Macromolecules **1992,** *25,* 999–1002 **999**

Selective Adsorption of Potassium Thiocyanate to a Zwitterionic Polymethacrylate

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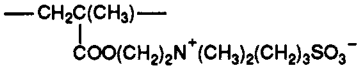
Received May 20, 1991
Revised Manuscript Received October 22, 1991

Introduction

N-(3-Sulfopropyl)-*N*-[(methacryloyloxy)ethyl]-*N*,*N*-dimethylammonium betaine (SPE) can be polymerized readily to yield the polymer (PSPE) having the following repeating unit:



$$\begin{array}{l}-\mathrm{CH_2C(CH_3)}-\\ \quad|\\ \quad\mathrm{COO(CH_2)_2N^+(CH_3)_2(CH_2)_3SO_3^-}\end{array}$$

PSPE is insoluble in water but dissolves in aqueous salt media due to disruption of intra- and interchain associations between the charges of the zwitterion.[1] Increasing the concentration of the salt enhances chain expansion particularly at low to medium salt concentration, as demonstrated by measurements of the intrinsic viscosity,[1-4] Study of the critical salt concentration for promoting dissolution[2] has shown that the effect of K^+ is roughly intermediate among the group of common cations. The most important role in this respect is played by anions, and, of these, CNS^- is more effective than OH^- and all the halide ions.

The swelling of cross-linked PSPE increases with the concentration of KCNS in the aqueous swelling medium, and the importance of the zwitterionic group has been demonstrated by the results of parallel experiments on the swelling of a cross-linked neutral polymer poly(2-hydroxyethyl methacrylate) in the same media.[5] Certain analogies exist between the behavior of a cross-linked polymer swollen in a liquid and that of the corresponding linear species dissolved in the same medium.[6-8] Our previous characterizations of linear PSPE in the perturbed[9] and unperturbed states[4] did not involve aqueous KCNS as solvent. In the present paper attention is focused on selective adsorption effects in the solution water (1)/linear PSPE (2)/KCNS (3) to compare them with results already obtained on the corresponding hydrogel system. Moreover, as far as we are aware, selective adsorption in PSPE or other sulfobetaine solutions has not been reported before.

Experimental Part

Materials. SPE (Rasching Co.), potassium thiocyanate (analytical grade; Aldrich Chemical Co.), and the initiator, ammonium persulfate (Hopkin and Williams), were used as received. Formamide (Aldrich Chemical Co.) was dried over anhydrous magnesium sulfate and distilled. Doubly distilled deionized water was employed in the polymerization and for preparation of the salt solutions.

Preparation of PSPE. The aqueous feed mixture containing SPE and initiator at concentrations of 0.54 and 0.011 mol dm^{-3}, respectively, was outgassed with gaseous nitrogen for 15 min, after which polymerization was carried out at 328 K for 9 h. The solution was then chilled to stop the reaction and allowed to reach room temperature. After precipitation in methanol, the resultant polymer was dried under vacuum for 2 days at 323 K. The conversion was ~70%.

Procedures. Refractive indices (n_0) of formamide and of aqueous KCNS solutions of five different concentrations C_3 (mol dm^{-3}) were measured on a Pulfrich refractometer. No filters were necessary, because there was sufficient clear displacement of the colored bands from the Hg lamp emission to obtain values of n_0 separately at each of three wavelengths in vacuo (λ_0), viz., 436, 546, and 578 nm. Specific refractive index increments (dn/dc_2) for solutions of PSPE in each of the solvents were measured as before[10] at λ_0 = 633 nm. Light scattering measurements were conducted with vertically polarized incident light (λ_0 = 633 nm) using a modified Sofica (Model 4200) light scattering photometer,[11] scattered intensities being registered on a digital voltmeter. Calibration was effected with purified benzene, taking the Rayleigh ratio R_{90}^{v} to be[12] $12.6 \times 10^{-4}\ m^{-1}$. Clarification was effected by means of 0.45-μm PTFE membrane filters (Gelman Sciences). Conductance measurements were made with an AGB-77 Laboratory Conductivity Meter (Scientific and Medical Products Ltd., Manchester, U.K.), calibrated with aqueous NaCl. All measurements reported here relate to 298 K.

Results

The weight-average molar mass of the polymer M_w obtained from light scattering in a single solvent, formamide, was 760 kg mol^{-1}. This and the other characteristics in formamide are listed in Table I.

The values of the relevant quantities measured for PSPE in the aqueous KCNS solutions are also given in Table I. The values of n_0 at 633 nm for the aqueous salt solvents were obtained from the measured values at the three different wavelengths by means of an accurately obeyed Cauchy dispersion relationship. These values of n_0 are seen to increase with C_3, and there is accordingly a decrease in dn/dc_2 with increasing concentration of KCNS in the aqueous solvent medium. The partial specific volume of PSPE in solution. $\bar{v}_2$, has been measured previously[9] as 0.717 $dm^3\ kg^{-1}$. By using the following Gladstone–Dale equation the refractive index of PSPE, n_2, can be calculated separately from data for each salt concentration.

$$dn/dc_2 = \bar{v}_2(n_2 - n_0) \quad (1)$$

The average value of n_2 was 1.540, which is not markedly different from the value of n_2 = 1.554 obtained by a similar procedure from corresponding data for this polymer in 2,2,2-trifluoroethanol.[9]

The molar mass of the polymer yielded by light scattering in a multicomponent solvent is an apparent value, denoted by M_w^*. The values of M_w^* increase with C_3 and are all greater than the true value, M_w, obtained in formamide. The root-mean-square radii of gyration in aqueous salt are also apparent values, denoted by $(\langle s^2\rangle_z^{1/2})^*$. These increase with C_3, indicating an apparent increase in chain expansion induced by the salt in breaking intra- and interchain associations in the polyzwitterionic chain, as is known from the influence of salt on the intrinsic viscosity.[1] However, although this effect is true qualitatively, it is not possible to obtain the true values $\langle s^2\rangle_z^{1/2}$ in a system wherein selective adsorption is considerable.[13] The apparent values, A_2^*, of the second virial coefficient remain sensibly independent of C_3, which is surprising if one considers increasing the KCNS concentration to induce increased polymer–solvent thermodynamic interaction. However, the true values, A_2, may be calculated from eq

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Table I
Light Scattering and Refractometric Parameters for a Sample of PSPE in Formamide and Aqueous KCNS Solutions

	formamide	C_3/mol dm^{-3} of aqueous KCNS 0.1	0.3	0.5	1.0	2.0
n_0	1.4433	1.3325	1.3357	1.3388	1.3465	1.3630
$dn/dc_2/(dm^3\ kg^{-1})$	0.080	0.150	0.147	0.142	0.138	0.127
$M_w^*/(kg\ mol^{-1})$		1080	1350	1600	1780	2080
$M_w/(kg\ mol^{-1})$	760					
$(\langle s^2\rangle_z^{1/2})^*/nm$		42.0	55.4	57.8	60.2	72.3
$\langle s^2\rangle_z^{1/2}/nm$	27.0					
$A_2^*/(10^{-4}\ m^3\ kg^{-2}\ mol)$		2.02	2.21	2.03	1.94	2.04
$A_2/(10^{-4}\ m^3\ kg^{-2}\ mol)$	1.03	2.87	3.93	4.27	4.55	5.58
χ_T		0.490	0.486	0.485	0.484	0.479
χ	0.492					
$\gamma_3/(dm^3\ kg^{-1})$		0.091	0.154	0.201	0.231	0.261

2.[14] As seen in Table I, the resultant values of A_2 do indeed

$$A_2/A_2^* = M_w^*/M_w \quad (2)$$

increase with C_3. The overall contributions of the different types of interaction χ_{ij} in the multicomponent polymer/aqueous KCNS solutions may be embodied into a total polymer–solvent interaction parameter χ_T, the values of which were calculated from eq 3 in which V_0 is the molar

$$0.05 - \chi_T = A_2 V_0/\bar{v}_2^{\,2} \quad (3)$$

volume of the aqueous KCNS. The molar volumes V_0 were obtained from eq 4 in which X_1 and X_3 are the mole fractions of water and salt, respectively, and V_1 ($=18 \times 10^{-3}$ dm^3 mol^{-1}) and V_3 ($=51.5 \times 10^{-3}$ dm^3 mol^{-1}) are the corresponding molar volumes, the two latter quantities being obtained from the densities of water ($=1.0$ kg dm^{-3}) and KCNS ($=1.886$ kg dm^{-3}).

$$V_0 = X_1 V_1 + X_3 V_3 \quad (4)$$

Although the concentrations of KCNS are quoted as molarities C_3 in Table I, weighings were also made in order to obtain also molalities m_3; hence, exact values of X_1 and X_3 were known. The polymer–solvent interaction parameter in the single solvent χ was calculated from the corresponding form of eq 3 in which V_0 denotes the molar volume of formamide. It is seen that the value of χ exceeds the values of χ_T, which in turn decrease with C_3.

The coefficients of selective adsorption γ_3 of KCNS to PSPE were evaluated via eq 5[14] in which $dn_0/d\phi_3$ expresses

$$\gamma = [(M_w^*/M_w)^{1/2} - 1][(dn/dc_2)/(dn_0/d\phi_3)] \quad (5)$$

the variation of the refractive index of aqueous KCNS with the volume fraction ϕ_3 of KCNS in it. Within the concentration range covered here this variation was independent of ϕ_3 and afforded a constant value of $dn_0/d\phi_3 = 0.318$. The values obtained thereby are all positive and indicate considerable selective adsorption of KCNS to an extent which increases with C_3 (see Table I). Thus, at $C_3 = 2.0$ mol dm^{-3}, $\gamma_3 = 0.261$ dm^3 of salt/kg of polymer, but even in the most dilute salt solution the selective adsorption of about one-third of this quantity is significant. A more physically meaningful picture of selective adsorption is provided in terms of the change in the molality of salt (m_3) with the molality of polymer subunits (m_2). On this basis the coefficient of selective adsorption N_3 is defined by eq 6 in which the derivative applies to conditions

$$N_3 = (\partial m_3/\partial m_2)_\mu \quad (6)$$

of constant chemical potential (μ) of diffusible low molar mass species, and the values of N_3 are calculated from eq 7 in which M_u is the molar mass of the subunit in PSPE. As shown in Figure 1, the values of N_3 increase from 0.49

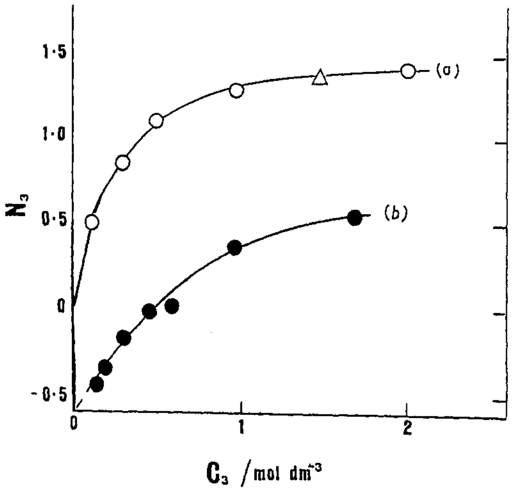

Figure 1. Selective adsorption coefficient on the basis of moles of KCNS per mole of the monomer unit in PSPE as a function of the concentration of KCNS in bulk solvent. (a) (○) Obtained via light scattering; (△) obtained via conductivity. (b) Calculated from binary interaction parameters.

$$N_3 = \gamma_3 M_u/V_3 \quad (7)$$

to 1.42 mol/mol as the bulk salt concentration in the medium increases from 0.1 to 2.0 mol dm^{-3}.

In a previous paper[15] we proposed a new procedure for determining the extent of selective adsorption (or desorption) of the salt. Essentially the ionic components of the solvent medium are considered as bound and free, with only the latter contributing to the measured conductance of the polymer solution. The treatment yielded the following expression:

$$N_3 = -M_u(d\kappa/dc_2)/(d\kappa/dC_3) \quad (8)$$

Here $d\kappa/dc_2$ is the change of the specific conductivity (κ) of the polymer solution with the concentration (c_2) of the polymer for a solvent having a particular molarity of salt. $d\kappa/dC_3$ relates to measurements in the absence of polymer and is the change of the specific conductivity of the salt solution with the molarity of salt at the same salt concentration as that used in the polymer solution. Figure 2a shows a linear decrease in κ with the polymer concentration for measurements in aqueous KCNS at $C_3 = 1.5$ mol dm^{-3}. The slope yields $d\kappa/dc_2 = -35$ (S m^{-1})/(kg dm^{-3}). Figure 2b gives the increase in κ with the concentration of salt in aqueous KCNS solutions. The plot displays a slight curvature, but at $C_3 = 1.5$ mol dm^{-3} the slope $d\kappa/dC_3 = 7.3$ (S m^{-1})/(mol dm^{-3}). Hence, as $M_u = 0.279$ kg mol^{-1}, eq 8 yields $N_3 = 1.34$ mol/mol. As seen in Figure 1a, this

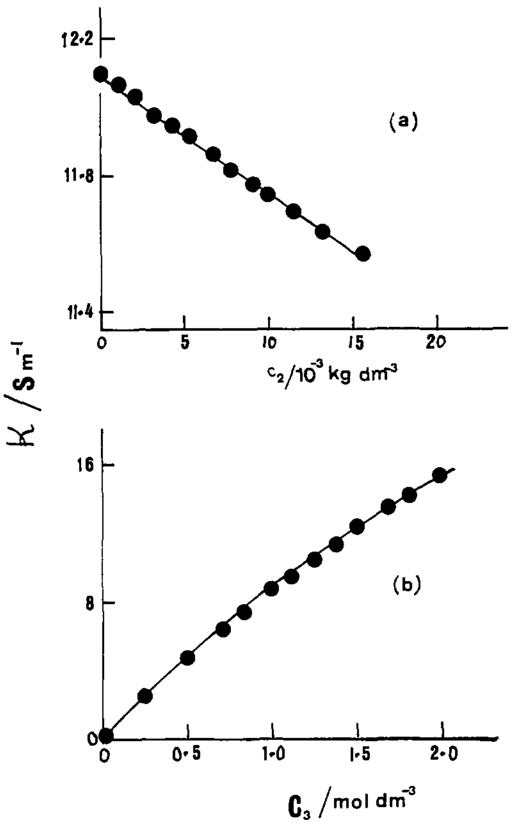

Figure 2. Variation of the specific conductivity with (a) the concentration of PSPE in 1.5 mol dm^{-3} aqueous KCNS and (b) the concentration of KCNS in the absence of polymer.

value lies in good accord with the variation of N_3 obtained by light scattering at different values of C_3.

Discussion

Selective adsorption to neutral polymers in binary liquid mixtures has been studied extensively. The coefficient of selective adsorption of one of the liquids can be positive, negative, or zero according to the composition of the liquid mixture.[16] Less work has been reported on neutral polymers in aqueous salt media. However, mention may be made of cellulose in the complex ionic solvent cadoxen, for which positive preferential adsorption of the tris(ethylenediamine)cadmium ion has been quantified by light scattering, differential refractometry, and conductivity.[15] Stejskal and Kratochvil[17] used the density increment method to measure the positive selective adsorption of salt to cellulose and other neutral polymers in concentrated aqueous $ZnBr_2$, the coefficient of selective adsorption being found to increase with $[ZnBr_2]$. The hitherto highest reported coefficient appears to be that of 1 mol of LiOH/mol of an anhydroglucose unit for cellulose in 6 wt % aqueous LiOH.[18]

In general polyelectrolytes behave differently.[19,20] At very high salt concentration positive selective adsorption of salt can occur[19] due to specific binding (as confirmed spectroscopically[21]), but otherwise the selective adsorption coefficients of salts are negative. Such desorption of salt increases with the concentration of salt in the bulk medium. Theory,[22,23] predicting a linear dependence of the square root of the absolute value of the adsorption coefficient of salt on the square root of the molarity of salt, has been confirmed experimentally.[19] For the present system the plot (not illustrated) of $N_3^{1/2}$ vs $C_3^{1/2}$ is markedly curved. This observation, coupled with the positive values of N_3 over the whole range of C_3, confirms the antipolyelectrolyte nature of PSPE. Moreover, even at low values of C_3 specific binding occurs to this polymer which contains both positive and negative charges, in contrast to a polyelectrolyte. Specific binding of KCNS to the charged groups is supported by the conductometric data that demonstrate decreased ionic mobility in the presence of polymer.

From previous work[5] on cross-linked PSPE hydrogels in aqueous KCNS the relevant pair interaction parameters χ_{ij} were derived. Values of γ_3 (and hence N_3, via eq 7) were calculated at each salt concentration using a theoretical relationship.[24] This expression gives γ_3 as a function of $\bar{v}_2$, ϕ_1, ϕ_3, V_3/V_1, χ_{12}, χ_{23}, and χ_{31}. Figure 1b shows that the resultant curve of calculated values of N_3 as a function of C_3 is of a similar general form to the experimental curve (Figure 1a), but at all concentrations the calculated values of N_3 are considerably lower and even assume negative values at $C_3 \leq$ ca. 0.5 mol dm^{-3}. In particular it should be noted that at zero salt concentration the system is no longer multicomponent and the value of N_3 must be zero. The calculated curve (Figure 1b) shows a large negative value of N_3 at $C_3 = 0$, indicating that the adoption of the relevant theoretical expression[24] for the selective adsorption coefficient is inadmissible. Effectively, although the Flory-Huggins treatment and interaction parameters[24,25] associated with it are often useful in nonpolar systems, they cannot be applied to an aqueous solution of ionic components in which specific ion binding occurs.

Finally some observations are made on the previous findings[5] on PSPE hydrogels in aqueous KCNS in relation to the present results. The overall total interaction parameter χ_T follows the same pattern qualitatively and quantitatively in both systems. The total uptake of aqueous KCNS as well as the partitioning coefficient of KCNS between the hydrogel and external solution exhibits sharp increases within the region 0 mol dm^{-3} < C_3 < 0.3 mol dm^{-3}. Thus the partitioning coefficient attains a value of unity at C_3 = 0.3 mol dm^{-3} and increases gradually to a value of 1.1 mol dm^{-3} at higher salt concentrations. A gel binding coefficient, expressed as moles of KCNS per mole of a segment in swollen hydrogel, increases continuously with C_3. Thus at C_3 = 0.3 mol dm^{-3} this coefficient has a value of unity, but at C_3 = 1.7 mol dm^{-3} the value is 6 mol/mol. For linear PSPE in dilute salt solution N_3 also increases sharply with C_3, a value of N_3 = 1 mol/mol being attained at C_3 = 0.4 mol dm^{-3}. This selective adsorption coefficient, however, increases in value only gradually at higher salt concentrations (see Figure 1a). In this context it is perhaps judicious not to emphasize the analogy between the hydrogel and solution. The binding coefficient of salt relates to the KCNS solution within the whole hydrogel network and not solely that in the immediate vicinity of the solvent sheath surrounding the linear polymer chain. Although specific binding of KCNS in solution can yield a value of N_3 = 1 mol/mol, the physical picture of the situation in which N_3 > 1 mol/mol (e.g., N_3 ~ 1.4 mol/mol at C_3 = 2 mol dm^{-3}) remains unclear. We offer the conjecture only that when the zwitterions in the chain have undergone complete specific binding, the observed value of N_3 thereafter relates to the preferential adsorption of the salt to a substrate which is essentially different in the respect that it is no longer zwitterionic. The fact that N_3 tends to a constant value would indicate that there is little affinity of KCNS for this substrate at high salt concentrations.

Acknowledgment. The provision of financial assistance by the Egyptian Government to M.A.R. is gratefully acknowledged.

References and Notes

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Registry No. PSPE (homopolymer), 41488-70-4; KCNS, 333-20-0.