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Thermodynamics of aggregation in associating ionomer solutions

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Small angle neutron scattering has been used to study the aggregation behaviour of a sodium sulfonated polystyrene ionomer (SPS) with a molecular weight of 10^5 g mol^{-1} and a sulfonation level of 0.95 mol% in dilute *p*-xylene solution. The variation with concentration of both the average aggregate molecular weight and the average aggregate radius of gyration at temperatures ranging from 25 to 60°C were obtained. All the results observed can be quantitatively interpreted by use of a closed association model in which single chains are assumed to be in equilibrium with aggregates of one size. At concentrations below 0.1 g dl^{-1} this ionomer exists in solution mainly as single collapsed chains with an average radius of gyration of 78 Å. By comparison, the single chain dimension of the unsulfonated polystyrene at infinite dilution is 130 Å in xylene. As the ionomer concentration is raised, an increasing fraction of the single chains associates to form small compact aggregates with a radius of gyration of 150 Å and consisting of three chains. Both the single chain and aggregate dimensions are temperature independent, as is the extent of aggregation at a given concentration. This shows that the free energy change on forming aggregates from single collapsed chains is primarily entropic in nature. (i.e. there is no enthalpy change on aggregation). Moreover, no enthalpic contribution to the free energy of mixing for the ionomer aggregates with the solvent is observed. A contrast matching method was used to probe the aggregate internal structure. Within an aggregate the individual chains were found to expand from their collapsed state to 115 Å. The combined results suggest that the aggregates and single chains consist of a compact core which is primarily ionic in nature surrounded by solvent swollen polystyrene chains. In this picture the aggregates would form because of the increase in both configurational entropy of the polymer chains and the greater mixing of the polystyrene chains with the solvent on single chain expansion within the aggregates. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Ionomers are macromolecules containing a small number (typically less than 10 mol%) of ionic groups chemically bound to a non-polar chain. Several recent reviews are available describing their properties in both the solid state and solution[1,2]. Theories on the ionomers' state of aggregation[3,4] and industrial applications[5] have also been reviewed. The industrial importance of these materials has arisen because of the very dramatic effects of the presence of low levels of charged groups on the properties of non-polar polymers in both the solid state and solution. In this regard, sulphonated polystyrene ionomers (SPS) are ideal model polymers to gain a fundamental understanding of the properties of ionomers as well as the behaviour of associating polymers in general. This understanding is aided by the large number of studies already carried out on polystyrene and its availability in both deuterated and monodisperse form spanning a wide range of molecular weights. Polystyrene is also easy to sulfonate and the degree of ionic substitution relatively easy to control. Recently, these ionomers have been extensively studied in polar solvents such as dimethyl formamide and dimethyl sulfoxide in order to understand the characteristic behaviour of salt-free polyelectrolyte solutions[6]. The aim of this work, however, is to focus on the factors controlling the aggregation of polymers in solution by the study of SPS ionomers in the non-polar solvent xylene. In this solvent environment, counterion dissociation does not occur in any substantial degree.

In low polarity solvents such as xylene, toluene and tetrahydrofuran, increasing the level of ionic substitution of SPS lowers the intrinsic viscosity until a critical charge level where the ionomer becomes completely insoluble.

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The lowering in viscosity is believed to be due to collapse of the single chains and consequent reduction in volume fraction by intramolecular ion pair associations. However, as the ionomer concentration is raised intermolecular ion pair associations form at the expense of intramolecular linkage, causing the viscosity to rise steeply. Attempts to correlate the initial gradients of reduced viscosity *versus* concentration, however, show little systematic variation with sulfonation level[7]. Recent results suggest that this is a result of the complex manner in which the aggregation of ionomers varies with sulfonation level[8–10].

Use of light[8] and small angle neutron[9,10] scattering (SANS) has provided conclusive evidence for single chain collapse of ionomers in the non-polar solvent xylene. Application of the aggregation equilibrium models, often termed the open and closed association models[11], has also enabled a quantitative analysis of the changes observed by these scattering techniques in average aggregate molecular weights and radii of gyration as a function of concentration. This has made it possible to determine the dimensions and weight fractions of different sized aggregates in solution as a function of concentration. SPS ionomers (molecular weight $10^5\,\mathrm{g\,mol^{-1}}$) with ionic substitution levels between 1.25 and 1.65 mol% were found to form aggregates of all sizes in xylene, with the open association model providing a good fit to all the results observed[9,10]. In these cases, at concentrations above $2\,\mathrm{g\,dl^{-1}}$ very large low density aggregates can be present which cause the solutions to 'gel'[12]. This type of viscosification with ionomers has led to their application as viscosifiers and stabilizers in oil drilling fluids[13].

Use of the above equilibrium models also allows the difference in free energy between the single chains and the aggregates to be determined in solution from either SANS or static light scattering data. For the ionomers with between 1.25 and 1.65 mol% ionic substitution, the negative free energy change on increasing the size of an aggregate by one chain was found to be independent of the number of chains in the aggregate and equal to $-9.4(\pm 1)\ RT$ (R is the gas constant and T is the temperature). From the temperature dependence of the aggregation, this free energy was found to be primarily entropic in nature. In these cases the free energy of mixing between the polymer and solvent is almost zero at all temperatures[9,10].

Neutron scattering measurements on contrast-matched ionomer solutions have also been used to determine the single chain dimensions within the aggregates in non-polar solvents[12,14,15]. This technique uses partially deuterated polymers and matches the scattering of the aggregates with the solvent, but a scattering contrast remains between the individual polymer molecules and their environment. This approach measures the average single chain dimension of all the isolated and aggregated single chains. By combining the information gained on the weight fractions of aggregates as a function of concentration with the observed changes in average contrast-matched single chain dimensions, the single chain dimensions in different environments can be estimated[16]. With 1.25 mol% SPS in xylene the isolated single chain radius of gyration is only 55 Å. Within an aggregate it can increase to a maximum size of 147 Å. These results suggest that the entropy change on aggregation of 1.25–1.65 mol% SPS is due to increased polymer conformational freedom within aggregates compared to the isolated collapsed chains.

On lowering the sulfonation level to 0.95 mol%, however, it was recently observed that only single chains and relatively compact three-chain aggregates are present in dilute solution[10]. In this case the closed association model describes the concentration dependence of the average aggregate molecular weights and the radii of gyration. With SPS at a sulfonation level of 0.95 mol% the negative free energy change on the formation of the three-chain aggregate was found to be −21.8 RT. This result compares with a slightly less negative value of −18.8 RT on formation of a three-chain aggregate with the 1.25–1.65 mol% SPS ionomers described above. It has been shown that only a small minimum in this free energy change as a function of the number of single chains in an aggregate is required for one size of aggregate to dominate in a system. Previous results suggest that the aggregate structure of this lower sulfonation level ionomer is much more compact than observed with the 1.25–1.65 mol% SPS ionomers. The purpose of this work is to investigate further why such a small change in the level of sulfonation changes the nature of the aggregation process in such a dramatic manner. In this study the effect of temperature on the extent of aggregation of very lightly sulfonated polystyrene (0.95 mol%) in xylene will be investigated in order to establish whether the aggregation process is entropy controlled, as with the higher sulfonation level (1.25–1.65 mol%). Furthermore, the single chain dimensions within the aggregates are measured in order to determine whether the chains are expanded even in the more compact three-chain aggregates.

EXPERIMENTAL

Sample preparation

Polystyrene of molecular weight 100 000 with a polydispersity $M_w/M_n < 1.05$ was sulfonated to a level of 0.95 mol% using methods described previously[12]. For contrast-matched measurements, a mixture of 20% perdeutero polystyrene of molecular weight 106 000 and 80% of the hydrogenous polystyrene was sulfonated to a level of 0.98 mol% as determined by Diertert sulfur analysis.

The intensity (as a function of the scattering vector q) due to the coherent scattering from a polymer solution can be written as[17]

$$I(q) = \kappa Mc[AS_s(q) + BS_p(q)] \qquad (1)$$

The constant κ can be calculated from an intensity standard (see later). $S_s(q)$ and $S_p(q)$ are the single chain and pair scattering functions, respectively, and the constants A and B are given by

$$A = (N_A/m_0^2)[(a_D - a_s^*)^2 x_D + (a_H - a_s^*)^2(1 - x_D)]$$

and

$$B = (N_A/m_0^2)(a_p - a_s^*)^2$$

where $a_p = a_D x + a_H(1 - x_D)$; N_A = Avogadro's number; c = total polymer concentration (in $\mathrm{g\,dl^{-1}}$); M = polymer molecular weight; m_0 = molecular weight of a monomer unit of the polymer; a_H and a_D = scattering lengths referring to the hydrogenous and deuterated monomers, respectively; x_D = mole fraction of deuterated polymer.

The corrected scattering length of the solvent is given by

$$a_S^* = a_S(V_m/V_s)$$

where a_s = average scattering length of the solvent; V_m and V_s = molar volumes of the monomer and solvent, respectively.

These equations can be simplified in the following two cases:

(i) *Hydrogenous polymer in a deuterated solvent.* In the following work the scattering from solutions of the hydrogenous ionomer in a deuterated solvent was obtained. In this case equation (1) reduces to the following expression

$$I_T(q) = \kappa McB[S_s(q) + S_p(q)] \qquad (2)$$

For the following work in order to account for the effects of temperature on the polymer concentration of a given solution and the ratio V_m/V_s, the effect of temperature on the densities of xylene and polystyrene solutions were measured.

(ii) *Average polymer scattering 'contrast-matched' with the solvent.* To obtain the single chain dimensions a mixture of a monodisperse 80% hydrogenous ionomer and 20% deuterated ionomer of identical molecular weight was dissolved in 67 wt% hydrogenous/33 wt% deuterated *p*-xylene. Under these conditions the polymer is 'contrast-matched', with the average scattering from the polymer being equal to that of the solvent (i.e. $a_P = a_s^*$). Then since $B = 0$ from equation (1) the following expression is obtained

$$I_s(q) = \kappa McAS_s(q) \qquad (3)$$

All the solutions were prepared at least two days prior to measurement.

Small angle neutron scattering

(i) *Non-contrast-matched solutions.* Small angle neutron scattering experiments on the non-contrast-matched solutions were performed using the D17 spectrometer at the Institut Laue Langevin, Grenoble, France. The samples were measured in 5 mm path length quartz cells at temperatures between 25°C and 60°C. The data were collected on a 64 × 64 cm detector. The sample-to-detector distance was 3.4 m and the incident wavelength, λ, was 15 Å. The scattering from water in a 1 mm cell was used as the intensity standard as well as a measure of detector response.

(ii) *Contrast-matched solutions.* Contrast-matched experiments were conducted on the NG7-30 Meter SANS instrument at the Cold Neutron Research Facility of the National Institute of Standards and Technology (NIST), USA. The samples were measured in 2 mm path length cells and the data collected on a 60 × 60 cm detector. The wavelength in this case was 5.5 Å, the sample-to-detector distance 6.81 m and a NIST standard sample was used to determine the absolute scale. The resulting intensity represents the single chain scattering that is mainly coherent but with a very small (and in this case negligible) flat incoherent component.

In both cases the data were corrected for background and incoherent scattering using the scattering from an empty cell and the solvent. The intensity was then scaled to absolute cross-section per unit volume (in units of cm^{-1}) by comparing it with the standard sample. Since the intensity of the scattering was isotropic, it was radially averaged to give intensity as a function of the magnitude of the scattering vector $q = (4\pi/\lambda)\sin\vartheta$, where 2ϑ is the scattering angle.

DATA ANALYSIS

Coherent scattering from hydrogenous polymer in a deuterated solvent

It has been shown that for $qRg < 1$, the total coherent scattering function from a non-contrast-matched ionomer solution can be given by the Zimm expression

$$\kappa cB/I_T(q) = 1/M_{agg}[1 + (q^2Rg^2_{agg})/3] + 2A_2c \qquad (4)$$

Rg_{agg} and M_{agg} are the z-average radius of gyration and weight average molecular weight, respectively, of all the aggregates and single chains in the solution. The term A_2 is the second virial coefficient which can be related to the excess Gibb's free energy of the solvent on dilution[18]. Using the Zimm expression the apparent average molecular weights and radii of gyration of the ionomer aggregates at different concentrations can be obtained from plots of $1/I_T$ *versus* q^2. These are defined, respectively, as

$$1/M_{app} = \kappa cB/I_T(0) = 1/M_{agg} + 2A_2c \qquad (5)$$

and

$$Rg_{app} = Rg_{agg}(M_{app}/M_{agg})^{1/2} \qquad (6)$$

Using the above-described SANS instruments, however, only a small range of the data is in the region $qRg < 1$ for the ionomer solutions in this study. Data with very little statistical error would therefore be required in order to obtain accurate values for M_{app} and Rg_{app}. Alternatively, the Debye model[19] for Gaussian chains (which can be fitted over a much wider q range) gives the single chain scattering function

$$S_s(q) = (2/\mu^2)[\exp(-\mu) - 1 + \mu] \qquad (7)$$

where

$$\mu = q^2Rg^2$$

This model has been fitted to scattering data in order to obtain extrapolated $I(0)$ values and thereby the molecular weights M, as well as radii of gyration Rg of polymers in theta solvents where $S_p(q)$ is small. It has also been successfully used to interpret the scattering from polymers contrast matched with good solvents. When fitted to the coherent scattering from dilute ionomer solutions it can also give radii of gyration and molecular weights comparable with the apparent values obtained using the Zimm expression. The advantage in using the Debye model, however, is that the whole scattering range measured in this work can be used.

Coherent scattering from contrast-matched solutions

Fitting of the Debye model (equation (7)) to the coherent scattering from the ionomers contrast matched in a mixture of hydrogenous and deuterated solvent gives a radius of gyration ($Rg_{\rm sin}$) equal to an average for all the single chains (both isolated and in aggregates). The extrapolated intensity at zero scattering angle should, from equation (3), be equal to $\kappa M_1 cA$, where M_1 is the uni-mer (unassociated polymer) molecular weight.

MODEL FITTING

Variation of average aggregate molecular weight (M_{agg}) *with concentration*

Previous work has shown that the closed association model can quantitatively explain the change in the average aggregate molecular weight of the SPS 0.95 mol% ionomer in xylene with concentration. In this model uni-mers (single chains represented by P_1) are assumed to be in equilibrium with n-mers of one size only, i.e.

$$nP_1 \Leftrightarrow P_n$$

where n is the number of chains in the aggregate P_n. With the closed association model the variation of weight average aggregate molecular weight with concentration is given by

$$^nK_c n(c/M_1)^{n-1} = (n-1)^{n-1}[x-1]/[n-x]^n \qquad (8)$$

where $x = M_{\rm agg}/M_1$. In this case the equilibrium constant is related to the molar concentrations of n-mers and uni-mers ($[P_n]$ and $[P_1]$, respectively) by

$$^nK_c = [P_n]/[P_1]^n \qquad (9)$$

The weight average aggregate molecular weight is given by

$$M_{\rm agg} = \Sigma w_i M_i = w_1 M_1 + (1 - w_1) n M_1 \qquad (10)$$

where w_i is the weight fraction of species consisting of i chains. This equation on rearrangement gives the weight fraction of single chains

$$w_1 = (n - x)/(n - 1) \qquad (11)$$

Equation (8) can be rearranged and rewritten in the form

$$c = f(x, n)/g(n, {}^nK_c) \qquad (12)$$

where

$$f(x, n) = \{[x-1]/[n-x]^n\}^{1/(n-1)}$$

$$g(n, {}^nK_c) = ({}^nK_c n)^{1/(n-1)}/(M_1(n-1))$$

In order to obtain initial estimates of n and ^nK_c, curves of $f(x,n)$ *versus* concentration for different values of the positive integer n were calculated. $f(x,n)$ was then divided by different constants (equal to $g(n, {}^nK_c)$) until good agreement (by eye) between the predicted curve and the observed apparent molecular weights at low concentrations was found. In the low concentration region the virial term in equation (5) will have negligible effect so that the apparent aggregate molecular weights can be taken as equal to their true weight average molecular weight (i.e. $M_{{\rm app}, c\to 0} = M_{\rm agg}$). A better fit to all the apparent molecular weights was then obtained by accounting for the second virial coefficient in the following manner.

Variation of apparent aggregate molecular weights (M_{app}) *with concentration*

The second virial coefficient, A_2, accounts for the non-ideality of the system arising from interactions of the solution components with the polymer molecules, but excludes non-ideal effects due to the inter-polymer interactions that result in aggregation. In this work at higher concentrations it is assumed that A_2 can be taken as a constant for a given ionomer. This simplification ignores the possibility of variation of interaction between polymer and solvent with aggregation. For the following work, however, $2A_2c$ becomes significant only after a majority of the chains are aggregated. The value obtained for A_2 is therefore primarily as a result of interactions between the solvent and the aggregates.

In order to account for the second virial coefficient at high concentrations, predicted curves of apparent molecular weight *versus* concentration were calculated using the expression

$$1/M_{\rm app} = 1/M_{\rm agg} + 2A_2\{f(x,n)/g(n, {}^nK_c)\} \qquad (13)$$

(from equations (5) and (12)). Once A_2 had been found from a best fit of equation (13) to the measured apparent molecular weights, true average molecular weights and radii of gyration were determined using equations (5) and (6).

The virial term obtained can be split into two parts[18]

$$A_2 = A_{2,\rm h} + A_{2,\rm s}$$

$$A_{2,\rm h} = -\Delta H_{\rm e}/RTc^2 V \qquad (14)$$

$$A_{2,\rm s} = \Delta S_{\rm e}/Rc^2 V \qquad (15)$$

where $\Delta H_{\rm e}$ and $\Delta S_{\rm e}$ are the excess enthalpy and entropy of the solvent on dilution, respectively, and V is the partial molar volume of the solvent. These quantities can be determined from the temperature dependence of the second virial coefficient using

$$A_{2,\rm h} = T\alpha A_2 - T(\delta A_2/\delta T)_{\rm P} \qquad (16)$$

and

$$A_{2,\rm s} = A_2(1 - T\alpha) + T(\delta A_2/\delta T)_{\rm P} \qquad (17)$$

where $(\delta A_2/\delta T)_{\rm P}$ is the gradient of A_2 *versus* temperature at constant pressure and α is the coefficient of thermal expansion.

Variation of average aggregate radii of gyration (Rg_{agg}) *with concentration*

The z-average radius of gyration is given by

$$Rg = \Sigma w_i M_i Rg_i / \Sigma w_i M_i$$

If only monodisperse single chains and aggregates of one size are present in solution then combining this with equation (10) gives

$$Rg_{\rm agg}(M_{\rm agg}/M_1) = [Rg_1 + (1 - w_1)(nRg_n - Rg_1)] \qquad (18)$$

where Rg_1 and Rg_n represent the radii of gyration of the uni-mers and n-mers, respectively. In this case the weight fraction of single chains (w_1) can be calculated from equations (8) and (11) once n and ^nK_c are known. A plot of $Rg_{\rm agg}(M_{\rm agg}/M_1)$ *versus* $(1 - w_1)$ should be linear over the whole concentration range if the closed association model explains the results in a quantitative manner.

Average single chain dimensions

The average single chain radius of gyration for a monodisperse polymer is given by

$$Rg^2 = \Sigma_i n_i Rg_i^2$$

where Σ_i represents the sum over all the polymer molecules in solution and n_i is the number fraction of chains with a radius of gyration Rg_i. If only single chains and aggregates of one size are present in solution then it is expected that the contrast-matched average single chain radius of gyration is given by

$$\begin{aligned} Rg_{\mathrm{sin}}^2 &= w_1 Rg_1^2 + (1 - w_1) Rg_{1,n}^2 \\ &= (1 - w_1)[Rg_{1,n}^2 - Rg_1^2] + Rg_1^2 \end{aligned} \tag{19}$$

$Rg_{1,n}$ represents the average single chain dimension within an n-mer. In the following discussion the weight fraction (w_1) and radius of gyration (Rg_1) of isolated chains are obtained using equations (11) and (18). $Rg_{1,n}$ can then be determined by fitting equation (19) to the variation in contrast-matched single chain radius of gyration with concentration.

Free energy of aggregation

For the closed association model the free energy of association for the formation of an n-mer is given by

$$\Delta G_n = -RT \ln {}^{n}K_{\mathrm{c}} \tag{20}$$

The corresponding (hypothetical) free energy change related to the addition of one chain onto an aggregate or another single chain is given by

$$\Delta G_2 = -RT \ln {}^{n}K_{\mathrm{c}}^{1/(n-1)} \tag{21}$$

Table 1 Apparent molecular weights and radii of gyration of the SPS ionomer (0.95 mol%) in xylene

c at 25°C	$10^{-5}\,M_{\mathrm{app}}$ (g mol^{-1})			Rg_{app} (Å)		
(g dl^{-1})	25°C	40°C	60°C	25°C	40°C	60°C
1.0	1.47	1.40	1.41	111	111	110
0.8	1.58	1.51	1.49	114	113	113
0.6	1.66	1.58	1.58	114	113	113
0.4	1.64	1.62	1.62	113	113	113
0.2	1.58	1.51	1.56	107	107	107
0.1	1.42	1.34	1.36	101	99	99
0.05	1.29	1.23	1.27	93	96	94

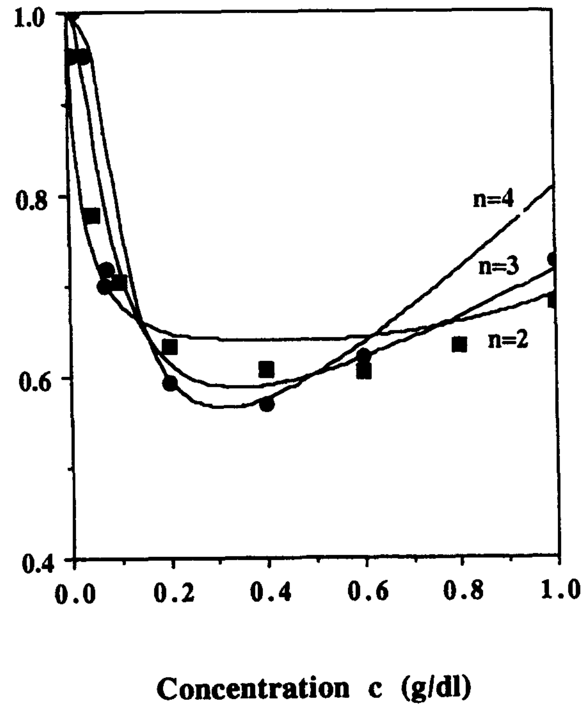

Figure 1 Inverse apparent aggregate molecular weight ($1/M_{\mathrm{app}}$) *versus* concentration for the SPS ionomer (0.95 mol%) in xylene at 25°C: (■) this data; (●) previous results[10]. Curves are the best fits to the data of equation (13) for values of n from 2 to 4

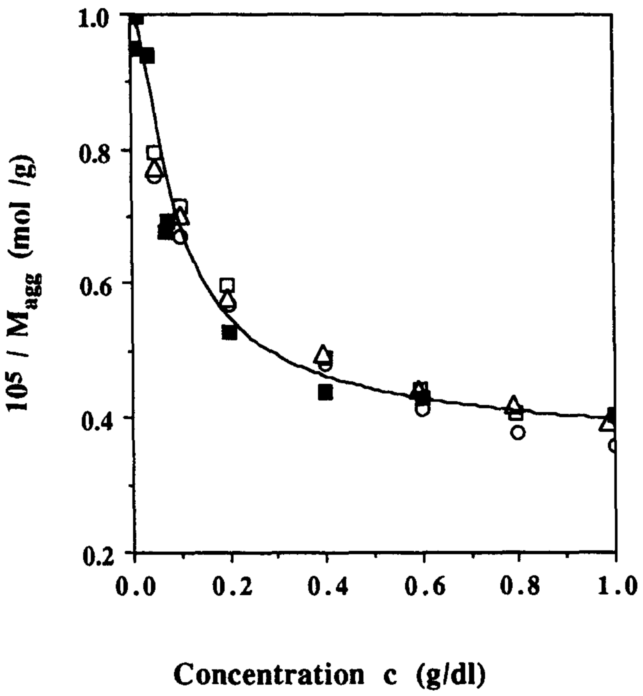

Figure 2 Inverse aggregate molecular weight ($1/M_{\mathrm{agg}}$) *versus* concentration for the SPS ionomer (0.95 mol%) in xylene: (■, □) 25°C; (○) 40°C; (△) 60°C. Curve is the best fit of the closed association model

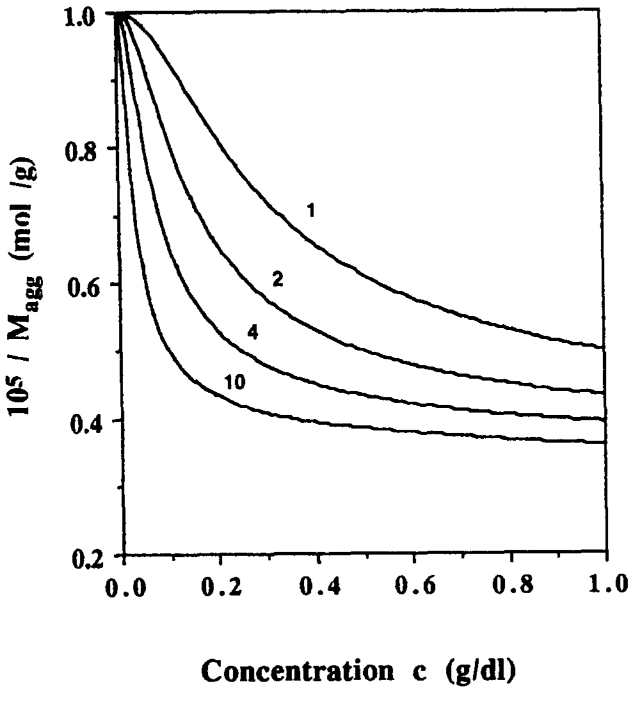

Figure 3 Curves predicted for the closed association model [equation (12)] with $n = 3$. Values of g are given on the curves

Table 2 Thermodynamic parameters for SPS ionomers in xylene

Sulfonation level (%)	$10^{-5} M_1$ (g mol^{-1})	ΔH_2 (kJ mol^{-1})	ΔS_2 (J K^{-1} mol^{-1})	$10^4 A_{2,h}$[a] (mol g^{-2} ml)	$10^4 A_{2,s}$[a] (mol g^{-2} ml)
0.95	1.0 ± 0.05	0 ± 3	88 ± 5	0 ± 0.5	1.6 ± 0.5
1.39	1.1 ± 0.05	0 ± 3	77 ± 4	-1.6 ± 0.3	1.6 ± 0.3

[a] Calculated using equations (16) and (17) with $\alpha = 1.2 \times 10^{-3}$ deg^{-1}

(NB this defines the standard state as 1 mol l^{-1} as used in reference 11). From the definition of the Gibbs function the change in free energy in a chemical reaction at constant temperature is given by

$$\Delta G = \Delta H - T\Delta S \qquad (22)$$

The van't Hoff equation gives

$$\mathrm{d}(\ln K)/\mathrm{d}(1/T) = -\Delta H/R \qquad (23)$$

These relationships provide the means for obtaining the enthalpy and the entropy of aggregation from the variation in $^{n}K_c$ with temperature.

RESULTS

Average aggregate molecular weights

Table 1 gives the apparent average aggregate molecular weights (M_{app}), obtained from the extrapolated zero angle coherent scattering, $I(0)$, (see equation (5)) from solutions of the ionomer SPS (0.95 mol%) in deuterated *p*-xylene. In *Figure 1* plots of $(1/M_{app})$ *versus* concentration at 25°C are shown combined with the previous results on this system that were determined at this temperature. Both sets of data are in good agreement considering the large effects that trace levels of solvents used during the preparation of the polymer (particularly methanol) can have on the aggregation of these ionomers[9]. With the results in *Figure 1* are given the best fits of the closed association model (equation (13)) to the data for values of n from 2 to 4. The best agreement between the model and the combined sets of data is found with $n = 3$, $g = 3.5(\pm 0.5) \times 10^2$ ml g^{-1} and $A_2 = 1.6(\pm 0.1) \times 10^{-4}$ mol g^{-2} ml.

Figure 2 shows the inverse aggregate molecular weights ($1/M_{agg}$) at 25°C calculated from apparent values using equation (5) and the above virial coefficient (A_2). The effect of g on the predicted curves (equation (12)) of ($1/M_{agg}$) *versus* concentration for $n = 3$ is shown in *Figure 3*. The large error for g arises primarily because of the difficulty in accurately determining the apparent molecular weights at concentrations below 0.2 g dl^{-1} where the second virial term can be considered negligible (compare *Figures 2* and *3*). *Figure 2* also shows a plot of $1/M_{agg}$ as a function of concentration at 40 and 60°C calculated using equation (5) and assuming the same virial term as above (i.e. $A_2 = 1.6 \times 10^{-4}$ mol g^{-2} ml). From this it can be seen that the best fit of equation (13) obtained at 25°C also describes the variation of molecular weight with concentration at 40 and 60°C. Despite the difficulty in accurately determining g it is clear from *Figure 2* that there is negligible systematic variation in n, g or A_2 with temperature since the molecular weights at 60°C are primarily between those at 25 and 40°C.

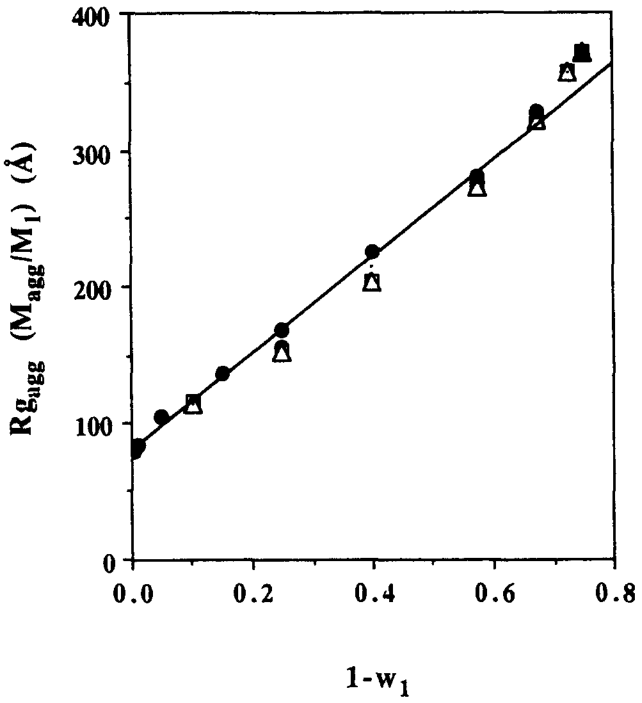

Figure 4 $Rg_{agg}(M_{agg}/M_1)$ *versus* $(1 - w_1)$ for the SPS ionomer (0.95 mol%) in xylene: (●, ○) 25°C; (□) 40°C; (△) 60°C. Line is the best straight line through the combined results at 25°C

Second virial coefficients

The second virial coefficient for the SPS ionomer (0.95 mol%) is approximately one-third the magnitude obtained for the unsulfonated polystyrene in xylene ($A_2 = 4.8 \times 10^{-4}$ mol g^{-2} ml)[11]. The relatively low second virial coefficient of this ionomer and its lack of strong variation with temperature mean that both $A_{2,h}$ and $A_{2,s}$ are small. Values estimated using equations (16) and (17) are given in *Table 2*. $A_{2,s}$ values for SPS 1.39 mol% are of similar magnitude in xylene. They are slightly smaller than the values obtained for non-sulfonated polystyrene in toluene (a very similar solvent to xylene) but very much smaller (between 10 and 20 times) than observed for polystyrene at the theta temperature in *trans*-decalin or cyclohexane[18]. In decalin and cyclohexane the large values of $A_{2,s}$ cancel with equally large but negative values for $A_{2,h}$ at the theta temperature. However, toluene is a good solvent at all temperatures for polystyrene, because although $A_{2,s}$ is small $A_{2,h}$ is close to zero. These results show that $A_{2,h}$ for the SPS ionomer (0.95 mol%) aggregates is also close to zero. This compares with a small but negative value for the SPS ionomer (1.39 mol%) aggregates (see *Table 2*).

Average aggregate radii of gyration

In *Table 1* the apparent average aggregate radii of gyration (Rg_{app}) for the SPS ionomer (0.95 mol%)

Table 3 Aggregate and single chain radii of gyration for SPS ionomers in xylene

	Radii of gyration (Å) of				
		aggregates of		single chains in aggregates of	
Sulfonation level (mol%)	isolated chains, Rg_1	2 chains, Rg_2	3 chains, Rg_3	2 chains, $Rg_{1,2}$	3 chains, $Rg_{1,3}$
0.95–0.98	78 ± 5	–	150 ± 10	–	115 ± 5
1.25–1.39[a]	55 ± 3	170 ± 20	–	101 ± 5	116 ± 5

[a] From references 9 and 16

obtained by a fit of the Debye model (equation (7)) to the coherent scattering from the ionomer in d-xylene are given as a function of concentration. $Rg_{agg}(M_{agg}/M_1)$ was calculated using equations (6), (12) and (13) using the values for n, g and A_2 obtained above. It is plotted against $(1 - w_1)$ (calculated from equation (11)) in *Figure 4*. Also given on this plot are the previous results at 25°C reanalysed using the Debye model. Within experimental error this plot is linear over the whole concentration range measured. This gives further evidence that the closed association model can interpret these results well and that the best fit of equation (13) has been found.

The single chain and three-chain aggregate radii of gyration (Rg_1 and Rg_3, respectively) at 25°C obtained from *Figure 4* (using equation (18)) are given in *Table 3*. The lack of temperature dependence of the average radii of gyration indicates that there is no significant change in the dimensions of either the single chains or the aggregates with temperature. Rg_1 is slightly larger than observed with the SPS ionomer (1.39 mol%) (also shown in *Table 3*) but much more compact than observed for polystyrene in xylene (130 Å)[9]. The smaller radius of gyration obtained for the SPS ionomer (0.95 mol%) three-chain aggregate compared with that for the two-chain aggregate formed with the SPS ionomer (1.39 mol%) indicates that the structure of these two aggregates must be very different.

Single chain dimensions within aggregates

In *Figure 5* the average single chain dimensions (Rg_{sin}) obtained by a fit of the Debye model to contrast-matched coherent scattering from the mixture of hydrogenous and deuterated SPS ionomer (0.98 mol%) are shown as a function of concentration. All the intercepts give $I(0)$ in agreement with equation (3), giving confidence that the solutions are correctly contrast matched. Within the range measured the effect of concentration on Rg_{sin} is very small. Also given in *Figure 5* is the best fit of equation (19) using an isolated single chain dimension, Rg_1, as 78 Å (as obtained above). This shows that very little effect of concentration on the average single chain dimensions is expected in the range over which it is possible to study without very long neutron beam exposure times. The best fit of equation (19) gives the single chain radius of gyration in the three-chain aggregate, $Rg_{1,3}$, as 115 Å. Therefore although the three-chain aggregates are compact, within these aggregates the single chains are expanded from their collapsed state when in isolation.

Free energies of aggregation

The lack of temperature dependence of g and therefore of the equilibirium constant ${}^{n}K_c$ (see equation (12)) for the SPS ionomer (0.95 mol%) in xylene shows (using equation (23)) that the free energy change on aggregation arises primarily as a result of entropic changes. Values obtained for the hypothetical entropy and enthalpy changes associated with an increase in the aggregate size by one chain (ΔS_2 and ΔH_2, respectively) for the SPS ionomer (0.95 mol%) are given in *Table 2*. These values and their errors were estimated from g and its error using equations (12), (21) and (23). ΔH_2 is zero as observed previously with the SPS ionomer (1.39 mol%). ΔS_2 for the SPS ionomers is slightly greater at a sulfonation level of 0.98 mol% than at 1.39 mol% (see *Table 2*).

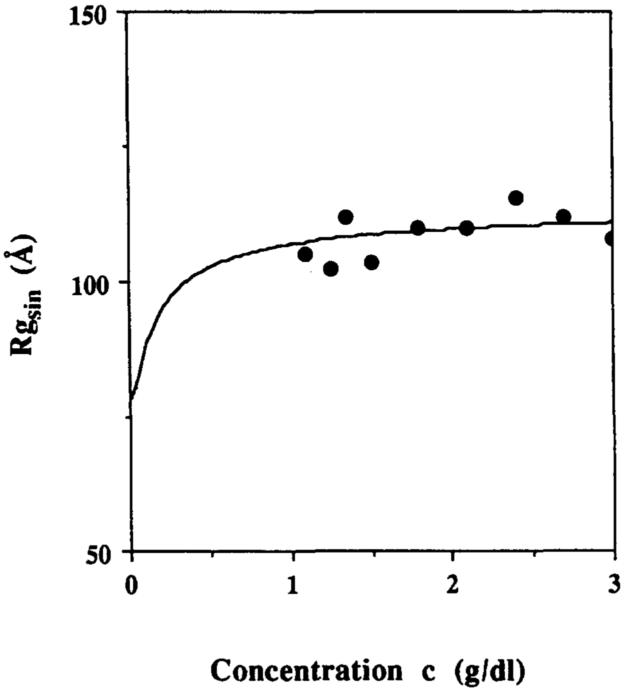

Figure 5 Average single chain radii of gyration (Rg_{sin}) of the SPS ionomer (0.98 mol%) in contrast matched xylene. Curve is the best fit of equation (19) as described in the text

DISCUSSION

For aggregating systems it requires only a small minimum in the negative free energy change on unimer addition to an aggregate *versus* number of chains already in the aggregate to result in the closed association model describing the data[20]. The above results show that the SPS ionomer (0.95 mol%) in xylene follows this model since an equilibrium is observed between compact aggregates of three chains and single chains. The relatively small difference between the single chain radius of gyration within the three-chain aggregates (115 Å) and the total aggregate size (150 Å) indicates that the individual chains must be strongly interpenetrating. Both the aggregates and single chains probably consist of a solvent-impenetrable core composed primarily of sodium sulfonate groups surrounded by polystyrene chains swollen by the solvent (i.e. a similar structure to an inverse micelle). This structure would reduce repulsive interactions between the solvent and ionic groups on the polymer. If these repulsive interactions had been significant then a positive enthalpic contribution to the excess free energy of the solvent on mixing with the aggregates might have been expected (i.e. $A_{2,\mathrm{h}}$ would have been negative, not zero as observed). The solvation of the polystyrene chains would account for the small excess entropy of the solvent on dilution with the ionomer aggregates. On aggregation of the single chains there is an increase in entropy but no overall change in enthalpy. Since the single chains expand on aggregation the increase in entropy is possibly due to both greater mixing of the more expanded polymer with the solvent and more configurational freedom of the polymer within the aggregates. The lack of enthalpy change on aggregation of the ionomer and the lack of enthalpic interaction between the ionomer and the solvent results in negligible change in the extent of ionomer aggregation or single chain and aggregate dimensions with temperature.

In comparison, the SPS ionomer (1.39 mol%) forms aggregates of all sizes in solution. These are much less dense than those observed with the lower ionic content ionomer described above. The large difference between the total two-chain aggregate radius of gyration (170 Å) and the single chain size within that aggregate (101 Å) suggests that the single chains are less interpenetrating for the SPS ionomer (1.39 mol%) than observed for the SPS ionomer (0.95 mol%). $A_{2,\mathrm{h}}$ for the SPS ionomer (1.39 mol%) aggregates is negative (although small), suggesting some repulsion between the ionic groups and the solvent. This is balanced, however, by an equal but positive value for $A_{2,\mathrm{s}}$. The aggregation of the SPS ionomer (1.39 mol%) results in an increase in entropy but no change in enthalpy. Single chain expansion is observed on aggregation but the average entropy change on increasing the size of an aggregate by one chain is smaller than obtained with the SPS ionomer (0.95 mol%). With the SPS ionomer (1.39 mol%), although there is a slight enthalpic repulsion between the aggregates and solvent it is too small for any significant effect of temperature on the aggregate or single chain dimensions or extent of aggregation at a given concentration to be observed.

Control of the aggregation of ionomers and its temperature dependence is important primarily because of the large effects that aggregation can have on solution viscosities[12]. These results suggest that the anomalous dependence of ionomer solution viscosity on temperature observed in some solvents as a result of changes in aggregation[21] may only be observed if there is a strong enthalpic interaction between the ionomer and solvent. An understanding of the factors controlling these interactions is therefore important in the application of ionomers as viscosity control agents, for example in lubricants[22] or drilling fluids[5]. The effect of aggregate size and structure on the viscosity of ionomer solutions will be discussed in detail in later work, as will ionomer systems where strong enthalpic interactions between the polymer and solvent are observed.

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REFERENCES

1 Tant, M. R. and Wilkes, G. L. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 1
2 Fitzgerald J. J. and Weiss, R. A. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 99
3 Mauritz, K. A. *JMS Rev. Macromol. Chem. Phys.* 1988, **C28**(1), 65
4 Eisenberg, A., Hird, B. and Moore, R. B. *Macromolecules* 1990, **23**, 4098
5 Lundberg, R. D. in 'Structure and Properties of Ionomers' (Eds M. Pineri and A. Eisenberg), Reidel, Dordrecht, 1987, pp. 429–438
6 Hara, M. in 'Polyelectrolytes: Science and Technology' (Ed. M. Hara), Marcel Dekker, New York, 1993, Ch. 4
7 Agarwal, P. K., Garner, R. T. and Graessley, W. W. *J. Polym. Sci. Polym. Phys.* 1987, **25**, 2095
8 Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Burchard, W. *Macromolecules* 1990, **23**, 1434
9 Pedley, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. *Macromolecules* 1990, **23**, 2494
10 Young, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. *Polymer* 1995, **36**, 691
11 Elias, H. G. in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, London, 1972, Ch. 9
12 Pedley, A. M., Higgins, J. S., Peiffer, D. G., Rennie, A. R. and Staples, E. *Polym. Commun.* 1989, **30**, 162
13 Peiffer, D. G., Lundberg, R. D., Newlove, J. C. and Werlein, E. R. US Patent 4,978,461 (12-18-1990), Exxon Research and Engineering Company
14 Lantman, C. W., MacKnight, W. J., Higgins, J. S., Peiffer, D. G., Sinha, S. K. and Lundberg, R. D. *Macromolecules* 1988, **21**, 1339
15 Gabrys, B., Higgins, J. S., Lantman, C. W., MacKnight, W. J., Pedley, A. M., Peiffer, D. G. and Rennie, A. R. *Macromolecules* 1989, **22**, 3746
16 Young, A. M., Higgins, J. S., Peiffer, D. G. and Rennie, A. R. *Polymer* in press
17 Ullman, R., Benoit, H. and King, J. S. *Macromolecules* 1986, **19**, 183
18 Schulz, G. V. and Lechner, in 'Light Scattering from Polymer Solutions' (Ed. M. B. Huglin), Academic Press, London, 1972, Ch. 12
19 Debye, P. J. *J. Phys. Colloid Chem.* 1947, **51**, 18
20 Hunter, R. J. in 'Foundations of Colloid Science', Vol. 1, Oxford University Press, New York, 1987, Ch. 10
21 Lundberg, R. D. and Makowski, J. S. *J. Polym. Sci. Polym. Phys. Edn* 1980, **18**, 1821
22 Marsden, K. *Lubrication Sci.* 1986, **1**, 265