength with increasing temperature may then be attributed to the destabilization of hydrogen bonding with increasing temperature[12]. Similar effects may also be observed in solutions of simple aliphatic dicarboxylic acids, as shown from a comparison of published data[13] on, for example, glutaric acid and alkyl-substituted glutaric acids. The absence of a similar effect in PEA may be attributed to the rigidity of the polymer backbone. Space filling molecular models are particularly useful in emphasizing the greatly restricted rotation about the C–C bonds of the chain in PEA compared with that in PMA. Thus, most hydrogen bonding possibilities in PEA would be precluded by steric factors and, for this reason, the acid strength of this polymer is essentially independent of temperature in the range under consideration.

ACKNOWLEDGEMENT

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