Dynamic light scattering by gels under hydrostatic pressure

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(*Received* 10 *October* 1980)

Measurements of variation with pressure of the collective diffusion constant D_c in polyacrylamide gels using both a good solvent (water) and a theta solvent (methanol 30% – water 70% by volume) are reported. From these observations the variation of ξ_h, the hydrodynamic screening length in the gel, is obtained, and compared with ξ_{st}, the static screening length. The latter is obtained from measurements of the density of the polymer solutions. In the concentration range studied (3%–10%) and for pressures up to 3 kbar, both ξ_h and ξ_{st} diminish with increasing pressure (i.e. the solvent quality improves), but the variation of ξ_h is more than an order of magnitude smaller than ξ_{st} for both the poor and good solvent cases.

INTRODUCTION

Hydrostatic pressures are frequently applied to semipermeable membranes in processes such as reverse osmosis, for example for water desalination. Although the pressures employed are relatively modest (generally less than 100 bars), they may measurably affect the transport properties within the membrane. Membranes used for these purposes are usually cross-linked polymer networks, the solution properties of which closely resemble those of the equivalent uncross-linked polymer in solution.

Quasi elastic light scattering can be used to measure the diffusion coefficient which governs the swelling of gels[1,2], and has also been used to measure the stiffness, or longitudinal elastic modulus of certain gel systems[3,4]. Although there have been several (static light scattering) investigations reported in the literature of the effects of hydrostatic pressure on dilute solutions of polymers[5,6], little attention seems to have been paid to the semi-dilute region, where the concentration of the polymer is such that the coils lose their separate identity and overlap. In this region polymer solutions bear a strong resemblance to gels, the slow moving entanglements between coils playing a rôle equivalent to the gel cross-links.

The collective diffusion constant D_c and the longitudinal elastic modulus E of the gel, which are both obtained by quasi elastic light scattering methods, are related to the screening length ξ of the solution

$$D_c = kT/6\pi\eta\xi_h \tag{1}$$

$$E = 3kT/4\pi\xi_{st}^3 \tag{2}$$

where ξ_h refers to the hydrodynamic screening length[7–9], and ξ_{st} is that obtained from static measurements[10,11]. In the above expressions, k is Boltzmann's constant and η is the solvent viscosity. The factor $3/4\pi$ in equation 2 is found to agree quite well with the experimental data[4]. At finite polymer concentrations ξ_h has a slightly weaker concentration dependence than ξ_{st}. One might intuitively expect in a good solvent, where the polymer segments display an affinity for the solvent molecules in preference to other polymer segments), that on account of the already favourable packing arrangement, the effect of an additional hydrostatic pressure will be small. Large effects, however, might be expected in poor solvents, because of the repulsive potential between polymer and solvent, which could cause precipitation as the pressure is increased.

Since the behaviour under pressure of liquid solutions is governed by the changes in volume occupied by each component, lattice models, in which such changes are set equal to zero, must therefore fail. It is customary[5,6] to analyse influence of pressure in terms of corresponding states theory[12].

Here we report dynamic light scattering measurements of two sets of gels under pressure, one in a moderately good solvent, and the other in a poor solvent. The gels used were polyacrylamide, cross-linked with N,N′ methylene bisacrylamide, in water and also in a mixture of methanol 30% (by volume) with water. The range of pressure explored was between 1 and 3000 bars. The theta temperature of the PA–methanol (30%)–water system is close to 15°C.

THEORY

For one g of polymer solution (assuming that the solvent consists of a single component) the change in Gibbs free energy is

$$dG = -SdT + VdP + \mu dw \tag{3}$$

where S, T, V and P are entropy, temperature, volume and pressure respectively, and μ is defined as[13]

$$\mu = \mu_1/M_1 - \mu_2/M_2 \tag{4}$$

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0032-3861/81/070877-05$02.00

Here μ_1 and μ_2 are the excess chemical potentials of the polymer and the solvent in the solution respectively, and M_1 and M_2 their corresponding molecular weights. The variable w represents the polymer weight fraction. Although equation 3 does not strictly apply to the PA–methanol–water system because of its ternary nature, the approximation involved is probably quite good for the present purposes, since water and methanol are good mutual solvents, while neither is so strongly attracted to polyacrylamide; we therefore neglect preferential absorption effects, and consider the mixed solvent to act as single fluid. The following Maxwell relation then holds

$$\frac{\partial \mu}{\partial P}_{T,w} = \frac{\partial V}{\partial w}_{T,P} \tag{5}$$

Now the intensity of the light scattered by the concentration fluctuations in a gel is proportional to[14]

$$\frac{I}{I_0} \propto \frac{kT}{\rho \partial\mu/\partial w}\left(\frac{\partial \varepsilon}{\partial w}\right)^2 \tag{6}$$

or alternatively[1]

$$\frac{I}{I_0} \propto \frac{kT w^2}{E}\left(\frac{\partial \varepsilon}{\partial w}\right)^2 \tag{7}$$

where E is the longitudinal elastic modulus of the gel and ε is the dielectric constant. It follows from equations 5, 6 and 7 that

$$\begin{aligned}\frac{\partial E}{\partial P} &= \frac{\partial}{\partial P}\left(\rho w^2 \frac{\partial \mu}{\partial w}\right)\\ &= E\kappa + w^2 \rho \frac{\partial^2 V}{\partial w^2}\end{aligned} \tag{8}$$

where ρ represents the density of the solution and κ its total bulk compressibility. To obtain equation 8 use is made of the fact that the polymer weight fraction is invariant under pressure. The values of E encountered here lie in the range 10^4–10^5 dynes cm^{-2}, while the bulk compressibilities are principally due to the solvent, and hence have values in the region of 10^{-10} cm^2 dyne^{-1}. The second term can be expressed in terms of the more familiar density variation, so that

$$\frac{\partial E}{\partial P} = E\kappa + \frac{w^2}{\rho}\left\{\frac{2}{\rho}\left(\frac{\partial \rho}{\partial w}\right)^2 - \frac{\partial^2 \rho}{\partial w^2}\right\} \tag{9}$$

In an ideal mixture of fluids the volumes of the constituent parts are additive, so that $\partial^2 V/\partial w^2$ is zero, and the term

$$\left\{\frac{2}{\rho}\left(\frac{\partial \rho}{\partial w}\right)^2 - \frac{\partial^2 \rho}{\partial w^2}\right\}$$

in equation (9) vanishes. In a less than ideal solution, this term becomes negative, while in a good solution it is positive. In general, $E\kappa$ is negligible compared to the second term in equation (9), so that the pressure variation of E is a sensitive indicator of the polymer–solvent interaction.

Because of technical considerations connected with the small size of the optical windows of the pressure cell, the intensity of the dynamically scattered light, and hence E, could not be reliably measured. What was measured instead was D_c, obtained from the rate of decay of the concentration fluctuations,

$$\Gamma = D_c K^2 \tag{10}$$

where K is the scattering wave vector.

EXPERIMENTAL PROCEDURE

The pressure cell, which was made of stainless steel and furnished with a choice of either sapphire or quartz windows, could withstand pressures in excess of 3000 atmospheres. The pressure transmitting fluid was chosen to be the same as the gel solvent (i.e. water or water–methanol), with a thin rubber membrane separating the gel from the fluid. This arrangement avoids the contamination that could occur if a gas were used as the pressure transmitting fluid. The whole cell was housed in a thermal jacket through which water could be circulated, and the temperature could be stabilized to within 0.5°C. The pressure was generated with a Nova single stroke hand pump, and was measured by a calibrated Bourdon gauge.

The light scattering equipment was standard, and has been described elsewhere[15]. The measurements were made at 454.5 nm using an argon ion laser (SP 164), with 90° geometry. The short wavelength of the incident light was chosen to discriminate against slower relaxation modes which tend to appear in the presence of poor solvents[16,38]; all the spectra observed, however, were close to being single exponentials. By using an interferometric configuration[17], we were able to confirm that the spectra obtained from the gels were in the heterodyne mode.

To correct for the variation in viscosity and refractive index of the solvent, light scattering spectra of polystyrene latex suspensions in the methanol–water solution were also measured as a function of temperature and pressure. The spectra were found to be homodyne. Difficulties were however encountered in this latter measurement, since the methanol–water solution dissolved the epoxy resin glue used to retain the pressure windows in place: the latex suspension became rapidly contaminated and the correlation spectra unusable. This obstacle was circumvented by placing a watertight housing round each window to prevent leakage of the impurities into the body of the cell; any residual contamination was minimized by performing the measurements immediately after injecting the suspension into the pressure cell. This difficulty was not encountered for the gels, since the rate of diffusion of the epoxy debris is negligible within the gel.

In the measurements on the latex suspensions, possible heterodyning from the stray light in the cell is a source of error. Because of the requirement stated above to perform these particular measurements quickly, it was not feasible to check for absence of heterodyning by performing an interferometric heterodyne experiment. Instead, a comparison was made between the viscosity of the water–methanol mixture obtained for different temperatures using a viscosimeter, and that calculated from the light scattering spectrum of the latex suspension in the same solvent at zero pressure. The two results were in good agreement, thus confirming the hypothesis of homodyne scattering.

In order to reduce multiple scattering within the cell in the gel with the poor solvent, the optical path of the laser beam was reduced by using two one-centimeter long quartz windows as entrance and exit window; the optical path through the gel was thereby reduced to 0.4 cm.

Concerning the measurement of the density of a series of gels difficulties were encountered associated with the volume changes and the formation of bubbles when the gel sets. These bubbles and the difficulties of cleaning the containing tube exclude the vibrating tube technique. The floating drop technique is open to criticism on account of the high sol fraction found in gels with a large surface area. We adopted the traditional pycnometer method, but using a series of *solutions* of PA in water and in methanol–water as opposed to the equivalent gels, on the assumption that the small amounts of cross-linking agent used (1 part in 75 by weight of polymer) would affect the solution density negligibly. This assumption was borne out by the agreement between previous measurements of the gel density[3] and the present ones. Use of the density bottle allowed the solution to be gently centrifuged to eliminate any bubbles introduced during the filling of the bottle, or appearing during the heating of the sample. The PA used for this purpose was made from the same batch of acrylamide as the gels, but without N N′ methylene–bisacrylamide; after polymerization and dilution with water the polymer was precipitated at 28°C using acetone. This operation was repeated to eliminate unreacted monomers and oligomers, and then the solution was lyophylized. The resulting polymer had a large polydispersity $M_w/M_n \simeq 1.5$ with $M_w = 10^6$ daltons. The solutions were allowed to come to equilibrium for several weeks, then transferred to the density bottle, which was placed in copper jacket thermostated to within 0.2°C. Any bubbles were removed by centrifugation at 1500 rpm.

The results are: for the concentration range $w = 0$ to 0.1 the densities were found to be linear in w, as follows:

PA–water 25°C $\rho(w) = 0.9967 + 0.3201\ w$ (11a)
PA–methanol–water 11.7°C $\rho(w) = 0.9647 + 0.3178\ w$ (11b)
PA–methanol–water 22.1°C $\rho(w) = 0.9603 + 0.3104\ w$ (11c)
PA–methanol–water 34.7°C $\rho(w) = 0.9544 + 0.2769\ w$ (11d)
PA–methanol–water 47.7°C $\rho(w) = 0.9460 + 0.2832\ w$ (11e)

The theta temperature of the PA-methanol-water system was determined by observing the cloud points of a set of semi-dilute solutions of varying concentration and then extrapolating to zero concentration. The temperature found was close to 15°C.

RESULTS AND DISCUSSION

According to equation 1 the gel diffusion coefficient is inversely proportional to the solvent viscosity. Corrections must be made for the pressure dependence of this parameter, as well as for possible variations in the refractive index n, which enters equation 10. For the relatively low concentration samples studied here, the refractive index is close to that of the pure solvent, and the error is not large if the refractive index correction is made for the solvent alone. For pure water, the variation of both η and n are available in the literature [18,19]. For the water–methanol mixture, the quasi-elastic light scattering spectra of calibrated polystyrene beads (Dow Chemical) in this mixture were measured as a function of pressure. This gives

$$\Gamma = \frac{n^2 K_0^2 kT}{6\pi\eta R} \tag{12}$$

where R is the radius of the beads (54.5 nm), the variation of which is taken to be negligible over the pressure range investigated. As stated in the previous section these measurements were made in the homodyne mode (*Figure 1*).

The light scattered from the gels however, was heterodyne. In *Figures 2* and *3* the values of $1/\xi_h$ obtained from these measurements corrected for the variation of η and n are shown. It is clear that for the gels in the good solvent (water), the variation of $1/\xi_h$ with pressure is rather small while in the poor solvent it is marked.

Although measurements of the scattered light intensity were not made, qualitative observations clearly showed that for the gel in the poor solvent, the scattered intensity fell markedly as the pressure increased. This observation is in agreement with measured variation of $1/\xi_h$. It differs however from the results of theta systems in the dilute regime[5,6], where increasing pressure was found to lower the quality of the solvent and to tend to precipitation.

To permit a quantitative appreciation of the present results, comparison should be made with equation 9 and the measurements of $\rho(w)$. At all the observed temperatures, $\rho(w)$ was found to be linear in w, both for the good solvent and for the water–methanol mixture. This means that $\partial^2 V/\partial w^2$ is positive in each case, and both solvents are better than ideal.

It follows from the linearity of $\rho(w)$ that the second derivative in equation 9 is zero, and as the first term is negligible, one obtains for PA–methanol–water at 22.5°C

$$\frac{\partial E}{\partial P} = 0.192\ w^2/\rho^2 \tag{13}$$

To appreciate the relative magnitude of this effect, we require a knowledge of E. In a poor solvent it is theoretically expected[20], and found experimentally[4] that

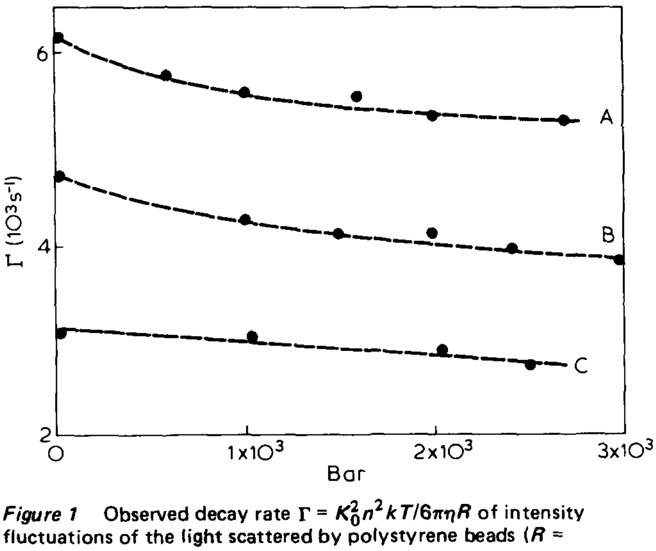

Figure 1 Observed decay rate $\Gamma = K_0^2 n^2 kT/6\pi\eta R$ of intensity fluctuations of the light scattered by polystyrene beads (R = 54.5 nm) in methanol (30%)—water as a function of pressure and temperature

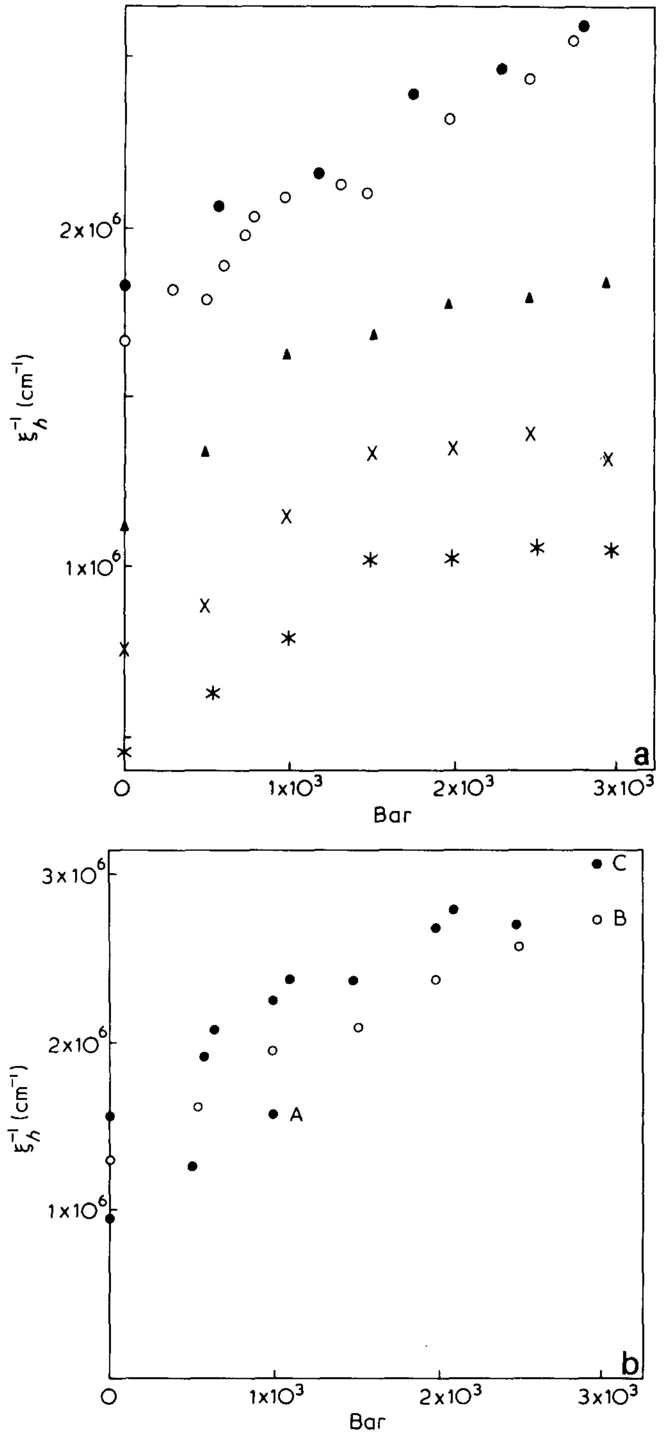

Figure 2 Pressure dependence of the inverse dynamic correlation length ξ_h^{-1} obtained from the observed decay rate of the concentration fluctuations in PA–methanol–water gels using equations 1, 10 and the values of n^2/η found from *Figure 1*. (a), w = 0.067; *, 11.9°C; X, 15.5°C; ▲, 24.6°C; ○, 34.3°C; ●, 44.6°C; (b), w = 0.112; (A), 11.4°C; (B), 16.2°C; (C), 21.0°C

the longitudinal elastic modulus E is proportional to w^3. Furthermore, it is found experimentally[21] that in a poor solvent E is equal to twice the shear elastic modulus μ of a gel. Measurement of μ in gels of two different concentrations using 30% methanol–water as a solvent at 20°C gave for the proportionality factor relating E to w

$$E = 5.9 \times 10^7\ w^3 \text{ dynes cm}^{-2} \qquad (14)$$

Combining equations 2, 13 and 14 gives

$$\begin{aligned}\frac{\partial(1/\xi_{st})}{\partial P} &= 0.131\,(T)^{-1/3} \\ &= 2.0 \times 10^{-2} \text{ cm dynes}^{-1}\end{aligned} \qquad (15)$$

at room temperature (poor solvent).

The static measurements leading to equation 15 may be compared with the numerical values of $\partial(1/\xi_h)/\partial P$ obtained from the dynamic measurements of *Figure 2*. In the poor solvent at 6% gel concentration one finds from the initial slopes

$$\partial(1/\xi_h)/\partial P = 3.6 \times 10^{-4} \text{ cm dynes}^{-1}$$

while for the 10% gel (16)

$$\partial(1/\xi_h)/\partial P = 6.0 \times 10^{-4} \text{ cm dynes}^{-1}$$

Both these values are more than an order of magnitude smaller than the slopes found from the static measurements. Also while the slope of ξ_{st}^{-1} with pressure is independent of the polymer concentration, the slope obtained from the dynamic measurements increases with increasing concentration.

In the good solvent case the exponent 3 in equation 14 should be replaced by 9/4, because of the presence of excluded volume[22]. Experimental measurements on the PA–water system at room temperature[3] give

$$E = 1.06 \times 10^8\ w^{2.35 \pm 0.06} \qquad (17)$$

(In what follows we shall neglect this small discrepancy between the experimental and theoretical exponents). The experimentally observed variation of $\rho(w)$ is almost identical to that of PA–methanol–water equation 11, so that equation 13 remains valid for the good solvent case.

Combination of equations 2, 13 and 17 gives

$$\partial(1/\xi_{st})/\partial P = 1.34 \times 10^{-2}\ w^{1/2} \text{ cm dynes}^{-1} \qquad (18)$$

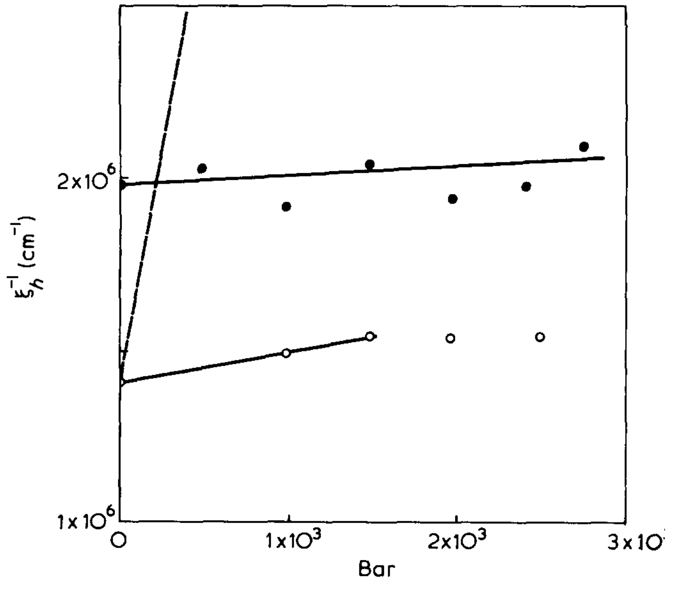

Figure 3 Pressure dependence of the inverse dynamic correlation length ξ_h^{-1} obtained from the observed decay rate of the concentration fluctuations in PA–water gels at 20°C, using equations 1 and 10 and the data of references 18 and 19 to correct for the variation with pressure of n and η. ○, w = 0.032; ●, w = 0.066. The broken line represents the initial pressure dependence of ξ_{st}^{-1} calculated from equations 2, 9 and 11a for the w = 0.032 sample at 20°C (equation 18)

at 20°C (good solvent). For the 3% sample, this gives a slope of 2.3×10^{-3} cm dynes^{-1}, and 3.2×10^{-3} cm dynes^{-1} for the 6% sample. These values are to be compared with $8.4\ 10^{-5}$ and $3.1\ 10^{-5}$ respectively in the same units for the dynamic slopes. In the last quoted result, however, the scatter in the experimental values causes an error which is comparable to the magnitude of the effect. The square root dependence on w of the static slope does not show up in the dynamic measurement; rather $\partial \xi_h^{-1}/\partial P$ *decreases* on increasing the polymer concentration.

The salient feature of these measurements is that for the theta system investigated, the solvent improves with increasing pressure. This is the reverse of the behaviour reported by Lechner[5b] for several dilute theta systems, where in each case the quality of the solvent becomes worse with increasing pressure. This reversal, however, is not too alarming. A similar change in sign of the excess volume of dilution, which determines the pressure properties of the solution, occurs with polystyrene–cyclohexane: at low concentrations the excess volume is positive[5], while at higher concentrations it is negative[23,24]. In contrast, other systems, such as polystyrene–*trans*–decalin, have positive dilution volumes which extend from the dilute into the concentrated regime[6,25–27]. Changes in sign of the volume of dilution are difficult to account for in the Flory theory.

In conclusion, in dilute theta systems, application of hydrostatic pressure causes the quality of the solvent to get worse[5,6], thereby raising the theta temperature. In the semi-dilute regime, for polystyrene–cyclohexane (as deduced from density measurements $\rho(w)$[23,24]) and for the system studied here, PA–methanol–water, this tendency is reversed. Although the static and dynamic screening lengths respond in the same way to applied hydrostatic pressure, quantitatively the dynamic screening lengths vary much more slowly than the static screening lengths. The effect of varying the polymer concentration on the pressure dependence of these parameters is quite different in the dynamic and the static cases. The present observations show that while fairly modest pressures will have a notable effect on the static properties of the gels (i.e. cause an increase in the elastic modulus E and the osmotic pressure), the dynamic properties are affected much more weakly for the range of concentrations we have explored.

An interesting feature which is unexplained is the appearance of a pronounced knee of $\xi_h^{-1}(P)$ in PA–methanol–water above a certain critical pressure. This may be connected with the crossover between the poor and good solvent regions[20]. In the PA–water curves, the scatter in the experimental points is too large to permit such a decomposition into two regions.

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