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Evidence of Polyion Hydration from X-ray and Neutron Small-angle Scattering Experiments

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Summary

The recently published small-angle scattering curves of semidilute solutions of poly (methacrylic acid) indicate some differences in neutron and X-ray data. At high degree of neutralization ($\alpha > 0.6$), with increasing α the neutron intensity decreases and X-ray intensity increases. A new series of experiments confirms this apparent discrepancy. We suggest an explanation of the observed phenomenon, based on a simple model which considers hydration of macroions. Using the proposed model, about one water molecule is estimated to be in excess in the hydration shell.

Introduction

The structure of semidilute polyelectrolyte solutions has been studied recently by employing both the small-angle neutron scattering (SANS) (COTTON and MOAN 1976, RINAUDO and DOMARD 1977, MOAN 1978) and X-ray scattering (SAXS) (PLEŠTIL et al.1979, ISE et al.1979, 1980). A characteristic feature of these experiments consists in the occurrence of a maximum on scattering curves. This result may be interpreted using models either with parallel rodlike macroions (COTTON and MOAN 1976) or with an irregular structure consisting of partially flexible chains (DE GENNES et al.1976), because the position of the scattering maximum is proportional to the square root of polymer concentration. Alternatively, ISE et al. (1980) proposed a model of regularly ordered coils.

A comparison of the results obtained by X-ray and neutron measurements (cf. PLEŠTIL et al. 1979, MOAN 1978) reveals several discrepancies. Part of them may probably be linked with the sample preparation or experimental technique. The most striking and interesting, however, is the opposite character of the dependence of scattered intensity on the degree of neutralization α and the difference between positions of the peaks on the X-ray and neutron scattering curves. In order to avoid some possible sources of discrepancies, we carried out both SAXS and SANS experiments with the same samples.

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Experimental

D_2O solutions of methacrylic acid polymerized by free radicals, M_w = 15 000, neutralized with NaOD or LiOD, were investigated. The SAXS curves were recorded with the Kratky camera. For a more detailed description of experimental conditions cf.PLEŠTIL et al.1979. The neutron studies were made in the Laboratory of Netron Physics of the Joint Institute for Nuclear Research (Dubna) using a spectrometer with axially symetric geometry (GLADKICH et al.1977).

RESULTS AND DISCUSSION

Experimental scattering curves (the dependence of scattered intensity on $h = (4\pi/\lambda) \sin\theta$ where λ is the radition wavelength and 2θ is the scattering angle) are shown in Fig.1. Using the position of the maximum h_m, one can determine the Bragg distance $d_B=2\pi/h_m$. The results in Table I show that the neutron experiments yield somewhat lower d_B and cd_B^2 values than X-ray ones. The reverse dependence of the scattered intensity on α for the two kinds of radiation can be seen directly in Fig.1. These differences, may be interpreted as a consequence of macroion hydration. A hydration shell of higher density as compared with that of bulk water is formed around the charged groups (IKEGAMI 1968).

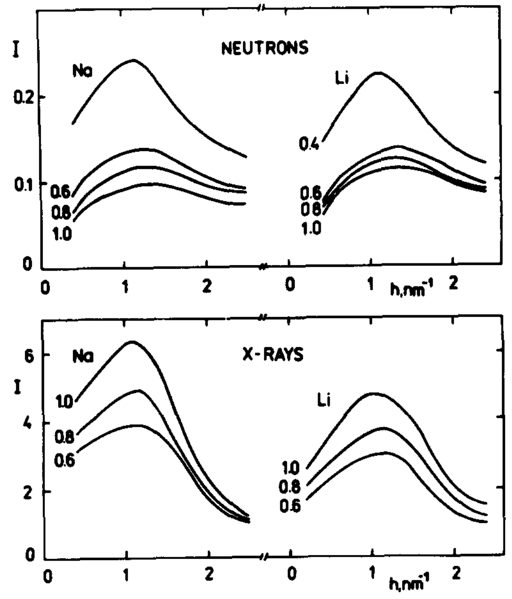

Fig.1 Neutron and X-ray small-angle scattering curves of polymethacrylic acid in D_2O (c=0.052 g/ml). Numbers at curves denote degree of neutralization; counterions Na^+ and Li^+.

Let us assume that the solution consists of domains inside which polymer chains of length L are situated parallel to each other, while the domains themselves are orientated randomly, so that the solution as a whole is isotropic.

The scattering law for such a system at $hL \gg 1$ may be written as (VAINSHTEIN 1966)

$$I(h) = |F(h)|^2 \cdot |B(h)|^2 / \pi hL \qquad (1)$$

where $F(h)$ is the scattering amplitude from one chain, $|B(h)|^2$ is an interference function, the form of which is given by the mutual chain order.

To construct the function $F(h)$, let it be assumed for the sake of simplicity that the hydrated polymer chain has cylindrical symmetry and can be characterized by the radii $r_1 < r_2$ and the excess scattering densities ρ_1 and ρ_2. The cross-section of such a model and the radial distributions of scattering density are shown in Fig.2.

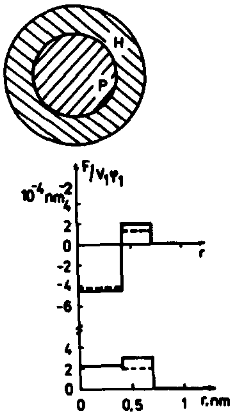

Fig.2 Cross-section and the assumed distributions of excess scattering density (cf. Eq.5) of the model of hydrated chain (upper curve - neutron, lower curve - - X-ray; —— $\alpha = 1$, - - - $\alpha = 0.6$)

For the chosen model, the scattering amplitude has the form (VAINSHTEIN 1966):

$$F(h) = 2 \left[(V_1+V_2)\rho_2 J_1(h\, r_2)/h\, r_2 + V_1 \; (\rho_1-\rho_2) J_1(h\, r_1)/h\, r_1\right] \qquad (2)$$

where V_1, V_2 are the respective volumes, $J_1(x)$ is the Bessel function.

Let us examine the effect of neutralization on $F(h)$. Neutralization is accompanied by ionization and the scattering density ρ_1 becomes a linear function of α:

$$\rho_1 = a_1 + b_1 \alpha \qquad (3)$$

Parameters of hydration shell also depend on the degree of neutralization. Let us assume, that the respective contribution to the scattering amplitude is also proportional to α :

$$\rho_2 V_2 = \alpha b_2 V_2 \tag{4}$$

where the combination b_2V_2 is unknown.
By combining expressions (2,3,4), it is easy to construct a linear function describing the dependence $F(\alpha)$:

$$F(\alpha) = V_1 \varphi(u_1)\left[a_1 + \alpha\left[b_1 + \rho_0 X \psi(u_1, u_2)\right]\right] \tag{5}$$

where $X = b_2V_2/\rho_0 V_1$ is a dimensionless combination proportional to the relative contribution of the hydration shell to the scattering amplitude; $\varphi(u) = 2J_1(u)/u$;

$$\psi(u_1, u_2) = \frac{\varphi(u_2)}{\varphi(u_1)} + \frac{\varphi(u_2) - \varphi(u_1)}{\varphi(u_1)} \cdot \frac{u_1^2}{u_2^2 - u_1^2} \tag{6}$$

is a function taking into account parameters of the model, $u_1 = h r_1$, $u_2 = h r_2$. For the estimated values ($r_1 \simeq 0.3$ nm, $r_2 \simeq 0.6$ nm), $\psi = 0.9$ at $h \simeq h_m$ for the investigated solutions, and it varies little with varying r_1 and r_2.

The values of the constants ρ_0, a_1 and b_1 from Eq. (5) calculated using the published coherent scattering lengths (JACROT 1976) are (in 10^{-4} nm^{-2} units), respectively, 6.40, - 4.02 and -0.61 for neutrons and 9.43, 2.37 and 0.0 for X-rays. By substituting these values into (5) and (1), one can see that at $0.1 < X < 0.8$ the scattering intensity of neutrons decreases with increasing α , while that of X-rays increases. At $X = 0$ (without considering hydration), an opposite dependence should be observed for neutrons, while for X-rays the intensity ceases to be dependent on α . The apparent discrepancy of experimental data seems to be resolved in this way. The different dependences of the intensity of the diffraction peak on α obtained by X-ray and neutron experiments demonstrate the essential effect of the macroin hydration on intensity.

It is possible to determine the parameter X from the observed dependence $I(\alpha)$, if the interference function $B(h)$ in Eq.(1) is independent of α . For $\alpha < 0.5$, this requirement is not satisfied, because the observed position of the maximum is strongly dependent on the degree of neutralization (PLEŠTIL et al.1979). At $\alpha > 0.5$, however, both d_B and the form of the peak become invariable. This allows us to expect that $B(h)$ remains constant at $\alpha > 0.5$, and the subsequent analysis is carried out using this assumption. The combined Eqs (1) and (5) may be represented as a linear function :

$$\left[I(\alpha)/I(\alpha=1)\right]^{1/2} = 1 - C\,(1-\alpha) \tag{7}$$

TABLE 1: Observed Bragg distances d_B (nm) and cd_B^2 (nm^2g/ml) values (in brackets) for PMA

Counterion (Concentration, g/ml)	Degree of neutralization			Method
	0.6	0.8	1.0	
Na^+	5.6			SANS a)
(0.0365)	(1.1)			
Na^+	7.3	7.2	7.0	SAXS b)
(0.0331)	(1.8)	(1.7)	(1.6)	
Na^+	5.5	5.5	5.6	SAXS
(0.052)	(1.6)	(1.6)	(1.6)	
Li^+	5.5	5.5	5.5	SAXS
(0.052)	(1.6)	(1.6)	(1.6)	
Na^+	4.8	4.8	4.7	SANS
(0.052)	(1.2)	(1.2)	(1.1)	
Li^+	4.8	4.8	5.0	SANS
(0.052)	(1.2)	(1.2)	(1.3)	

TABLE 2: Scattering amplitudes b_I (10^{-5}nm), number of excess water molecules per one PMA repeat unit (ΔN_1) and the same parameter obtained without considering counterion condensation (ΔN_o).

Method	Counterion	b_I	ΔN_o	ΔN_1
SANS	Na^+	0.36	1.30	1.27
SAXS	Na^+	2.82	1.45	
SANS	Li^+	-0.18	0.98	1.03
SAXS	Li^+	0.56	1.14	

If C has been determined from the experimental data, the quantity X is expressed as follows:

$$X = \frac{a_1}{\rho_o} \left(\frac{C}{1-C} - \frac{b_1}{a_1} \right) \cdot \frac{1}{\psi} \qquad (8)$$

Fig.3 shows experimental data corresponding to the construction of Eq. (7). The linear dependence is indeed lost at $\alpha < 0.5$. At $\alpha \geq 0.6$, the values of the parameters X for four cases investigated by us lie within 0.2 - 0.4.

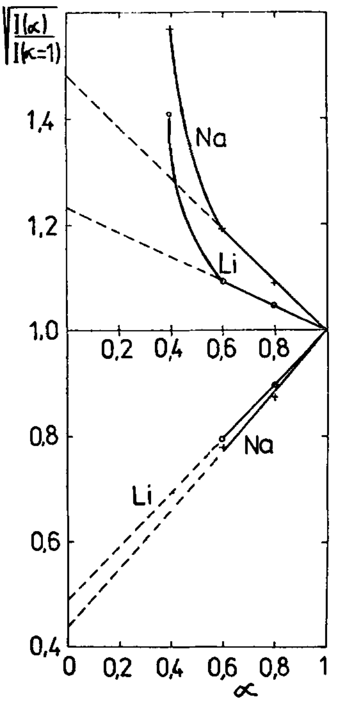

Fig.3 Dependence of relative scattering amplitude on the degree of neutralization for PMA solutions (upper part - neutron, lower part - X-ray).

The quantity ΔN_o

$$\Delta N_o = x \cdot \frac{v_M}{v_o} \qquad (9)$$

has the meaning of the averaged excess number of water molecules (compared with bulk water) in the hydration shell per one repeat unit (υ_M and υ_o are molar volumes of the repeat unit and solvent respectively). The numerical values of ΔN_o summarized in Table 2 seem to be plausible (cf. IKEGAMI 1968), but markedly depend on the nature of the counterion and of the radiation used. The latter fact indicates that the hydration layer includes the counterion, i.e. there occurs a perceptible condensation of counterions. If β is the fraction of condensed counterions, then the actual number of excess water molecules may be written as

$$\Delta N_1 = \Delta N_o - \frac{\beta b_I}{b_o} \qquad (10)$$

where b_I and b_o, respectively, are the scattering amplitudes of the counterion and water molecule. The values of β may be determined from our data, upon the requirement that ΔN_1 determined from X-ray and neutron experiments should coincide.

In spite of the schematic character of the model and rather few experimental data, the N_1 values thus obtained (Table 2) may be regarded as satisfactory. β is very sensitive to the error in ΔN_o; therefore, a reliable determination of β calls for more detailed experimental data. The respective β values for Na and Li counterions are 0.2 and 0.5.

Hence, by simply taking into account the hydration effects, it is possible to explain the dependence of scattered intensity on the degree of neutralization. Within the accepted assumptions, these data allow to estimate the number of excess water molecules in the hydration shell. Further and more detailed experiments are needed in the range $\alpha > 0.6$, both in order to check the assumptions made and to obtain more precise conclusions. The second effect mentioned at the beginning, it is, that of variation of the positions of diffraction maxima, will be dealt with separately.

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