Studies on the Mechanical and Swelling Behavior of Polymer Networks Based on the Scaling Concept. 4. Extension of the Scaling Approach to Gels Swollen to Equilibrium in a Diluent of Arbitrary Activity

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ABSTRACT: An equation of state has been constructed to describe the mechanical and swelling behavior of gels at different activities of the diluent. The actual polymer concentration of the gel and the extent of the deformation of chains were chosen as independent variables. The validity of the proposed relationships was checked on a series of chemically cross-linked poly(vinyl acetate) gels prepared from polymers of different molecular masses and molecular mass distributions, using both toluene and acetone as swelling agents. Elastic moduli were determined through unidirectional compression measurements; deswelling was achieved by the equilibrium swelling degree decreasing method. It was established that the osmotic contribution of the network chains obeys the same power law as semidilute polymer solutions. Agreement between the predicted and experimentally determined relationships has been found.

Introduction

Polymer gels in swelling equilibrium with a pure diluent can be considered as a set of closely packed coils kept together by cross-links. This situation is similar to a semidilute solution with a concentration of c_e, which is proportional to overlap concentration, c^* (c^* theorem).[1]

In our previous papers we reported mechanical measurements carried out on polymer gels swollen to equilibrium in a pure good diluent.[2-4] It was established that the only parameter that controls the elastic and swelling properties of permanent network systems is the screening length, ξ, which depends on the concentration,[5] c ($\xi \propto c^{-3/4}$), and this dependence is not altered by the network topology.

It was found for chemically different gel systems under good solvent conditions that according to the c^* theorem, the elastic (shear) moduli, E, obey the power law

$$E = A_1 c_e^{9/4} \tag{1}$$

where c_e is the equilibrium polymer concentration of the gel and A_1 is a constant characterizing the polymer–diluent system.

Supposing the elastic modulus to be proportional to the density of contact points between the chains ($E \propto \xi^{-3}$), one can directly deduce eq 1 from the concentration dependence of ξ.

On the other hand, it may be argued quite generally that in the semidilute regime the osmotic pressure of a solution, Π, measures the number of contact points. According to the equation of state of des Cloiseaux,[6] under good solvent conditions the concentration dependence of the osmotic pressure obeys the relation

$$\Pi = A_2 c^{9/4} \tag{2}$$

where A_2 is another constant, the value of which depends on the interaction between polymer and solvent. Comparing eq 1 and 2, one can see that E and Π have the same concentration dependence except for a difference in the prefactors.

Previous experimental works confirm the validity of eq 1 and 2 for gels swollen to equilibrium in good diluents[2,3,7-9] and polymer solutions in the semidilute regime.[5,10]

In spite of the several available methods for decreasing the activity of the diluent inside the gel, only a few studies have been published so far on the scaling behavior of gels at different diluent activities.[11-13]

The aim of the present work is to study the mechanical and swelling behavior of gels at different activities of the swelling agent. An attempt is made to establish a scaled relationship for that case.

Theory

According to thermodynamic considerations, the swelling pressure of a gel, ω, can be expressed as

$$-\omega = (\mu_1 - \mu_1^\circ)/\bar{V}_1 = E - \Pi_n \tag{3}$$

where μ_1 is the chemical potential of the diluent in the swollen gel, μ_1° is that of the pure diluent, $\bar{V}_1$ means the partial molar volume of the swelling agent, and Π_n is the osmotic contribution of the network chains. The classical theory of rubber elasticity contains a further term (usually designated as a cross-linking or logarithmic term), the existence of which has not been clarified yet. It has been shown by careful experiments that eq 3 is valid within the limits of the experimental error.[14,15]

A satisfactory molecular theory taking into account the effect of all molecular parameters of the network on E and Π_n has not yet been elaborated. Recently, a new mechanism, which considers the topological rearrangements of network chains during swelling and deswelling, has been proposed.[24] The basic idea of this mechanism is that the network chains are widely interspersed. Some recent experiments on polystyrene gels seems to support this idea.[25,26] This picture suggests that the elastic properties of polymer gels can be described in terms of c/c^*, similar to the case for semidilute polymer solutions.

For evaluation of the equilibrium swelling degree of gels surrounded by either a solution of the network polymer or a pure swelling agent and for estimation of the partition coefficient of linear polymer chains between the solution and the gel phase, a new approach has been proposed.[13]

Our analysis differs from that of ref 13 in the following respects:

(i) We consider the elastic (shear) moduli of gels rather than the elastic free energy, since E can be determined directly by mechanical measurements. Other thermodynamic quantities related to swelling such as swelling pressure are evaluated with the aid of E and Π_n.

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(ii) The main purpose of our work is to establish general relationships to describe the concentration dependence of ω and E for gel systems at different activities of the diluent. The applicability of our approach is not restricted to the case in which the gel is equilibrated by a semidilute solution of the network polymer as in ref 13.

The scaling approach presented here is completely phenomenological. We consider E as a function of the polymer concentration of the gel, c, and the ratio of c to overlap concentration, c^*. These two quantities can be considered as independent variables, since c is proportional to the concentration of the elastically active network chains, while c/c^* represents the extent of the deformation or interspersion (if any) of chains.

If E is supposed to be a generalized homogeneous function of these variables, we may write

$$E = f(c, c/c^*) \propto c^x (c/c^*)^y \tag{4}$$

The values of the exponents x and y can be determined since eq 4 is expected to fulfill the following requirements:

(i) In swelling equilibrium with a pure good diluent the elastic moduli of different network systems must depend on the swelling equilibrium concentration according to eq 1:

$$E \propto c_e^{9/4} \tag{5}$$

(ii) The concentration dependence of the elastic modulus for a given swollen gel must obey the relation[16,17]

$$E \propto c^{1/3} \tag{6}$$

Taking into account eq 5 and 6, one gets for the exponents

$$x = 9/4 \qquad y = -23/12 \tag{7}$$

Accepting the c^* theorem, one can write eq 4 as

$$E = A_1 c^{9/4} (c/c_e)^{-23/12} \tag{8}$$

For the osmotic contribution of the network chains we apply the power law derived for the semidilute solutions

$$\Pi_n = A_3 c^{9/4} \tag{9}$$

where A_3 is a constant that differs from that of the solution of the same polymer. The difference is a consequence of the chemical modification of the polymer and the decreasing of external degrees of freedom of the chains by cross-links.

Introducing eq 8 and 9 into eq 3, one obtains

$$-\omega = A_1 c^{9/4} (c/c_e)^{-23/12} - A_3 c^{9/4} \tag{10}$$

Taking into account that at swelling equilibrium with the pure diluent ($c = c_e$) $\omega = 0$, we get

$$A_1 = A_3 = A \tag{11}$$

Thus the concentration dependence of the swelling pressure can be given as

$$\omega = A c^{9/4} [1 - (c/c_e)^{-23/12}] \tag{12}$$

The combination of eq 8, 11, and 12 results in

$$\omega = E[(c/c_e)^{23/12} - 1] \tag{13}$$

in which the numerical factors are omitted. It is worth mentioning that eq 13 contains no molecular parameters that characterize the individual gel systems; thus it can be considered as an equation of state of gels, which provides a correspondence between the most important measurable quantities.

Experimental Section

Table I[a]
Characteristics of the PVA Samples

sample	$\bar{M}_w$	$[\eta]_{303\,K}$
I	22 300	0.26
II	52 600	0.45
III	102 700	0.70
IV	139 600	0.84
V	345 500	1.50

[a] $[\eta]$ (intrinsic viscosity) is given in 100 cm^3/g units. $\bar{M}_w$ (average molecular mass) was calculated through the equation[20] $[\eta]_{303\,K} = 4.28 \times 10^{-4} \bar{M}_w^{0.64}$.

Table II
Solids Content of PVA and PVAc Gels

	solids content of gels, g		
		PVAc	
symbol[a]	PVA	exptl	calcd
12/50	0.0943	0.1812	0.1843
6/400	0.0450	0.0863	0.0879
9/50	0.0705	0.1328	0.1378
3/100	0.0210	0.0401	0.0410
12/200	0.0928	0.1791	0.1814
6/200	0.0435	0.0832	0.0850

[a] Symbol of the gels: (polymer concentration at cross-linking)/(degree of cross-linking).

Materials. The poly(vinyl acetate) (PVAc) gels were prepared by total acetylation of poly(vinyl alcohol) (PVA) gels.[18,19] PVA samples with narrow molecular mass distributions were obtained by fractionation of a hydrolyzed Poval 420 (Kuraray Co., Japan) product. Some characteristics of the PVA fractions are summarized in Table I.

In addition, six series of polydisperse samples were prepared by mixing different amounts of fractions I and V and fractions II and V. $\bar{M}_w/\bar{M}_n$ ratios for these mixtures were between 1.6 and 4.4. The PVA molecules were cross-linked with glutaraldehyde (Merck, GFR) at pH 1.5 and 298 ± 0.1 K in solutions of concentrations c_0 = 3.0, 6.0, 9.0, and 12.0 wt %. At each concentration, we prepared four series of gels, each characterized by a different degree of cross-linking (DC = 50, 100, 200, and 400). DC means moles of monomer units per mole of cross-linking agent.

Cylindrical gel specimens of equal height and diameter were obtained by mixing a homogenized solution of the polymer, the cross-linking agent, and the catalyst (2 N HCl solution) in cylindrical containers of a suitable frame. Gelation was completed under isothermal conditions at 298 ± 0.1 K in 2 h. After removal from the frame the gel cylinders were placed in closed vessels and were left standing in a thermostat for the duration of the reaction.[21] Then the media of the gels were replaced with a mixture of pyridine (50 vol %)-acetic anhydride (40 vol %)-acetic acid (10 vol %). The acetylation was carried out at 363 K for 8 h. A fresh mixture was provided each hour. In the last 3 h the acetic acid was omitted from the fresh mixture in order to shift the equilibrium in the direction of acetate formation. After acetylation the media of the gels were replaced with both toluene and acetone.[18,19]

Table II shows the solids content of some PVA and PVAc gels. It can be seen that the experimentally determined polymer content agrees with that calculated on the basis of stoichiometry within 1-2%.

Methods. Unidirectional compression measurements (at constant volume) were carried out on gel samples swollen to equilibrium in toluene or acetone at different activities of the diluents in an apparatus that allowed us to measure force-deformation relations over a wide range (from 0.0001 to 2.0 N and from 0.006 to 3.333 mm) with an accuracy of ±0.0001 N and ±0.006 mm. The gel cylinders were subjected to deformation between two flat glass plates in a thermostable sample holder.[21]

For evaluation of force-deformation measurements we applied the equation

$$f = 2C_1(\Lambda - \Lambda^{-2}) + 2C_2(\Lambda - \Lambda^{-2})\Lambda^{-1} \tag{14}$$

where f is the force of retraction at compression ratio $\Lambda = L/L_0$ (L and L_0 are the heights of the deformed and undeformed gel

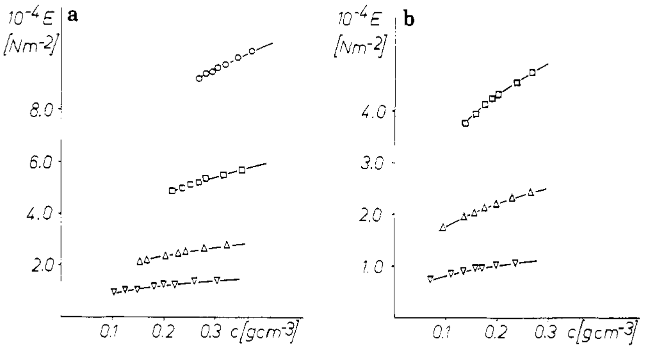

Figure 1. Elastic modulus, E, as a function of gel concentration, c, for PVAc/toluene (a) and PVAc/acetone (b) systems. Gel samples were prepared from fraction V by cross-linking at 9.0 wt % initial polymer concentration. Degree of cross-linking: (○) 50; (□) 100; (△) 200; (▽) 400.

Table III[a]
Characteristics of Polymers Used for Decreasing the Activity of Diluents

material	$\overline{M}_w$	$\overline{M}_n$	d_2, kg dm^{-3}
PS	37 000	34 000	1.05
PVAc	130 000	122 000	1.17

[a] $\overline{M}_n$ = number-average molecular mass; d_2 = density of the polymer.

cylinder, respectively) and C_1 and C_2 are constants. For all the PVAc gels C_2 was found to be equal to zero. The absence of volume change and barrel distortion was checked. The reproducibility of the mechanical measurements was within 5%. All compression measurements were carried out at deformation ratios $0.7 < \Lambda < 1.0$.

The elastic (shear) moduli of the gels were calculated from $2C_1$ data through the relation

$$E = 2C_1F^{-1} \tag{15}$$

where F is the swollen unstrained cross section. In Figure 1 the dependence of the elastic moduli on the concentration can be seen.

Deswelling was realized by means of the equilibrium swelling degree decreasing method.[22] This method differs from other osmotic deswelling methods as the swollen gel specimen is surrounded by a semipermeable membrane (Kalle A.G. Wiesbaden, GFR) that prevents the penetration of the polymer molecules used for lowering the activity of the diluent into the gel phase. Thus difficulties arising from either the unknown influence of the penetrating polymer molecules or the determination of the concentration of the gel sample taken from the high-viscosity polymer solution can be avoided. The precondition of these measurements is the knowledge of the solvent activity in the equilibrium polymer solution. This value has to be determined through independent experiments, e.g., by osmotic pressure measurements. This method enables one to determine ω vs. c plots for gels with an accuracy of 2–3%. The activity of the diluents, a_1, varied in the range $0.9950 < a_1 \leq 1.0000$. For decreasing the activity of the swelling agent low molecular mass polystyrene (PS) and poly(vinyl acetate) with a known activity–concentration dependence were used.[23] In the following stage the polymer solutions were dialyzed in order to remove the fraction that can diffuse through the semipermeable membrane. This procedure was continued until the polymer could not be detected in the equilibrium liquid phase even by interferometry. Characteristics of the polymers after this treatment are given in Table III.

High-accuracy osmotic pressure data for these polymers, prepared the same way, are available in the literature.[23] These data were checked in the concentration range 0.02–0.12 kg dm^{-3}, and agreement within 5% was found.

Since in swelling equilibrium the activity of the diluent inside and outside the gel must be equal, the swelling pressure of a gel can be determined from the known solvent activity of the polymer solution in equilibrium with the gel according to

$$\omega = -(RT/\bar{V}_1) \ln a_1 \tag{16}$$

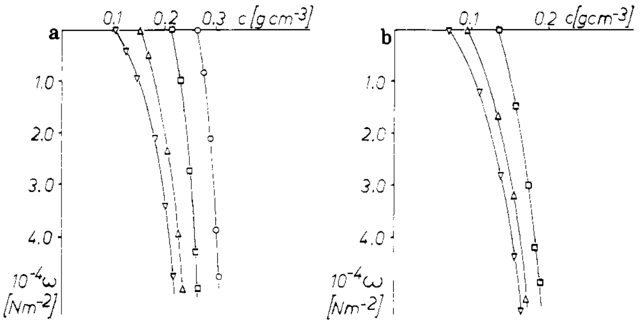

Figure 2. Swelling pressure, ω, vs. polymer concentration, c, plots for PVAc/toluene (a) and PVAc/acetone (b) systems. Gel samples were prepared from fraction V by cross-linking at 9.0 wt % initial polymer concentration. Degree of cross-linking: (○) 50; (□) 100; (△) 200; (▽) 400.

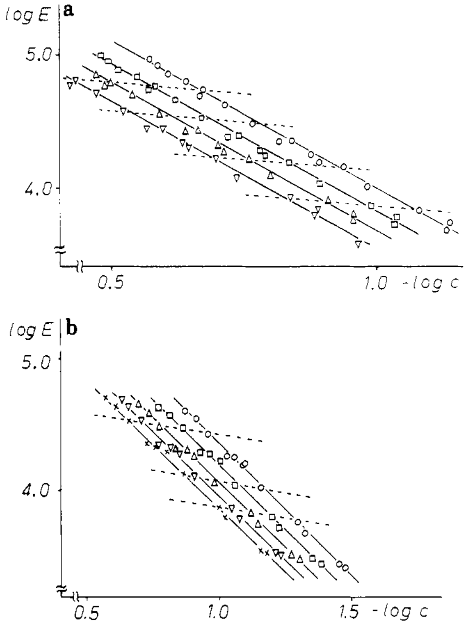

Figure 3. log–log representation of the elastic modulus, E, vs. the polymer concentration of the gel, c, for PVAc/toluene (a) and PVAc/acetone (b) systems at different c/c_e. The E values were obtained from the smoothed curves shown in Figure 1. (a) c/c_e: (○) 1.00, (□) 1.25, (△) 1.50, (▽) 1.75; (b) c/c_e: (○) 1.00, (□) 1.25, (△) 1.50, (▽) 1.75, (×) 2.00. The slopes of the straight lines are 2.38 and 2.09, respectively. Dashed lines show the variation of log E with log c for the same gel samples. The average value of the slopes is equal to 0.34 for both kinds of systems.

Table IV
Activity-Concentration Data for Two PVAc Gels Swollen in Toluene

gel A		gel B	
$-10^5 \times \ln a_1$	c, g cm^{-3}	$-10^5 \times \ln a_1$	c, g cm^{-3}
0	0.107	0	0.022
9	0.124	4	0.048
16	0.135	14	0.073
28	0.146	31	0.102
59	0.170	59	0.133
81	0.185	82	0.151
114	0.201	125	0.177
139	0.212	193	0.206
204	0.234	230	0.219
295	0.256	348	0.252

In Figure 2 ω vs. c curves are shown for several PVAc/toluene and PVAc/acetone gels. In Tables IV and V some representative ln a_1 vs. c data are tabulated.

All the experiments were carried out at 298 ± 0.1 K.

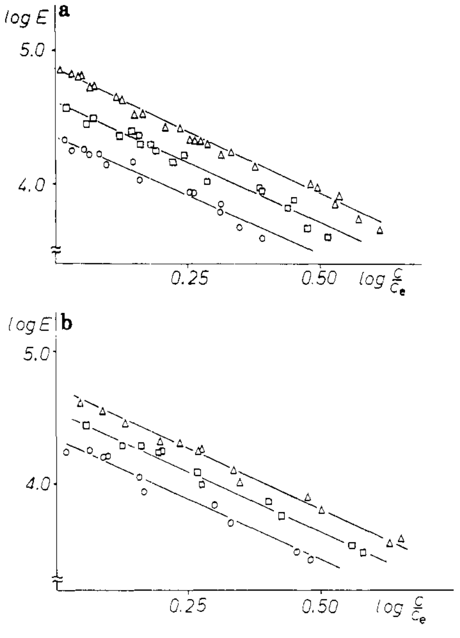

Figure 4. Plot of log E as a function of log c/c_e for PVAc/toluene (a) and PVAc/acetone (b) gels at different polymer concentration c: (a) (○) 0.15, (□) 0.20, (△) 0.25; (b) (○) 0.100, (□) 0.125, (△) 0.150. The straight lines are the best least-squares fits, with slopes of −1.87 and −1.88, respectively.

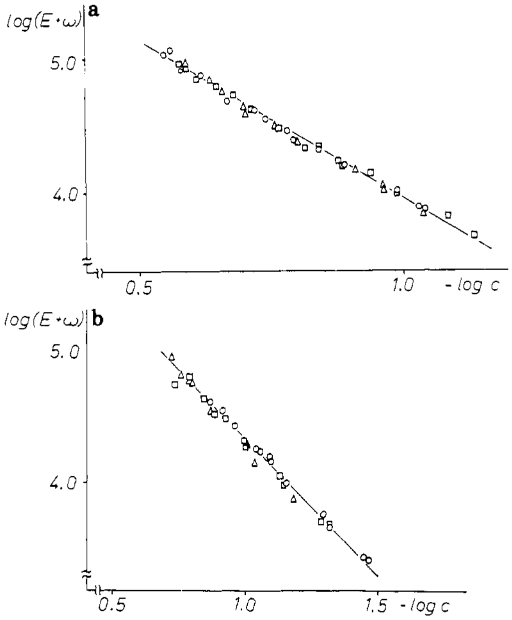

Figure 5. Variations of log ($E + \omega$) as a function of log c at different c/c_e for PVAc/toluene (a) and PVAc/acetone (b) systems. c/c_e: (a) (□) 1.00, (○) 1.25, (△) 1.50; (b) (○) 1.00, (□) 1.50, (△) 2.00. The E and ω values were obtained from the smoothed curves of Figures 1 and 2, respectively. The slope of the continuous line is equal to 2.46 for PVAc/toluene gel and 2.16 for PVAc/acetone gel.

Results and Discussion

In order to examine the applicability of eq 8, we have plotted log E vs. log c at fixed c/c_e (Figure 3) and log E vs. log (c/c_e) at given c values (Figure 4) for both PVAc/toluene (a) and PVAc/acetone (b) gels. It can be seen that the experimental points for the different systems are on straight lines with slopes of 2.38 and −1.87 for the PVAc/toluene system and 2.09 and −1.88 for the PVAc/acetone system. These exponents differ slightly from the theoretical values $^{9}/_{4}$ and $-^{23}/_{12}$, respectively. The dashed lines in Figure 3 show the variation of log E with log c for

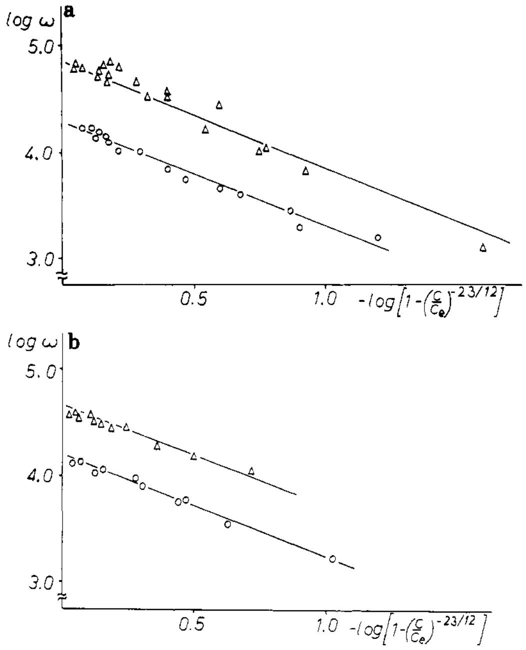

Figure 6. log–log plot of swelling pressure, ω, vs. $[1 - (c/c_e)^{-23/12}]$ for PVAc/toluene (a) and PVAc/acetone (b) systems at different polymer concentration. c: (a) (○) 0.15, (△) 0.25; (b) (○) 0.10, (△) 0.15. The slopes of the straight lines are 0.96 for PVAc/toluene gel and 0.94 for PVAc/acetone gel.

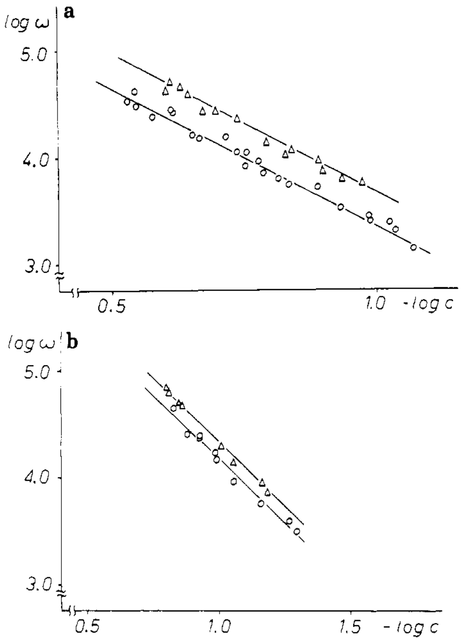

Figure 7. Double-logarithmic representation of variations in swelling pressure, ω, with the polymer concentration of the gel, c, for PVAc/toluene (a) and PVAc/acetone (b) systems at different degrees of interpenetration. c/c_e (a) (○) 1.25, (△) 1.75; (b) (○) 1.50, (△) 2.00. The slopes of the lines are equal to 2.56 and 2.41, respectively.

the same samples. Their slopes are equal to 0.34, which satisfies the requirement given by eq 6.

In Figure 5 log ($E + \omega$) vs. log c plots are presented for both kinds of system. It is apparent that all the experimental points are on the same straight line independently of the c/c_e values. The exponents found for the systems are close to the predicted value, $^{9}/_{4}$. This means that eq 9 is valid; i.e., the osmotic contribution of the network chains in the gel obeys the same concentration dependence as the semidilute polymer solutions. Furthermore, it can be concluded that there are no other terms (e.g., a cross-

Table V
Activity-Concentration Data for Two PVAc Gels Swollen in Acetone

gel A		gel B	
$-10^5 \times \ln a_1$	c, g cm^{-3}	$-10^5 \times \ln a_1$	c, g cm^{-3}
0	0.111	0	0.035
12	0.121	5	0.044
34	0.136	23	0.078
50	0.145	47	0.104
61	0.151	61	0.116
88	0.162	81	0.130
120	0.172	120	0.149
159	0.183	174	0.166
225	0.194	212	0.173

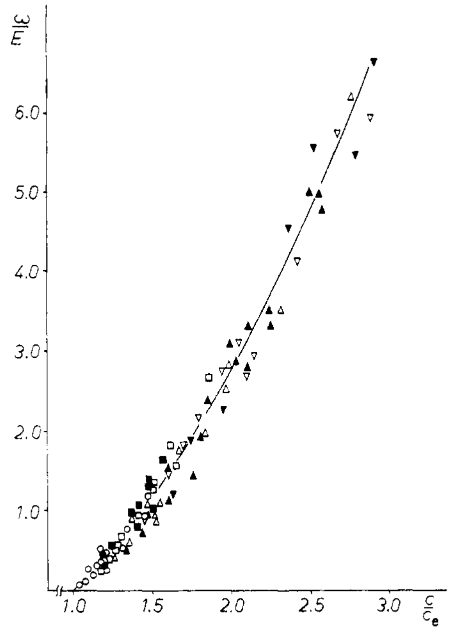

Figure 8. Values of ω/E against c/c_e for both PVAc/toluene and PVAc/acetone gel systems. The continuous curve corresponds to the prediction of eq 13. Different symbols refer to gel samples characterized by different degrees of cross-linking (DC) values. DC of PVAc/toluene gels: (○) 50; (□) 100; (△) 200; (▽) 400. DC of PVAc/acetone gels: (■) 100; (▲) 200; (▼) 400.

linking term) in eq 3. The existence of additional terms would cause functions plotted in Figure 5 to depend on c/c_e.

The validity of eq 12 has been checked in two different ways. In Figure 6 log ω values are plotted against log $[1 - (c/c_e)^{-23/12}]$ at fixed c for PVAc/toluene and PVAc/acetone systems. According to eq 12, straight lines are expected with a slope of 1. Lines of slope 0.96 and 0.94 for PVAc/toluene and PVAc/acetone gels were found, respectively. The agreement is satisfactory. In Figure 7 we have plotted log ω vs. log c at fixed c/c_e. We found parallel straight lines with slopes differing slightly from the predicted value, $^9/_4$.

Comparison of the experimentally determined exponents of PVAc/toluene to PVAc/acetone systems shows that, at fixed c/c_e, the exponents are always smaller if acetone is used as a diluent.

In order to avoid the necessity of interpolation between the experimental points and to check the universality of the proposed equation of state, the directly measured quantities of both PVAc/toluene and PVAc/acetone gel systems are presented in Figure 8. Equation 13 predicts that ω/E is the only function of c/c_e. It would be desirable to compare other experimental results on gels with eq 13 but unfortunately, to the best of our knowledge there are no data available in the literature. Figure 8 shows that there is no systematic deviation from the predicted relation. Considering the uncertainty of the separate measurements, including the determination of E, ω, c, and c_e, it may be established that agreement between the prediction and the experimental results is quite satisfactory.

Finally, we may conclude that the scaling approach can be applied with success to describe the mechanical and swelling behavior of gels even if the activity of the diluent differs from that of the pure swelling agent.

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