Phase Transition in Swollen Gels. 2. Effect of Charge Concentration on the Collapse and Mechanical Behavior of Polyacrylamide Networks[†]

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ABSTRACT: The mechanical and swelling behavior of ionized networks of copolymers of acrylamide with a small amount of sodium methacrylate (molar fraction of sodium methacrylate $x_{\mathrm{MNa}} = 0$–0.024) in acetone–water mixtures at pH 7.5 was investigated. In the range $x_{\mathrm{MNa}} \geq 0.008$, a phase transition of the gels was detected; the extent of the transition Δ (given by the difference in the volume change of the network) and the critical value of the interaction parameter χ_c in the transition (given by the composition of the acetone–water mixture) can be described in terms of a molecular theory suggested earlier describing the swelling equilibria of polyelectrolyte networks. The modulus value in the phase transition also exhibited a jumpwise change adequately correlated to a volume change in the network collapse.

The coexistence of two polymer phases differing in the chain conformation and concentration of segments in the swollen polymer network has been predicted theoretically[1-3] and proved experimentally on polyacrylamide (PAAm) networks swollen in acetone–water mixtures.[4-7] The decisive role in the formation of phase transition (collapse) of PAAm networks was played by the time of gel ageing[4-6] (or curing). The original explanation[4] that the network density ν markedly increases with the gel ageing has not been confirmed experimentally; mechanical experiments showed that ν remains constant with curing.[6] The most recent experiments have demonstrated the presence of charges (due to the hydrolysis of the PAAm chain) in the collapse of PAAm gels;[7,8] also, theoretical analysis of the Flory equation,[9] originally suggested in 1953 for free energy of an ionized swollen network, ΔF, demonstrated the conclusive effect of charges on the existence of the phase transition.[7]

In our preceding paper[10] based on a quantitative analysis of a more advanced theory of swelling equilibria of polyelectrolyte networks (including both the reference state of the polymer network and the change in the free energy of electrostatic interactions with swelling), the possible existence of a phase transition in the PAAm gels was analyzed; it was found that approximately 1 mol% of the charges on the PAAm chain affects the free energy ΔF to such a degree that the gel may collapse. So far, however, there are no quantitative experimental data between the occurrence of the collapse and its intensity, on the one hand, and the charge concentration on the chain, on the other. Also, the mechanical behavior during the collapse has not yet been studied, and it can be expected that the jumpwise change in the gel volume will cause a jumpwise change also in other physical characteristics and, consequently, in the modulus.

This paper is concerned with an investigation of the effect of charge concentration on the intensity and position of the collapse and also on the mechanical behavior of PAAm gels in acetone–water mixtures. The charge concentration on the PAAm chains is quantitatively controlled by the copolymerization of acrylamide with a low amount of sodium methacrylate and by a suitably chosen pH value of the mixture.

Experimental Section

Sample Preparation. The gels were prepared by using 5 g of acrylamide (AAm), 0.135 g of *N,N'*-methylenebis(acrylamide) (MBAAm), 20 mg of ammonium persulfate, and 20 mg of sodium pyrosulfite (the latter was used instead of the usual tetramethylenediamine in order to suppress as much as possible the spontaneous hydrolysis of the PAAm chain, enhanced by the basic character of tetramethylenediamine[4,5]). Six series of networks were prepared—A, B, C, D, E, and F—in which the molar fraction of sodium methacrylate x_{MNa} was, respectively, 0, 0.004, 0.008, 0.012, 0.016, and 0.024. All ingredients, with the exception of sodium pyrosulfite, were dissolved in water, and the solutions were flushed with nitrogen, after which pyrosulfite was added and the solution was taken to a 100-mL volume. On stirring, the solution was dosed into test tubes ~1 cm in diameter; the test tube contents was again flushed with nitrogen, and the tubes were sealed. At room temperature the polymerization proceeded ~3 h; after that, the gels were removed from the test tubes and cut into samples ~1 cm long.

Swelling. Acetone–water solutions in the range 0–80 vol % acetone prepared from redistilled water and acetone (analytical purity grade) were used for swelling (Table I). Swelling in mixtures with a low content of acetone (<50 vol %) was carried out on samples immediately after completion of polymerization. About half of the samples were partly dried after polymerization and used for swelling in mixtures with a high content of acetone (>40 vol %); if the samples were used directly after polymerization, in mixtures with a high content of acetone, heterogeneities appeared due to microsyneresis, and the samples remained unhomogenized even after 2 months' time. On the other hand, direct swelling of dried samples in mixtures with a low content of acetone caused destruction of the networks as a result of the fast swelling of the sample surface. Series A was swollen for 2 weeks in water–acetone mixtures prepared earlier (pH ~6–6.5) and also in mixtures with pH adjusted to 7.5. The other series were first swollen 7 days in the original mixtures, and after that the pH of the mixture was adjusted to 7.5 with concentrated NaOH (pH 7.5 guarantees that in the networks B–F the degree of ionization α equals the molar fraction of sodium methacrylate x_{MNa}, with an accuracy better than 0.5% of the originally weighted amount). After another 7 days of swelling (measurement of the time dependences of the gel weight showed that such a time was sufficient for attaining equilibrium swelling), the swelling ratio X, related to the state of network formation, was determined from the relation

$$X = (D^*/D)^3 = V^*/V \tag{1}$$

where D and D^*, respectively, are the sample diameters after swelling in mixtures and after preparation and V and V^*, respectively, are the sample volumes after swelling in mixtures and after preparation. The sample diameters were measured with an Abbé comparator (Zeiss Jena, accuracy ±0.002 mm); the X values summarized in Table I are the average from at least four measurements.

Mechanical Measurements. The deformation experiments in a simple compression were carried out with an apparatus described earlier[11] at room temperature on the same samples as those used in the swelling measurement. A cylindrical sample was compressed between Teflon surfaces in the respective ace-

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[†] For part 1, see: Ilavský, M. *Polymer* 1981, *22*, 1687.

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Table I
Swelling and Deformation Characteristic

acetone, vol %	A[a] log X^f	A[a] log G^d	A[b] log X^f	A[b] log G^d	B[c] log X^f	B[c] log G^d	C[c] log X^f	C[c] log G^d	D[c] log X^f	D[c] log G^d	E[c] log X^f	E[c] log G^d	F[c] log X^f	F[c] log G^d
0	-0.246	1.290	-0.249	1.245	-0.534	1.220	-0.782	1.188	-0.901	1.245	-0.997	1.240	-1.141	1.225
5	-0.213	1.312	-0.238	1.255	-0.490	1.199	-0.790	1.161	-0.894	1.260	-0.994	1.239	-1.078	1.321
10	-0.187	1.315	-0.190	1.278	-0.477	1.236	-0.746	1.217	-0.843	1.307	-0.992	1.277	-1.045	1.348
15	-0.177	1.314	-0.159	1.292	-0.490	1.290	-0.713	1.220	-0.862	1.283	-0.957	1.294	-1.004	1.405
20	-0.137	1.362	-0.117	1.329	-0.366	1.274	-0.685	1.238	-0.801	1.352	-0.943	1.280	-1.021	1.355
25	-0.044	1.406	-0.040	1.377	-0.421	1.322	-0.629	1.352	-0.798	1.336	-0.900	1.331	-0.987	1.397
30	0.075	1.461	+0.077	1.493	-0.340	1.343	-0.535	1.320	-0.789	1.301	-0.866	1.334	-0.970	1.407
35	0.304	1.669	0.268	1.632	-0.221	1.412	-0.470	1.400	-0.709	1.408	-0.803	1.398	-0.923	1.442
38	0.536	1.705	0.566	1.789	-0.115	1.477	-0.244	1.646						
40	0.654	1.763	0.666	1.861	+0.286	1.648	-0.267	1.533	-0.661	1.533	-0.706	1.431	-0.871	1.484
42	0.708	1.966	0.740	1.881	0.723	1.845	-0.118	1.593[e]						
							0.534	2.102[e]	-0.621	1.378	-0.674	1.445		
									-0.501	1.480[e]				
45	0.816	2.078	0.857	2.085	0.818	2.020	0.800	2.223	0.604	2.389[e]	0.609	1.436	-0.793	1.512
											-0.472	1.505[e]		
47	0.929	2.104	0.905	2.073	0.877	2.176	0.862	2.365	0.807	2.456	0.725	2.462[e]	-0.605	1.566
													-0.591	1.528[e]
50	0.915	2.163	0.945	2.091	0.927	2.368	0.935	2.393	0.888	2.451	0.873	2.596	0.834	2.518[e]
53									0.961	2.523	0.931	2.428	0.934	2.585
55	0.998	2.225	0.985	2.197	0.981	2.373	1.001	2.464	0.989	2.581	0.938	2.491	0.950	2.541
58													0.983	2.539
60	1.067	2.342	1.033	2.321	1.015	2.438	1.069	2.546	1.033	2.701	1.007	2.569	1.023	2.581
65	1.074	2.378	1.062	2.445	1.054	2.529	1.103	2.591	1.074	2.699	1.060	2.649	1.058	2.568
70	1.122	2.455	1.120	2.571	1.097	2.586	1.122	2.644	1.102	2.780	1.097	2.613	1.077	2.565
75	1.145	2.534	1.143	2.726	1.129	2.688	1.152	2.727	1.120	2.809	1.103	2.680	1.111	2.655
80	1.157	2.678	1.181	2.917	1.168	2.966	1.165	2.867	1.175	3.021	1.140	2.776	1.150	2.887

[a] Swollen 14 days at pH ~6. [b] Swollen 14 days at pH 7.5. [c] Swollen 7 days at pH ~6 and 7 days at pH 7.5. [d] Values of the modulus G in g cm^{-2}. [e] Values at the phase transition. [f] Swelling ratio determined by eq 1.

Table II
Basic Characteristic and Parameters of Phase Transition

series	x_{MNa},[a] mol %	$\nu_e \times 10^5$,[b] mol cm^{-3}	log G^c	log X^d	Y_1^e	Y_2^f	Y_3^g	χ_c^h	Δ^i
A	0	2.6					0.414		
B	0.004	3.5			0.031	0.030	0.310		
C	0.008	5.1	0.509	0.652	0.018	0.029	0.162	0.600	0.170
D	0.012	6.3	0.909	1.105	0.027	0.014	0.131	0.635	0.240
E	0.016	7.0	0.957	1.197	0.018	0.015	0.141	0.668	0.295
F	0.024	8.0	0.990	1.425	0.037	0.027	0.180	0.720	0.348

[a] Content of sodium methacrylate in the polymerization mixture. [b] Network density eq 3. [c] Change in the modulus at collapse. [d] Change in the volume at collapse. [e] Magnitude of time effect before collapse. [f] Magnitude of time effect after collapse. [g] Magnitude of time effect in the mixture of 80 vol % acetone. [h] Critical value of the interaction parameter determined by Maxwell's construction of experimental data. [i] Intensity of collapse determined by Maxwell's construction of experimental data.

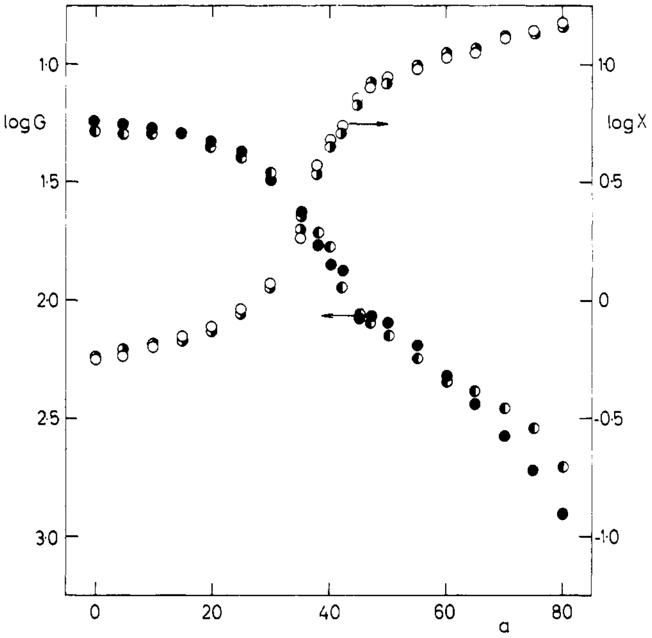

Figure 1. Dependence of the swelling ratio X (○, ◑) and modulus G (g cm^{-2}) (●, ◐) on the acetone content a (vol %) in the mixture acetone–water for networks of series A: (○, ●) networks swollen at pH 7.5; (◑, ◐) networks swollen at pH ~6.

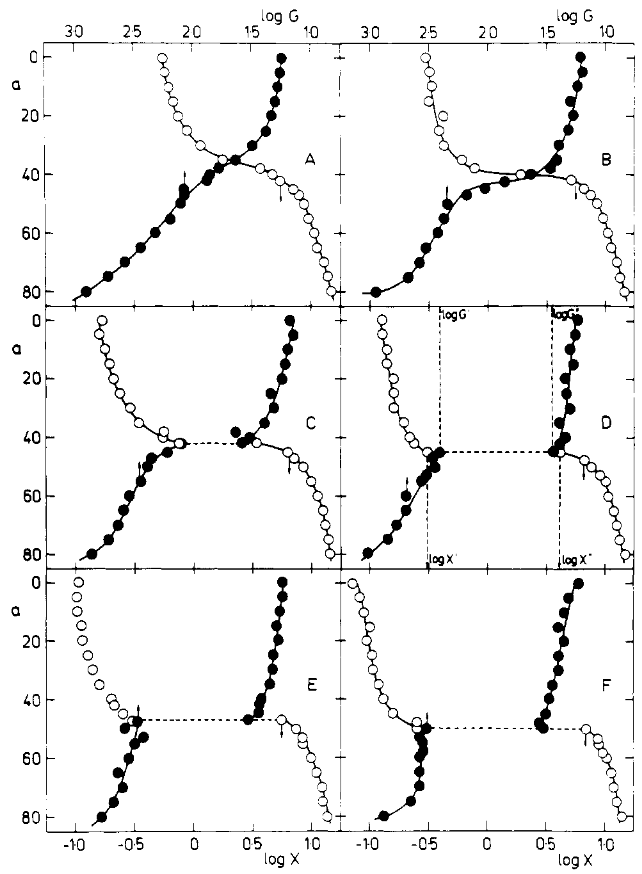

Figure 2. Dependence of the swelling ratio X and modulus G (g cm^{-2}) on the acetone content a (vol %) in the mixture acetone–water with pH 7.5: (○) X; (●) G.

tone–water mixture through which nitrogen was passing. The force was recorded with a force transducer, range 1 kg (Hottinger Baldwin Messtechnik); the deformation transducer operated with an accuracy of ±0.002 mm. Two types of experiments were performed: (a) Measurements of the time dependences of force $f(t)$ at constant deformation $\epsilon = (1 - \lambda) \approx 0.05$ ($\lambda = l/l_0$, where l and l_0, respectively, are the deformed and initial sample heights) were made in the time interval 10–3600 s. These measurements were used in the detemination of the time dependence of Young's modulus $E(t) = f(t)/\epsilon S_0$ (S_0 is the initial swollen cross section of the sample) and the fraction $Y = \log [f(10)/f(3600)]$ characterizing the magnitude of time effects in the mechanical behavior. The experiments were carried out on chosen samples, usually in the acetone–water mixture before the collapse and after it and in the mixture with 80 vol % acetone in all series of networks. (b) Measurements of the dependence of force f on compression λ each time after relaxation for 30 s at a given λ_i were made in the compression range $0.7 \le \lambda_i \le 1$. These measurements were used to determine the shear modulus G from the equation

$$G = f/S_0(\lambda^{-2} - \lambda) \qquad (2)$$

The G values given in Table I are the average from measurements on at least two samples.

Results and Discussion

Swelling and Mechanical Characteristics. Figure 1 shows that the dependence of the swelling ratio X on the acetone concentration in networks of series A is continuous and is not affected by the pH of the mixture. This allows one to infer that a gel swelling during 2 weeks at pH 7.5 does not virtually lead to detectable spontaneous hydrolysis of the PAAm chain. These results are in accord with those obtained earlier[4,6], in which gels after 15 days of ageing in water exhibited a continuous dependence of X on the composition of the mixture; with this time of curing, efficient hydrolysis occurs only at much higher pH values (~12) (cf. ref 5). While in series B with $x_{\mathrm{MNa}} = 0.004$ the dependence of X on the composition of the mixture is continuous, similar to series A, in the other series (C–F), with $x_{\mathrm{MNa}} \geq 0.008$, a collapse takes place, the extent of which (given by the magnitude of the change in volume during the collapse) and the acetone content in the mixture in which the collapse appears increase with increasing content of sodium methacrylate (Figure 2, Table I). Thus, the increasing content of sodium methacrylate is reflected qualitatively in the same way as the time of ageing of PAAm gels[4-8] (cf. Figure 1 in ref 7).

Figure 3, which shows photographs of samples of the individual series at the critical composition of the mixture where the phase transition takes place, also demonstrates the increasing change in the sample volume during collapse with increasing x_{MNa}; such an increase is mainly caused by the increasing swelling of networks in the expanded state. Along with collapsed and expanded samples, at the critical composition of the mixture there also exist samples which are partly expanded and partly collapsed (cf., e.g., sample 3 of series F at 50 vol % acetone, Figure 3). The existence of inhomogeneities in swelling indicates the coexistence of both the expanded and collapsed phases in a single sample. The coexistence of phases is probably stressed by inhomogeneities in the network density (as a consequence of high dilution at network formation), which also affects the critical composition of the mixture during the collapse (cf. the discussion below).

Similarly to the swelling ratio X, the dependence of the modulus G on the composition of the mixture in series A is independent of pH of the mixture (Figure 1). While in the range $x_{\mathrm{MNa}} \leq 0.004$ the dependence of G on the acetone concentration is continuous, at a higher content of sodium methacrylate G exhibits a jumpwise change in the collapse region, which increases with increasing x_{MNa} (similarly to the swelling ratio X, Figure 2).

The dependence of the modulus G on the swelling ratio X is shown in Figure 4. In networks of series A, log G increases with log X in the range of high swelling with the slope $s = 0.65$, which is twice that theoretically predicted by the kinetic theory of rubber elasticity[2] ($s = 0.33$). The increasing content of sodium methacrylate shifts the

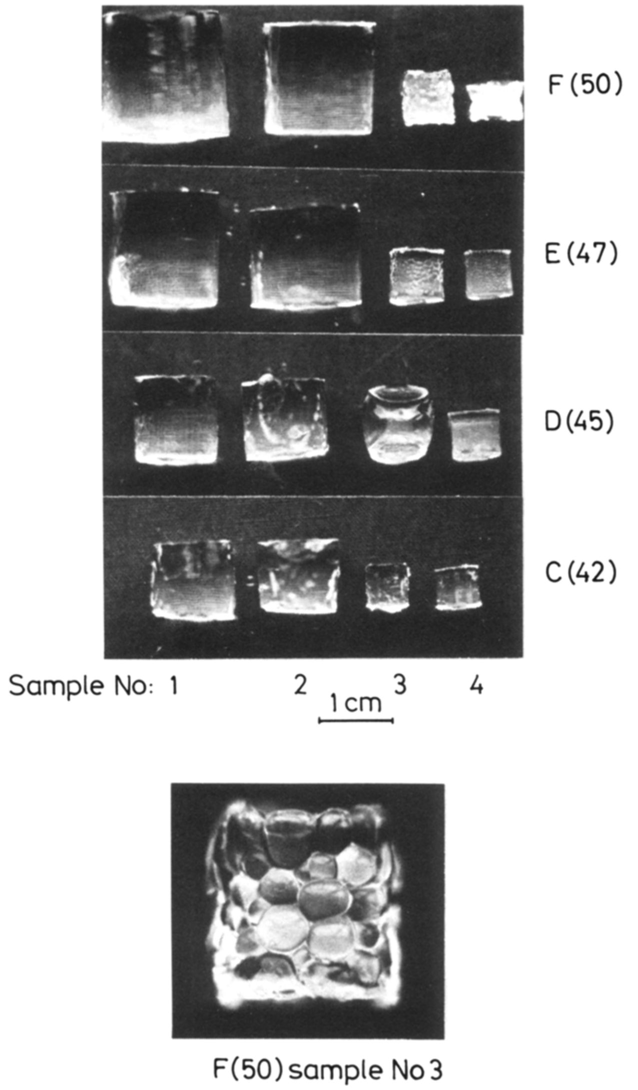

Figure 3. Sample dimensions determined at critical concentrations of the mixture acetone–water in which phase transition takes place. Capital letter denotes series of networks, and figure in parentheses denotes volume percent acetone in the mixture.

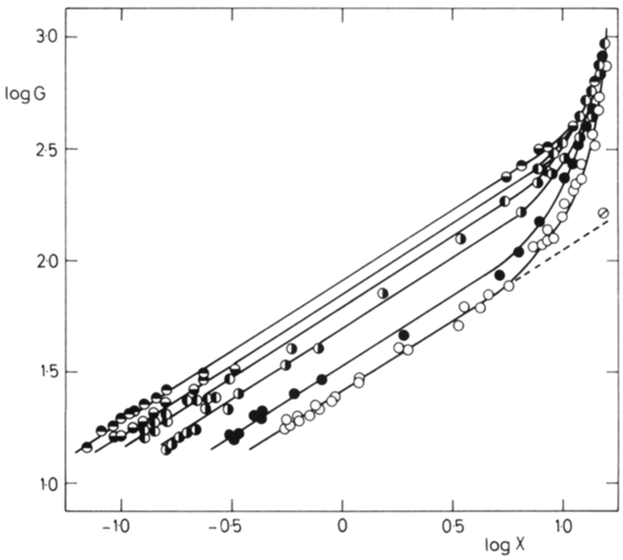

Figure 4. Dependence of the modulus G (g cm^{-2}) on the swelling ratio X for networks of series (○) A, (●) B, (◑) C, (◐) D, (◒) E, and (◓) F; (⊘) shows the extrapolated equilibrium G value of sample A swollen in the mixture with 80 vol % acetone.

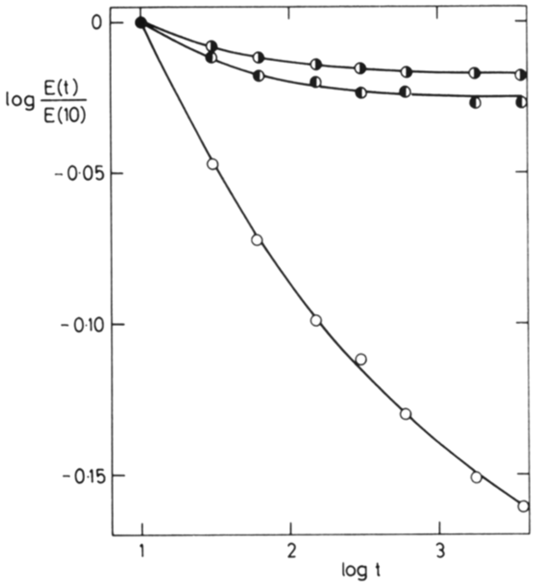

Figure 5. Dependence of the reduced modulus of networks of series C on time t (s) in various acetone–water mixtures. Acetone content (vol %): (○) 80; (◐) 45; (◑) 35.

modulus toward higher values; in all cases the log G vs. log X dependence in the range of large swelling is linear, with slope $s = 0.65$. Departures from the straight line in the range of low swelling, $X > 8$ (in these gels the volume $V_{\mathrm{pol}} \approx V_{\mathrm{solvent}}$), are due to the influence of the main transition region at high acetone concentrations.

A detailed measurement of the time dependences showed that the experimentally used regime, i.e., reading off the force values after 30 s of relaxation is sufficient to achieve equilibrium in samples with high swelling at $X < 8$. The mixture with 80 vol % acetone exhibited pronounced time dependences of the modulus (example in Figure 5); extrapolation to the equilibrium with an earlier procedure[12,13] has in all cases considerably reduced the modulus, virtually to the expected dependence (Figure 4). The same extrapolation procedure applied to samples in the range $X < 8$ gave extrapolated equilibrium values of the modulus that differed from those experimentally determined after 30 s of relaxation by less than 2.5%. The value $Y = \log [f(10)/f(3600)]$ characterizing the magnitude of time effects is also in agreement with such a conclusion (Table II). In samples of all series it holds that both immediately before (Y_1) and after (Y_2) the collapse $Y_1 \approx Y_2 \approx 0.025$ (decrease in the force by ~5% of the initial value, with more than half of the decrease occurring within the first 30 s), whereas in samples with 80 vol % acetone the corresponding value Y_3 is approximately 10 times higher (decrease in force by more than 70% of the initial value) and Y_3 decreases with increasing x_{MNa} as expected (cf. Figure 4).

The jumpwise change in the modulus occurring in the collapse and characterized by the parameter $\Delta(\log G)$ (=log $G'' - \log G'$, where G' is the modulus of the expanded gel at X' and G'' is the modulus after the collapse at X'' (cf. Figure 2D)) can be correlated with the volume change

$\Delta(\log X)$ ($= \log X'' - \log X'$) (Table II). As expected, the $\Delta(\log G)$ on $\Delta(\log X)$ dependence can, with good accuracy, be described by the slope determined earlier, $s = 0.65$ (i.e., $\Delta(\log G) \approx 0.65\Delta(\log X)$).

Using extrapolated values of the modulus G for $X = 1$, one can determine the concentration of elastically active network chains related to the dry state ν_e (Table II):

$$\nu_e = (G/RTv^0)\langle r^2\rangle_i/\langle r^2\rangle_0 \qquad (3)$$

where R is the gas constant, T is temperature, v^0 is the volume fraction of the polymer at network formation ($v^0 = 0.037$, calculated from the density of the dry polymer $\rho = 1.35$ g/cm^3), and $\langle r^2\rangle_i$ and $\langle r^2\rangle_0$, respectively, are the mean-square end-to-end chain distances in the isotropic and reference states.[2] Since G has been determined at $X = 1$, i.e., the state of measurement (isotropic) is the same as the state of network formation, it may be assumed[2,12] that $\langle r^2\rangle_i = \langle r^2\rangle_0$. $\nu_e = 2.6 \times 10^{-5}$ mol cm^{-3} of the PAAm network (series A) is in good agreement with the value determined earlier ($\nu_e = 2.9 \times 10^{-5}$ mol cm^{-3}) from torsional measurements.[6] ν_e increases approximately 3 times with increasing content of sodium methacrylate (Table II). The determined low experimental values of ν_e indicate the low efficiency of the cross-linking reaction (~6–20%), probably mainly as a result of large cyclization accompanying high dilution used in the network formation.

Comparison between Theory and Experiment. In our preceding paper[14] the inclusion of the effect of electrostatic interactions on the chain made possible a generalization of the kinetic theory of rubber elasticity and allowed us to derive relations describing the deformational, swelling, and potentiometric equilibria of polyelectrolyte gels. The swelling equilibrium is described in terms of the relation[10,14]

$$P = \phi_1 + \phi_2 + \phi_3 + \phi_4 \qquad (4)$$

where P is the swelling pressure, ϕ_1 is the contribution corresponding to mixing of the polymeric segments with the solvent (Flory–Huggins equation with the interaction parameter χ), ϕ_2 corresponds to the difference between the osmotic pressure in the gel and in solution (mixing of ions with the solvent), ϕ_3 corresponds to a change in the configurational free network energy with swelling, and ϕ_4 corresponds to a change in the free energy of electrostatic interactions with swelling. The detailed form of ϕ_i ($i = 1$–4) in molecular parameters is given by eq 2–5 in the preceding paper (cf. ref 10).

A characteristic feature of the coexistence of two phases and thus of the collapse of the swollen network consists in the van der Waals loop which appears in the dependence of P on the volume fraction of the polymer in the swolen state v_2 ($v_2 = v^0X = V_d/V_{sw}$, where V_d and V_{sw}, respectively, are volumes in the dry and swollen states). The composition of phases (v_2' and v_2'') is given by the condition[10]

$$\int_{v_2'}^{v_2''} Pv_2^{-2}\, dv_2 = 0 \qquad (5)$$

In the case of free swelling, eq 5 gives for v_2' and v_2''

$$\int_{v_2'}^{v_2''} (\tilde{\chi} - \chi_c)\, dv_2 = 0 \qquad (6)$$

where the dependence of the interaction parameter $\tilde{\chi}$ on the gel composition (given by v_2) is determined by eq 4 for $P = 0$. Equation 6 also determines the constant critical value of the interaction parameter χ_c (Maxwell's construction is carried out on the $\tilde{\chi}$ vs. v_2 dependence[10]) at which the collapse occurs. The difference $\Delta = v_2'' - v_2'$ can be regarded as a measure of the extent of the collapse.

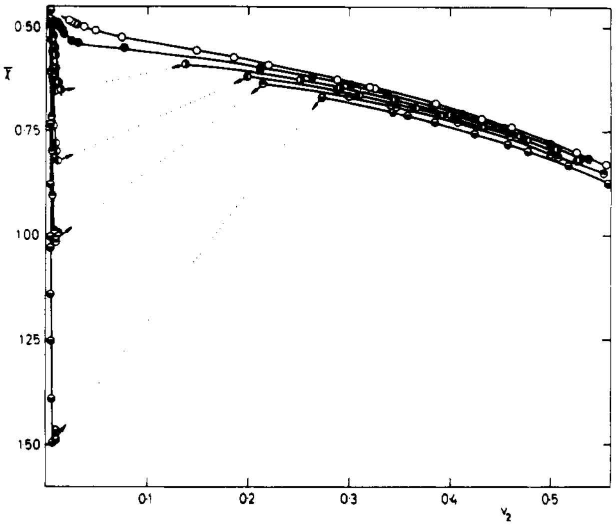

Figure 6. Dependence of the interaction parameter $\tilde{\chi}$ (eq 4 for $P = 0$) on the degree of swelling of gels. Samples denoted as in Figure 4.

Using the known molecular parameters, i.e., molecular mass of the monomeric unit $M_0 = 71$ g mol^{-1}, density of the dry polymer $\rho = 1.35$ g cm^{-3}, $T = 298$ K, $v^0 = 0.037$, dielectric constant $D = 80$, molar volumes V_1 of the mixture acetone–water (determined earlier[6]), experimental network densities ν_e, and the experimental degree of ionization $\alpha = x_{\mathrm{MNa}}$, the dependences of the interaction parameter $\tilde{\chi}$ on v_2 were calculated from experimental v_2 by means of eq 4 (due to free swelling, $P = 0$, Figure 6). In the range $\alpha \le 0.004$, $\tilde{\chi}$ increases monotonically with v_2; the increase in $\tilde{\chi}$ with v_2 (or with the polymer concentration in polymer solutions) is commonly observed in many polymer systems; in this case it is related to the solvent quality becoming increasingly poorer with increasing acetone content. In the range $\alpha \ge 0.008$ there is a discontinuity in the $\tilde{\chi}$ vs. v_2 dependence associated with the collapse of the gel. By applying eq 6 to the dependences in Figure 6, it was possible to determine the composition of the mixtures, i.e., v_2' and v_2'' (i.e., the extent of the collapse Δ) and the critical value of the interaction parameter χ_c (see the example given in Figure 7).

In series C–F, in which the collapse takes place, one can see (Figure 6) that $\tilde{\chi}$'s of expanded samples immediately before the collapse are higher than $\tilde{\chi}$'s of collapsed samples immediately after the transition. As a consequence, the experimental $v_{2,e}'$ values are higher than would correspond to the applied eq 6, and virtually reach the values of the minimum in the $\tilde{\chi}$ vs. v_2 dependence. On the other hand, the experimental $v_{2,e}''$ values are always lower after the collapse than the v_2'' values determined by Maxwell's construction and are shifted towards the maximum in the $\tilde{\chi}$ vs. v_2 dependence (see example for series D in Figure 7). Thus, the experimental values $v_{2,e}'$ and $v_{2,e}''$ lie in a metastable region, the limits of which, $v_{2,s}'$ and $v_{2,s}''$, are determined by the spinodal condition

$$(\partial P/\partial v_2)_{T,p} = 0 \qquad (7)$$

in which p is the external pressure. For instance, if eq 7

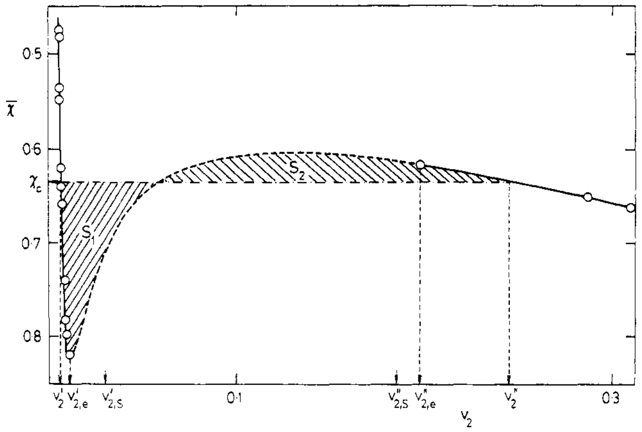

Figure 7. An example of Maxwell's construction in the dependence of $\bar{\chi}$ on v_2 (eq 6) used in the determination of the extent of the collapse $\Delta = v_2'' - v_2'$ and critical values of the interaction parameter χ_c of networks of series D: (○) experimental data; (---) course determined by eq 4 with $P = 0$ and critical parameters χ_c and Δ defined by the condition $S_1 = S_2$.

combined with eq 4 is applied to data in the series D, we have $v_{2,s}' = 0.0295$ and $v_{2,s}'' = 0.184$ (in eq 4, $\chi = 0.635$). The shift of $v_{2,e}'$ and $v_{2,e}''$ to the metastable region resembles the behavior of the van der Waals gas (supercooled gas and superheated liquid) and is associated with the manner in which the collapse was reached (i.e., by decreasing swelling in the region of the expanded state using samples directly after the polymerization and by raising swelling in the range of the collapsed state using partly dried samples). The temperature dependence of the results of swelling cured PAAm networks[4] in the mixture 44:56 vol % acetone–water also indicates a shift of $v_{2,e}'$ and $v_{2,e}''$ to the metastable region toward the spidonal determined by the light scattering measurement.

Due to the shift of $v_{2,e}'$ and $v_{2,e}''$ to the metastable region, the experimentally determined extent of the collapse Δ is smaller than the one determined experimentally by employing Maxwell's construction (Figure 8). Also, in all cases the critical values of the interaction parameter χ_c found by applying eq 6 to experimental data are somewhat higher than the respective χ of the mixture acetone–water at which the collapse takes place and which have been determined for the PAAm network alone (Figure 8).

The $\bar{\chi}$ vs. v_2 dependence also allows one to infer that the inclusion of electrostatic effects (mixing of ions with the solvent ϕ_2 and a change in electrostatic interactions with swelling ϕ_4) in relation 4 describing the swelling equilibrium of polyelectrolyte gels has led to $\bar{\chi} = 0.46$–0.48 for gels of all series, A–F, swollen in water alone. The same values, $\bar{\chi} = 0.47$–0.48, were obtained for the system PAAm–water earlier,[6] both from measurements carried out on networks and from viscosity measurements in PAAm solutions. The agreement between the $\bar{\chi}$ values for series B–F in water can be expected, because $\bar{\chi}$ expresses the measure of polymer–diluent affinity, when all charges are screened and one cannot expect that the low content of sodium methacrylate will affect $\bar{\chi}$ to any marked extent. Thus, eq 4 describes the swelling equilibria of ionized PAAm networks better than the relation without electrostatic interactions used earlier[6] (only mixing of polymeric segments with the diluent ϕ_1 and a change in the configurational network energy with swelling ϕ_3 have been considered; i.e., $\phi_1 + \phi_3 = 0$), which gives high negative $\bar{\chi}$ values for cured PAAm networks in pure water and in mixtures with a low acetone content. It was the existence of such negative $\bar{\chi}$ that actually suggested the two-phase model describing the swelling of cured PAAm networks in acetone–water mixtures.[6] It is obvious that in order to remove the negative $\bar{\chi}$ values it is sufficient to include electrostatic interactions into the swelling pressure, without any need to consider the two-phase model as in the earlier case.[6]

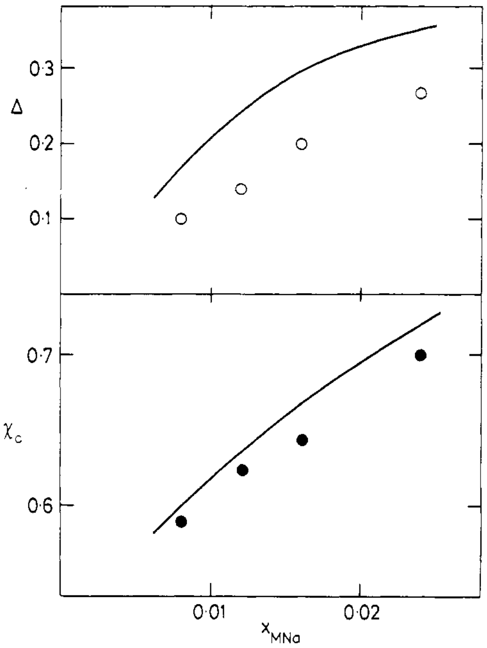

Figure 8. Dependence of the extent of the collapse Δ and of the critical value of the interaction parameter χ_c on the content of sodium methacrylate x_{MNa}: (—) course determined by Maxwell's construction of experimental data $\bar{\chi}$ vs. v_2 (cf. Figure 5); (○) experimental $\Delta = v_{2,e}'' - v_{2,e}'$; (●) correspond to χ of the acetone–water mixture in which the collapse is observed.

Various opinions exist in the current literature on changes occurring in the course of the ageing of aqueous PAAm solutions (reflected, for example, in a decrease in their viscosity with time) as long-term conformational changes,[15] degradation processes caused by radicals[16] or by microorganisms,[17] disentanglement of polymer chains,[18,19] etc. Recent light scattering experiments have shown[20] that the ageing in water brings about only hydrolysis of the PAAm chain; though hydrolysis at room temperature is very slow, it proceeds more rapidly at elevated temperatures. Indeed, potentiometric titration has revealed[21] the existence of acid groups in an amount lower than 1% in a solution of linear PAAm, but more titration data are needed, especially in the course of ageing. Nevertheless, we believe that during the ageing of PAAm solutions and also of gels chiefly the hydrolysis of the amide groups takes place; naturally, pH of the environment and the temperature of ageing determine the velocity and extent of hydrolysis. In this respect it is interesting to note that swelling data[8] obtained for cured PAAm gels up to 90 days (also for short curing times where phase transition does not occur) in water and in NaCl solutions can be described by the theory discussed above,[10] accounting only for the effect of charges on swelling equilibria. The agreement of the theory with experiment is conditioned by the existence of a fraction of charges on the PAAm chain up to ~0.012 for a curing time up to 60 days (cf. Figures 3 and 4 from ref 10), so that the expected extent of hydrolysis is small.

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Effect of Charge Density and Simple Salts on the Diffusion of Polyelectrolytes in Aqueous Solution

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ABSTRACT: Translational diffusion coefficients of the sodium salts of acrylamide/acrylic acid copolymers of different charge densities and identical degrees of polymerization have been determined at 25 °C in 0.1 and 0.5 M NaBr by quasi-elastic light scattering. At a fixed concentration of NaBr, the limiting diffusion coefficients, obtained by extrapolation of concentration-dependent diffusion coefficients to zero polyelectrolyte concentration, decrease linearly with the square root of the polyelectrolyte charge density. The lower the simple salt concentration, the larger is the rate of decrease with increasing charge density. A "critical" polyelectrolyte concentration has been observed, at which the diffusion coefficients are independent of both the polyelectrolyte charge density and the concentration of simple electrolyte. Above the critical concentration the polyelectrolyte diffusion coefficients increase with increasing charge density; below the critical concentration the diffusion coefficients decrease with increasing charge density, approaching the limiting values. The Mandelkern–Flory constant $\Phi_0^{1/3}P_0^{-1}$ is shown to be constant over the wide range of charge densities investigated and independent of the simple salt concentration.

Introduction

While studies dealing with the diffusion of counterions and coions in polyelectrolyte solutions have provided important information regarding the interactions of small ions with polyelectrolytes,[1-5] the measurement of polyelectrolyte diffusion coefficients has been problematic and few studies dealing with this subject have been reported. The development of quasi-elastic light scattering techniques[6-8] has given impetus to this area of investigation, since it allows for the determination of polymer diffusion coefficients more rapidly and accurately than previously possible. Quasi-elastic light scattering techniques have been utilized to study the effects of salts on the diffusion coefficients of polyelectrolytes in aqueous solution.[9-14] However, no systematic study of the effects of polyelectrolyte charge density on diffusion coefficients has been reported, even though it is well recognized that the charge density of ionic polymers is the most important structural variable which affects their solution properties. It was therefore the purpose of the present investigation to explore this area.

To focus upon the effect of charge density on the diffusion of a polyelectrolyte while minimizing specific nonelectrostatic effects, it is necessary to keep the primary structure and degree of polymerization of the polyelectrolyte constant, while varying the degree of ionic character. Acrylamide/acrylic acid copolymers are excellent model polyelectrolytes for this purpose, since their charge density may be varied by changing the ratio of acrylamide to acrylic acid, and they may be prepared readily by hydrolyzing nonionic polyacrylamide (PAM) to any desired extent without altering the degree of polymerization.

Presently, we report the diffusion coefficients of the sodium salts of fully neutralized acrylamide/acrylic acid copolymers of four different charge densities whose acrylic acid content ranged from 0.6 to 65 mol %. Intrinsic viscosities and counterion activity coefficients for the same series of polyelectrolytes have previously been reported.[15-17] The effect of NaBr concentration on the diffusion coefficients of each of these polyelectrolytes in aqueous solution has been investigated, and the effects of charge density on the measured diffusion coefficients are discussed in terms of the dimensionless charge density parameter ξ that is frequently used to characterize polyelectrolytes when a line charge model is employed

$$\xi = e^2/DkTb \qquad (1)$$

where e is the protonic charge, k is the Boltzmann constant, T is the absolute temperature, D is the bulk dielectric constant, and b is the spacing between ionic groups along the contour length of the polyelectrolyte. The importance of ξ in governing the solution properties of polyelectrolytes has been proposed in theoretical treatments,[18,19] particularly that of Manning.[20,21] Empirical relationships between ξ and counterion activity coefficients[15,16] and intrinsic viscosities[17] of polyelectrolyte so-

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