Static viscoelastic properties of swollen polyelectrolyte gels in equilibrium with water and aqueous electrolyte solutions

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The static viscoelastic properties of covalently crosslinked anionic polyelectrolyte gels—condensation products of *p*-phenolsulphonic acid and formaldehyde—are studied. They are loaded with different kinds of counterion species and are in swelling equilibrium with water and aqueous electrolyte solutions respectively. The Young's modulus of the gels decreases with increasing water content as well as with increasing temperature, indicating that in swelling equilibrium the chain segments of the network are stiff and largely stretched. Creep experiments show that the deformation of the gels consists of an elastic, a viscous and a plastic (irreversible) component. An analysis of the viscous component leads to two relaxation times τ_2 and τ_3 ($\tau_2 \simeq 50$ min, $\tau_3 \simeq 1$ min). The results are interpreted by assuming that the gels have an inhomogeneous structure. They are assumed to be formed by highly crosslinked regions, which are connected by loose links. The dimensions of the structural components are smaller than the wavelength of visible light. The irreversible deformation is caused by a disentanglement and/or breaking of the loose links. The reversible deformation is attributed to reversible deformations of the highly crosslinked regions and a reversible stretching of the loose links.

(Keywords: viscoelastic properties; polyelectrolyte gels)

INTRODUCTION

To optimize the effectiveness of ion-exchange membranes in membrane separation processes it is necessary to know their transport properties. The most complete information in this respect can be obtained by determining experimentally the matrix of phenomenological transport coefficients based on the linear laws of thermodynamics of irreversible processes. However, in many cases it is sufficient to know the values of only a small set of parameters introduced by a suitable model which takes into account the chemical composition and the physicochemical properties of the membrane matrix. The transport coefficients can then be estimated by model calculations. The model of the membrane with narrow pores[1] has been very successful for characterizing the transport properties of ion-exchange membranes. For phenolsulphonic acid (PSA) membranes, which are condensation products of *p*-phenolsulphonic acid (containing small amounts of phenol) and formaldehyde[2,3], a detailed comparison between the values of the transport coefficients calculated on the basis of the model of the membrane with narrow pores with those obtained on the basis of the linear laws has been carried out[4]. Characteristic differences between the two sets of data have been found. They can be explained by assuming that PSA membranes, which are transparent to visible light, have a heterogeneous structure. It is the aim of this study to contribute to a elucidation of the structure of PSA membranes by studying the static viscoelastic properties of PSA gels. A similar but less detailed study has been carried out by Koschel and Schlögl[5].

EXPERIMENTAL

Gels

PSA gels were prepared by a condensation reaction of *p*-phenolsulphonic acid with formaldehyde in the presence of sulphuric acid[6,7]. Equal volumes of molten *p*-phenolsulphonic acid containing sulphuric acid and a small amount of phenol (about 10%)[8] and an aqueous solution of formaldehyde (30%) were slowly mixed at a temperature below room temperature. The mixture was freed of air bubbles and poured into moulds covered by two glass plates (see *Figure 1*). The condensation reaction took place at about 62°C. The water content and the fixed ion concentration of the gels were varied by changing the condensation time (1.5 h to 8 h). The condensation reaction was stopped by treatment of the moulds with water at room temperature. Thereafter the moulds were taken apart and the gel samples were brought to swelling equilibrium with a concentrated KCl solution. Several gel samples were prepared from a given batch of a reactive mixture to obtain a set of samples with the same properties. Finally, the gels were characterized by determining their water content (*w* is mass fraction of water in the swollen gel) and fixed ion concentration. The dimensions of the sample in swelling equilibrium with water and aqueous electrolyte solutions respectively were

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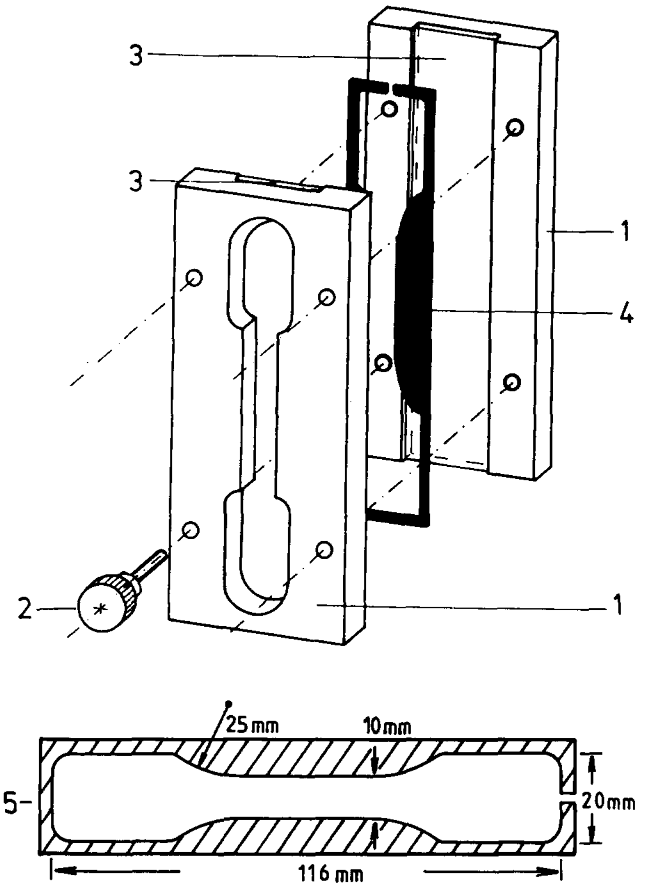

Figure 1 Preparation of gel samples: 1, aluminium frame; 2, screw; 3, glass plates; 4, brass spacer (mould); 5, mould

determined in separate experiments (thickness ~1 ± 0.01 mm, effective length ~100 ± 0.2 mm, width ~10 ± 0.1 mm).

Measurements of static viscoelastic properties of PSA gels

The apparatus for measuring the static viscoelastic properties of PSA gels is shown schematically in *Figure 2*. *Figure 3* shows the construction of a device to attach a gel sample to the clamps of the stress–strain apparatus.

The digital control of the apparatus allowed two different kinds of experiments to be carried out: (a) Experiments at constant displacement rate—measurements of stress σ at constant displacement rate u $[\varepsilon = (L-L_0)/L_0 = (u/L_0)(t-t^\circ)]$. This mode of operation is used to measure the Young's modulus of the gel at zero stress $[\lim \sigma = 0, E = (\partial\sigma/\partial\varepsilon)_T]$. (b) Creep experiments—measurements of strain ε $[=(L-L_0)/L_0]$ at constant stress σ_0 $(=F_0/a)$ as a function of time (L and a are effective length and cross section of the sample respectively; F_0 is applied force). The difference between the constant force F_0 to be applied to the gel sample and the value of the actual force acting was monitored three times per second. By changing the rotational speed of the spindle (see *Figure 2*) this difference was adjusted to zero. Three different rotational speeds of the spindle were available corresponding to displacement rates between 1 and 160 μm s^{-1}.

Preconditioning of gel samples

Before a stress–strain experiment was started with a given gel sample it was taken through several cycles of counterion exchange K^+/H^+) associated with changes of the swelling of the gel. Thereafter the sample was exposed to several cycles of strain at constant stress at 40°C followed by a relaxation period at zero stress. This treatment was necessary to remove non-equilibrium swelling states generated by the condensation reaction.

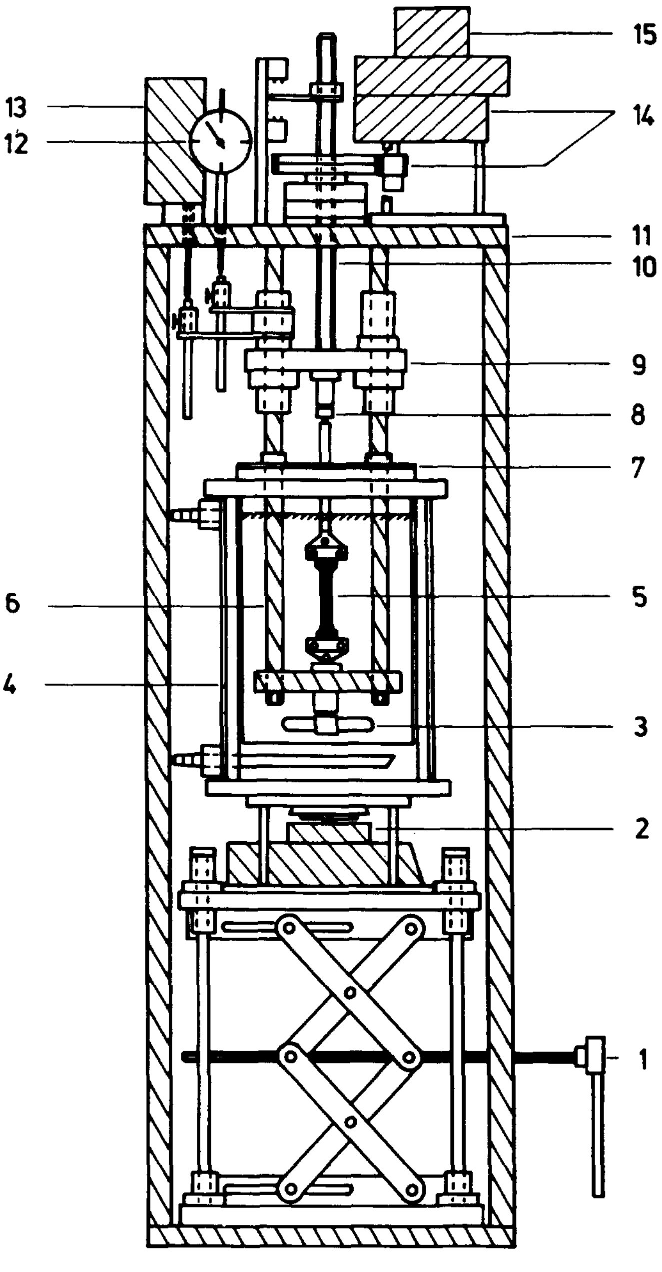

Figure 2 Apparatus to measure the static viscoelastic properties of PSA gels: 1, jack to adjust die position of the thermostated external solution ($V = 3.5\,\text{dm}^3$); 2, magnetic stirrer; 3, magnetic stirring bar; 4, thermostating jacket; 5, gel sample; 6, rigid frame fixed to plate (11); 7, cover; 8, force transducer (Sensotec, type 31, range 0 to 20 N (± 0.15%); Burster, Gernsbach, FRG); 9, brass bar which is moved up and down by rotating the spindle (10)—the mechanical length-measuring device as well as the displacement transducer are connected with this bar; 10, spindle; 11, plate to which the rigid frame (6) is fixed; 12, mechanical length-measuring device; 13, displacement transducer (Digital Transducer, type MT 30; Haidenhain, Traunreut, FRG); 14, gear driven by the motor (15); 15, motor

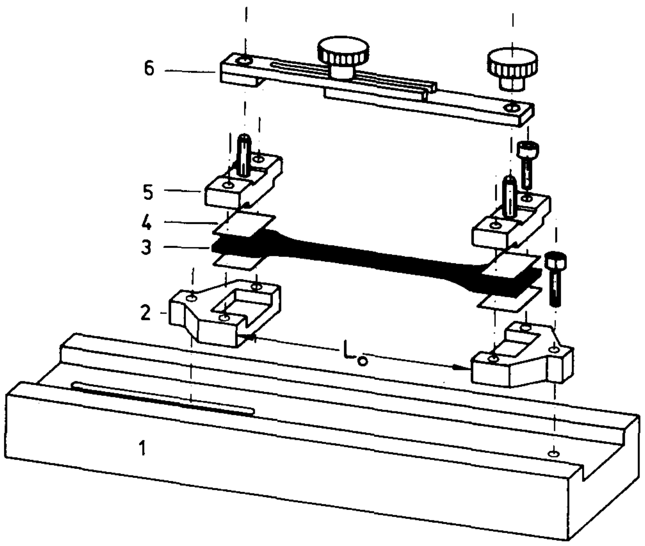

Figure 3 Device to attach a gel sample to the clamps of the apparatus shown in *Figure 2*: 1, aluminium frame; 2, 5, clamps; 3, gel sample; 4, thin Pertinax plates; 6, distance holder, which is removed after positioning the gel sample in the stress–strain apparatus. A torque wrench is used to adjust the pressure exerted by the clamps

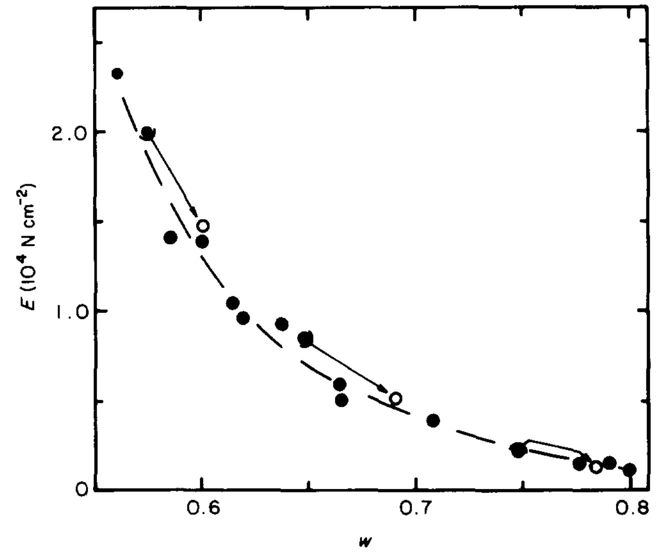

Figure 4 Young's modulus E of PSA gels loaded with K^+ ions as a function of the water content (w = mass fraction of water). The samples are in swelling equilibrium with water. $T = 25°C$.Treatment of the gel samples at a temperature of 70°C for 24 h leads to an increase of the water content and to a corresponding change (decrease) of the Young's modulus (indicated by arrows)

RESULTS AND DISCUSSION

Young's modulus of PSA gels

Experiments at constant displacement rate are used to measure the Young's modulus of PSA gels under different conditions. *Figures 4* and *5* show typical results obtained with PSA gels loaded with K^+ ions in swelling equilibrium with water and KCl solutions of different concentrations, respectively. Values of the Young's modulus of PSA gel loaded with different counterion species in swelling equilibrium with water are shown in *Figure 6*. These experimental data demonstrate (see *Figure 7*) that the Young's modulus of PSA gels does not follow the $(1/\gamma_{rel})^{1/3}$ dependence predicted by the statistical theory (γ_{rel} = swelling ratio)[9]. Such behaviour is typical for polyelectrolyte gels (e.g. refs 10 to 12). All this indicates that the chain segments between crosslinks are largely extended in the swollen state. Furthermore it is found that the Young's modulus decreases with increasing temperature (see *Figure 8*).

Figure 9 shows the results of a standard thermodynamic analysis[9] of the data in terms of the

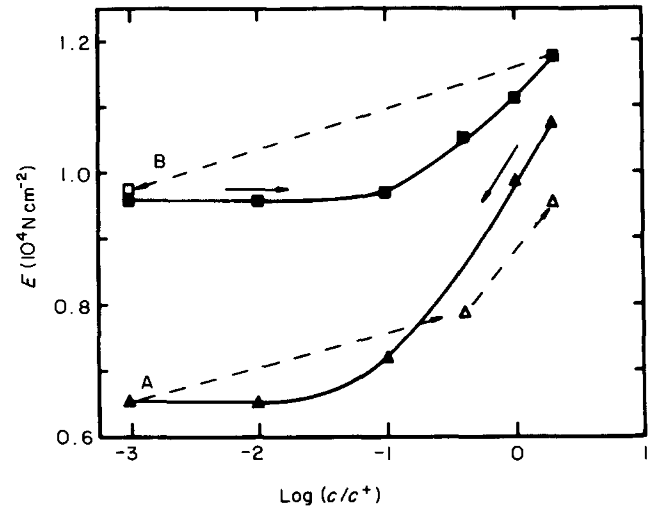

Figure 5 Young's modulus E of PSA gels loaded with K^+ ions as a function of KCl concentration of the external solution. $T = 25°C$. $c^+ = 1$ mol dm^{-3}. The gels differ in water content (w = mass fraction of water). Curve A: Water content of the gel in swelling equilibrium with water, $w = 0.67$; the experiments are carried out with three different samples taken from the same batch. Curve B: Water content of the gel in swelling equilibrium with water, $w = 0.62$; the experiments are carried out with three different samples taken from the same batch. The arrows indicate the sequence of the measurements. The data points connected by the broken lines were obtained one week after the data points connected by the full curves

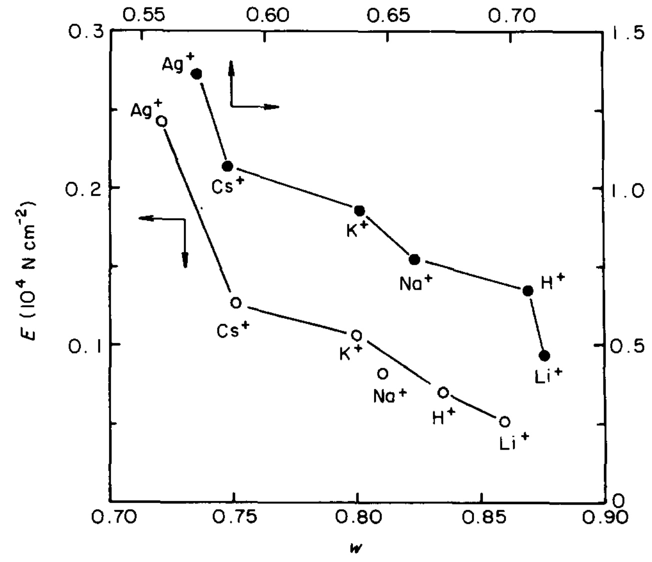

Figure 6 Young's modulus E of PSA gels taken from the same batch loaded with different counterion species. The samples are in swelling equilibrium with water. The data refer to two different gel samples differing in their degree of crosslinking

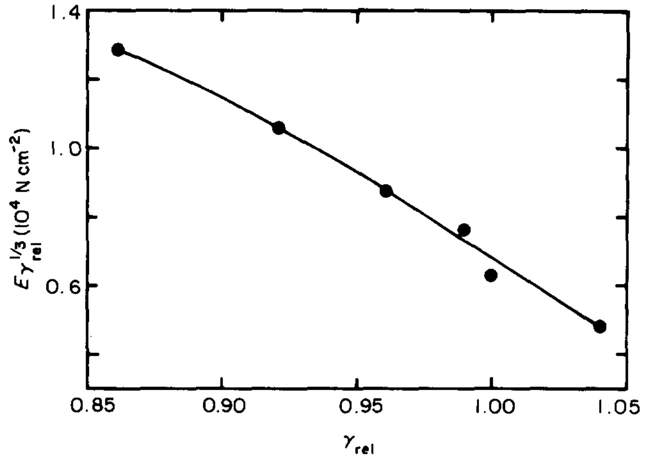

Figure 7 Plot of $E\gamma_{rel}^{1/3}$ as a function of the relative swelling ratio γ_{rel} ($= V(Me^+)/V(H^+)$). $V(H^+)$, $V(Me^+)$ = volume of a piece of gel loaded with H^+ and Me^+ ions respectively in swelling equilibrium with water. $T = 25°C$. Water content in the K^+ form in swelling equilibrium with water $w = 0.64$

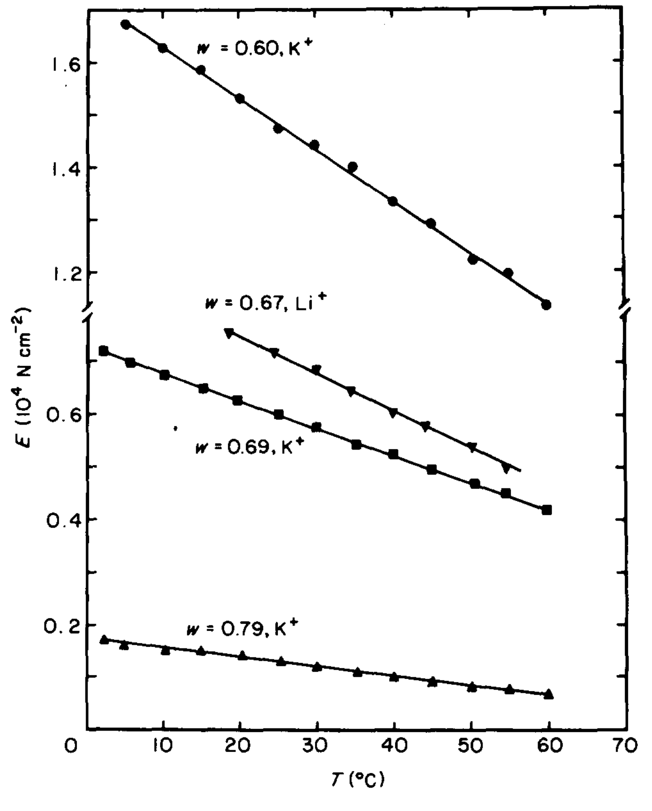

Figure 8 Young's modulus E of PSA gels in swelling equilibrium with water as function of temperature. The gels differ in water content (w = mass fraction of water) and counterion species

equations:

$$-(\partial S/\partial L)_{T,V} \simeq a(\partial\sigma/\partial T)_{P,L} + (1+\varepsilon)a\alpha_P^*(\partial\sigma/\partial\varepsilon)_{P,T} \qquad (1)$$

$$(\partial U/\partial L)_{T,V} = a\sigma + T(\partial S/\partial L)_{T,V} \qquad (2)$$

where S is the entropy, U the internal energy and α_P^* the linear coefficient of thermal expansion, $\alpha_P^* = (\partial L/\partial T)_P/L$. It is found that α_P^* has a value of about $\alpha_P^* \simeq 5 \times 10^{-5}$ K^{-1} ($w = 0.6$). α_P^* depends slightly on the water content of the gel.

The internal energy change $(\partial U/\partial L)_{T,V}$ as well as the entropy change $T(\partial S/\partial L)_{T,V}$ associated with deformations is positive. Both quantities have values which are of the same order of magnitude. The internal energy term has a positive value even under zero strain. The sample with the lower water content has the larger $(\partial U/\partial L)_{T,V}$ value. This is another indication of the fact that PSA gels in swelling equilibrium with water or aqueous electrolyte solutions are in a strained state.

Creep experiments

Figure 10 shows typical results of creep experiments of PSA gels loaded with K^+ ions in contact with water. The gels differ in water content. The deformation of PSA gels exhibits an elastic, a viscous and a plastic (irreversible) component. The contribution of the plastic component increases with increasing water content. The curves reflect the phenomenon of elastic delay after releasing the stress: the relaxation curves at constant stress are characterized by shorter relaxation times than those characterizing the recovery period after releasing the stress. The analysis of the creep experiments is based on a Voigt's model modified empirically (see *Figure 11*):

$$\varepsilon(t) = \sigma_0\left\{\frac{1}{E_1} + \frac{1}{E_2}\left[1 - \exp\left(-\frac{t}{\tau_2}\right)\right] + \frac{1}{E_3}\left[1 - \exp\left(-\frac{t}{\tau_3}\right)\right] + \frac{t}{\eta_1}\right\} \qquad (3)$$

where $E_1 = \sigma_0/\varepsilon_1$, $\tau_i = \eta_i/E_0$ ($i = 1, 2$), $\eta_1 = L_0\sigma_0/v$ and v is the rate of plastic deformation.

Equation (3) is fitted to the experimental data using a non-linear regression program of the BMDP library[13]. The results of this analysis are compiled in *Table 1*. It turns out that the viscoelastic deformation observed in a time interval of up to 360 min can be represented satisfactorily by two relaxation times (see *Figure 12*).

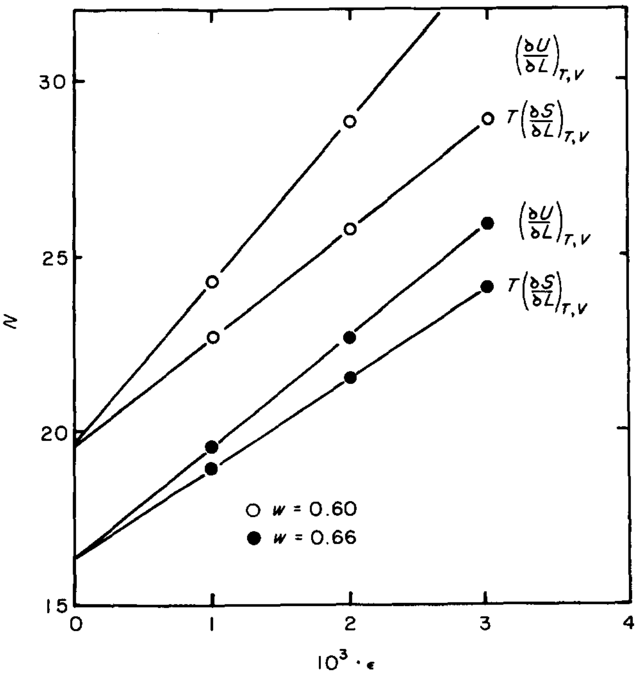

Figure 9 Thermodynamic analysis of elastic deformations of PSA gel loaded with K^+ ions in swelling equilibrium with water: ●, $w = 0.66$; ○, $w = 0.60$

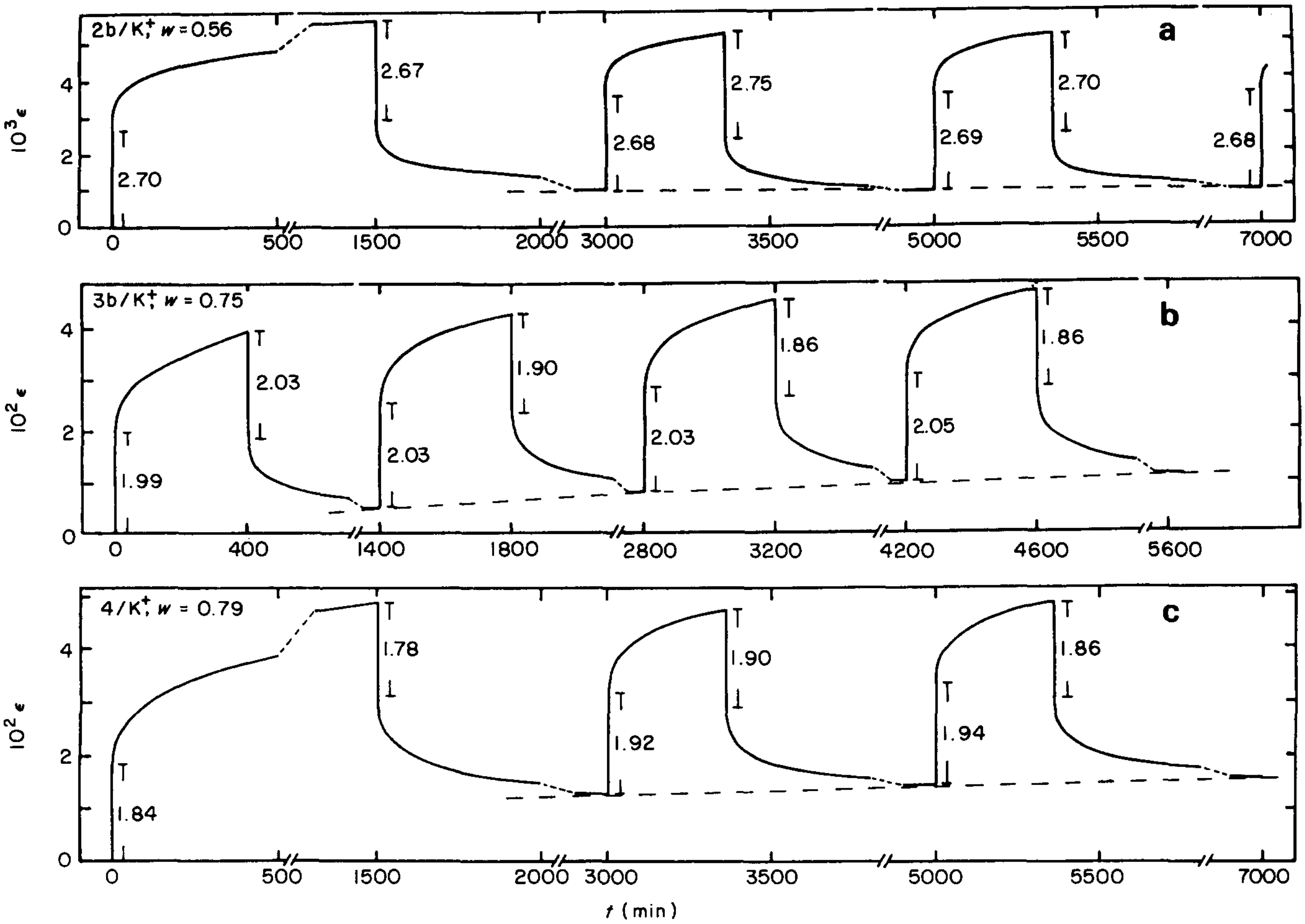

Figure 10 Creep experiments with PSA gels of different water content at $T=25°C$. $\varepsilon=(L-L_0)/L_0$; $\sigma_0=F_0/a$; L, a = effective length and cross section of gel sample respectively; w = mass fraction of water. (a) $\sigma_0=48.0\,\mathrm{N\,cm^{-2}}$; (b) $\sigma_0=28.5\,\mathrm{N\,cm^{-2}}$; (c) $\sigma_0=19.4\,\mathrm{N\,cm^{-2}}$

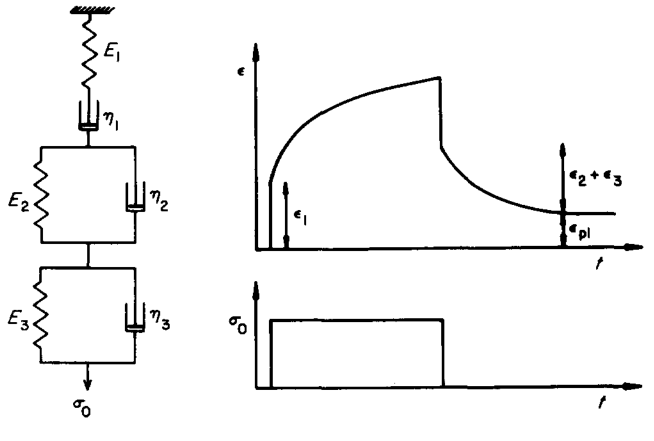

Figure 11 Evaluation of creep experiments: mechanical equivalent circuit composed of springs and dashpots

There remains a difference between η_1(fit) and η_1(expt) ($=L_0\sigma_0/v$). Here η_1(fit) is smaller than η_1(expt) because the experimentally observed rate of irreversible deformation contains a contribution from viscous deformations with relaxation times longer than τ_2. The moduli E_2 and E_3 of the viscous deformation have a larger value than the elastic modulus E_1. Furthermore E_2 associated with the longer relaxation time τ_2 (about 50 min) is smaller than E_3 associated with the shorter relaxation time τ_3 (about 2 min). An explanation of this finding cannot be given. Similar results are obtained from creep experiments with gels taken from one batch and loaded with different counterion species (see *Table 2*) as well as with gels loaded with K^+ ion in swelling equilibrium with aqueous KCl solutions of different concentrations (see *Table 3*).

STRUCTURAL MODEL

To a first approximation PSA gels can be considered to be formed by a covalently crosslinked network carrying negatively charged groups ($-SO_3-$) covalently bound to the gel matrix. The fixed charges are compensated by mobile ions of opposite charge (counterions). In contact with water and aqueous electrolyte solutions respectively, the gels swell. The fixed ion concentration in the swollen state has a value of the order of $1c^+$ ($c^+=1\,\mathrm{mol\,dm^{-3}}$ imbibed water). It is not a function of pH, since the $-SO_3H$ group is a strongly acidic one. In swelling equilibrium the medium within the network is under a hydrostatic pressure of the order of 100 bar generated by the contractive forces of the stretched chain segments. The value of the swelling pressure π_{ion} caused by the presence of the fixed charges can be estimated on the basis of the fixed ion concentration using the Donnan equilibrium condition and van't Hoff's law of ideal dilute solutions. The contribution of the matrix to the swelling pressure is neglected. For z, $-z$ valent electrolytes π_{ion} is

Table 1 Evaluation of creep experiments with PSA gels loaded with K^+ ions in swelling equilibrium with water in terms of equation (1). The samples differ in their water content. w = mass fraction of water of the gel. X = fixed ion concentration. $T = 25$°C. $\eta_{pl} = \eta_1(\mathrm{expt})$; $\eta_1 = \eta_1(\mathrm{fit})$

	Cycle	σ_0 (N cm^{-2})	E (10^4 N cm^{-2})			τ (min)		η (N s cm^{-2})			
			E_1	E_2	E_3	τ_2	τ_3	$\eta_2\ 10^{-7}$	$\eta_3\ 10^{-6}$	$\eta_1\ 10^{-5}$	$\eta_{pl}\ 10^{-5}$
$w=0.56$ $X=1.83c^+$	1	14.6 ±0.2	0.162 ±0.010	0.430 ±0.012	0.562 ±0.016	85.4 ±2.5	3.50 ±0.13	2.20 ±0.12	1.06 ±0.07	0.246 ±0.024	0.394 ±0.030
	2		0.164 ±0.010	0.408 ±0.011	0.512 ±0.016	60.0 ±1.4	2.83 ±0.11	1.40 ±0.07	0.87 ±0.06	0.328 ±0.020	0.790 ±0.070
	3		0.164 ±0.010	0.408 ±0.012	0.454 ±0.015	86.0 ±3.0	3.50 ±0.14	2.07 ±0.13	0.95 ±0.07	0.394 ±0.030	1.40 ±0.15
$w=0.65$ $X=1.35c^+$	1	71.4 ±1.2	0.652 ±0.037	1.91 ±0.06	3.78 ±0.15	62.6 ±1.3	3.6 ±0.2	7.18 ±0.37	8.18 ±0.73	0.79 ±0.05	1,21 ±0.01
	2		0.641 ±0.036	1.99 ±0.06	3.06 ±0.12	64.8 ±1.4	4.5 ±0.2	7.73 ±0.44	8.27 ±0.71	0.93 ±0.07	1.86 ±0.14
	3		0.641 ±0.036	1.99 ±0.07	3.22 ±0.07	57.9 ±1.7	3.6 ±0.2	6.94 ±0.45	6.96 ±0.54	1.10 ±0.08	2.83 ±0.03
$w=0.75$ $X=1.08c^+$	1	28.5 ±0.3	0.143 ±0.005	0.401 ±0.011	0.769 ±0.030	72.9 ±1.3	7.13 ±0.23	1.75 ±0.08	3.29 ±0.24	0.208 ±0.007	0.329 ±0.020
	2		0.141 ±0.005	0.426 ±0.013	0.715 ±0.029	72.0 ±1.6	6.95 ±0.25	1.84 ±0.10	2.98 ±0.23	0.278 ±0.015	0.614 ±0.080
	3		0.141 ±0.005	0.419 ±0.011	0.661 ±0.022	79.9 ±1.4	7.23 ±0.18	2.00 ±0.08	2.87 ±0.17	0.300 ±0.017	0.75 ±0.17
	4		0.139 ±0.007	0.434 ±0.011	0.678 ±0.021	75.2 ±1.1	7.69 ±0.16	1.96 ±0.08	3.23 ±0.20	0.320 ±0.017	0.96 ±0.18

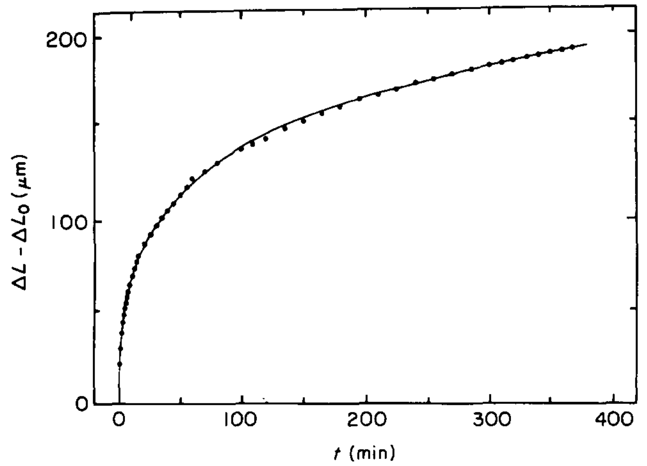

Figure 12 Evaluation of creep experiments using equation (1). The viscoelastic and plastic contributions to the strain of PSA gels at constant stress can be characterized to a good approximation by two moduli E_2 and E_3 and two relaxation times τ_2 and τ_3

given by:

$$\pi_{ion} = 2RT\{[X^2/(2z^2) + c^2]^{1/2} - c\} \qquad (4)$$

where π_{ion} is the swelling pressure, X the fixed ion concentration, c the electrolyte concentration and z the valency of counterions.

Figure 13a shows a graphical representation of equation (4) as a function of electrolyte concentration. Measurements of the water content of PSA gels as a function of electrolyte concentration exhibit a concentration dependence similar to that of π_{ion} (see *Figure 13b*). This indicates that the swelling behaviour of PSA gels is mainly determined by the amount of substance X' of the fixed charges per mass unit of the dried gel and the degree of crosslinking ($X' = (2.4 \pm 0.3) \times 10^{-3}$ mol g^{-1} for the PSA gels used in this study). Owing to the complexity of the chemistry of the gelation process in PSA gels it is not possible to determine the degree of crosslinking directly. Only the water content of the gel can be determined. It is a measure of the degree of crosslinking and can be modified by the temperature and/or the condensation time. The dominating characteristic dimension of the meshes of the PSA network is in the range between 1 nm and several 10 nm. This can be concluded from the fact that the transport properties of PSA gels are described by the model of a membrane with narrow pores. This model is applicable to ion-exchange gels in which the charge density formed by the counterions is smeared out continuously over the cross section of the pores by the thermal motion of the counterions.

These considerations give the physical basis for the conclusions drawn from the measurements of the temperature dependence of the Young's modulus: the network of PSA gels in swelling equilibrium with water and aqueous electrolyte solutions respectively is in a state of high tension.

To interpret the results of the measurements of the Young's modulus further and to analyse the creep experiments it is necessary to develop a more detailed structure model of the PSA gels. Such a model was first proposed by Koschel and Schlögl[5] in 1957 (see *Figure 14*). According to this model PSA gels have a heterogeneous structure. They are composed of highly crosslinked regions connected by loose links. The dimensions of the structural elements are smaller than the wavelength of visible light. The gels are transparent. The space between the highly crosslinked regions constitutes a system of wide pores. The highly crosslinked regions have a narrow pore structure (see above). Measurements of transport properties of PSA membranes lead to the assumption (see below) that the number of fixed charges per unit length of

Table 2 Evaluation of creep experiments with PSA gels loaded with different counterion species in swelling equilibrium with water in terms of equation (1). The gels are taken from the same batch and have the same degree of crosslinking. A new sample is used for each experiment. w = mass fraction of water. X = fixed ion concentration ($c^+ = 1$ mol dm^{-3}). $T = 25$°C. $\eta_{pl} = \eta_1$(expt); $\eta_1 = \eta_1$(fit)

		E (10^4 N cm^{-2})			τ (min)		η (N s cm^{-2})			
	σ_0 (N cm^{-2})	E_1	E_2	E_3	τ_2	τ_3	$\eta_2\ 10^{-7}$	$\eta_3\ 10^{-6}$	$\eta_1\ 10^{-5}$	$\eta_{pl}\ 10^{-5}$
Li^+ $w = 0.67$ $X = 1.20c^+$	35.5 ±2.0	0.67 ±0.05	2.48 ±0.08	3.42 ±0.13	41.2 ±1.5	2.04 ±0.11	6.13 ±0.44	4.19 ±0.39	1.12 ±0.09	2.52 ±0.28
		0.64 ±0.04	2.19 ±0.10	2.85 ±0.13	56.9 ±3.2	2.71 ±0.14	7.47 ±0.77	4.64 ±0.47	1.26 ±0.10	2.73 ±0.23
		0.66 ±0.04	2.57 ±0.12	3.01 ±0.14	49.2 ±3.2	2.40 ±0.16	7.59 ±0.90	4.33 ±0.50	1.36 ±0.12	—
		0.63 ±0.04	2.58 ±0.11	2.76 ±0.12	48.8 ±3.3	2.30 ±0.14	7.56 ±0.90	3.81 ±0.38	1.35 ±0.14	—
Cs^+ $w = 0.55$ $X = 1.51c^+$	40.0 ±0.5	1.15 ±0.07	3.85 ±0.18	5.47 ±0.27	51.0 ±3.0	2.71 ±0.15	11.8 ±1.3	8.9 ±1.0	4.33 ±0.25	—
		1.19 ±0.08	4.04 ±0.27	6.15 ±0.35	53.2 ±3.5	2.80 ±0.15	12.8 ±2.0	10.3 ±1.3	4.26 ±0.45	—
		1.21 ±0.08	4.88 ±0.27	7.43 ±0.35	56.9 ±3.5	2.70 ±0.15	16.7 ±2.0	12.0 ±1.3	3.90 ±0.45	8.5 ±2.0
		1.17 ±0.07	4.31 ±0.16	8.43 ±0.07	47.4 ±1.0	2.21 ±0.10	12.2 ±0.7	11.1 ±1.0	3.61 ±0.38	4.60 ±0.62

Table 3 Evaluation of creep experiments with PSA gels loaded with K^+ ions in swelling equilibrium with different concentrated electrolyte solutions. w = mass fraction of water. X = fixed ion concentration ($c^+ = 1$ mol dm^{-3}). $T = 25$°C. $\eta_{pl} = \eta_1$(expt); $\eta_1 = \eta_1$(fit)

			E (10^4 N cm^{-2})			τ (min)		η (N s cm^{-2})		
	c (mol dm^{-3})	σ_0 (N cm^{-2})	E_1	E_2	E_3	τ_2	τ_3	$\eta_2\ 10^{-7}$	$\eta_3\ 10^{-6}$	$\eta_1\ 10^{-5}$
$w(H_2O) = 0.66$ $X(H_2O) = 1.12c^+$	0.001	22.3 ±0.5	0.52 ±0.03	1.42 ±0.13	1.35 ±0.07	69.0 ±3.0	2.33 ±0.12	5.86 ±0.81	2.59 ±0.44	0.99 ±0.05
	2	24.3 ±0.5	0.89 ±0.05	2.86 ±0.15	3.10 ±0.11	59.0 ±3.5	3.88 ±0.30	10.1 ±1.1	7.21 ±0.94	1.28 ±0.07
	0.001	22.3 ±0.5	0.53 ±0.03	1.10 ±0.03	1.63 ±0.06	70.1 ±1.9	3.00 ±0.14	4.60 ±0.26	2.92 ±0.25	0.41 ±0.01
$w(H_2O) = 0.68$ $X(H_2O) = 1.08c^+$	0.001	22.3 ±0.5	0.43 ±0.04	0.96 ±0.03	1.32 ±0.05	50.1 ±1.1	2.30 ±0.11	2.89 ±0.15	1.82 ±0.15	0.93 ±0.04
	2	24.0 ±0.5	0.79 ±0.05	2.22 ±0.11	2.80 ±0.11	65.6 ±1.9	2.44 ±0.12	8.75 ±0.98	4.10 ±0.36	1.03 ±0.04
	0.001	21.4 ±0.5	0.42 ±0.03	0.97 ±0.03	1.37 ±0.05	60.4 ±1.5	2.70 ±0.12	3.50 ±0.19	2.22 ±0.18	0.45 ±0.02

the links connecting the highly crosslinked regions is smaller than that of the chain segments within the highly crosslinked regions.

The viscoelastic properties of PSA gels reported in this study can be interpreted on the basis of this structural model in the following way: the plastic (irreversible) deformation generated by a one-sided stress of the order of only 1 bar, which is small compared with the value of the swelling pressure, is caused by a disentanglement and/or breaking of loose links. The contribution of plastic deformation increases with increasing water content. The reversible deformations are attributed to deformation of the already largely extended chain segments of the loose links and the highly crosslinked regions.

It is found that the Young's modulus of gels loaded with a given counterion species increases with decreasing water content of the gels. This finding can be interpreted by assuming that the volume fraction of the highly crosslinked regions increases with decreasing water content (longer condensation time of the gel). The chain segments in this structural element are rather stiff due to the repulsion of the fixed charges and the swelling of the gel. This assumption finds support by the observation that the mechanical permeability d_h of PSA gels decreases with decreasing water content (see *Figure 15*). The volume of d_h will be determined mainly by the volume fraction of wide pores.

The finding that the Young's modulus of a given gel sample increases with increasing electrolyte solution can also be explained. With increasing electrolyte concentration of the external solution the electrolyte concentration within the gel increases (Donnan distribution). This concentration increase is higher in the domains with the lower fixed ion concentration (space between the highly crosslinked regions) and leads there to a more effective screening of the fixed charges attached to the loose links. Consequently the loose links coil up. The result is an apparent increase of the volume fraction of the highly crosslinked regions.

In the creep experiments the relaxation time τ_3 (several

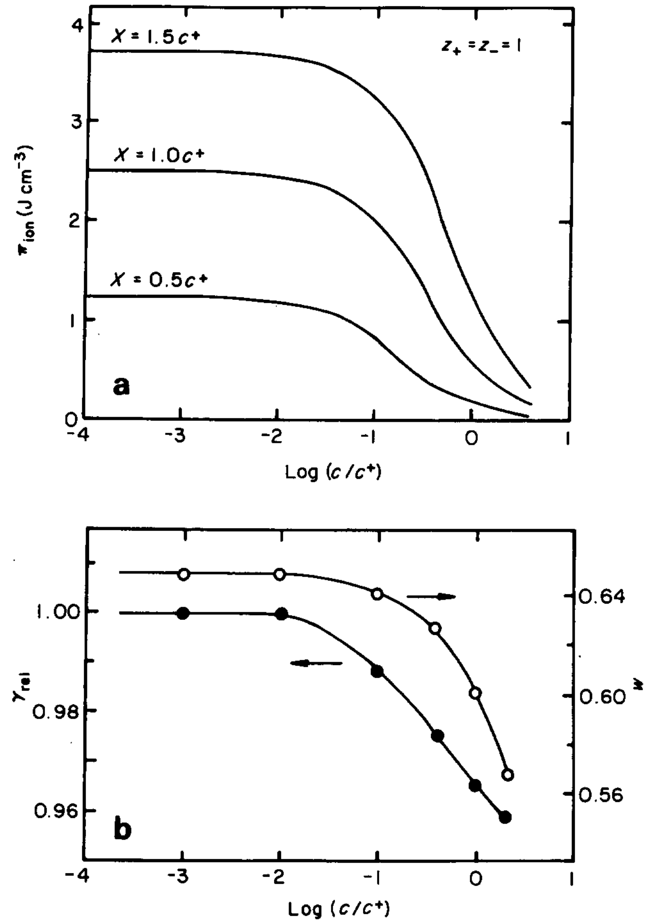

Figure 13 (a) Swelling pressure π_{ion} produced by the presence of counterions within the pore medium as a function of electrolyte concentration in the equilibrium solution. Graphical representation of equation (4). X = fixed ion concentration; $c^+ = 1\ \mathrm{mol\ dm^{-3}}$ imbibed water. (b) Water content w and relative swelling ratio of a PSA gel loaded with K^+ ions as functions of electrolyte concentration. $\gamma_{\mathrm{rel}} = V(c)/V(c=0)$; $V(c)$, $V(0)$ = volume of the gel in swelling equilibrium with KCl solution of concentration c and water ($c = 0$) respectively

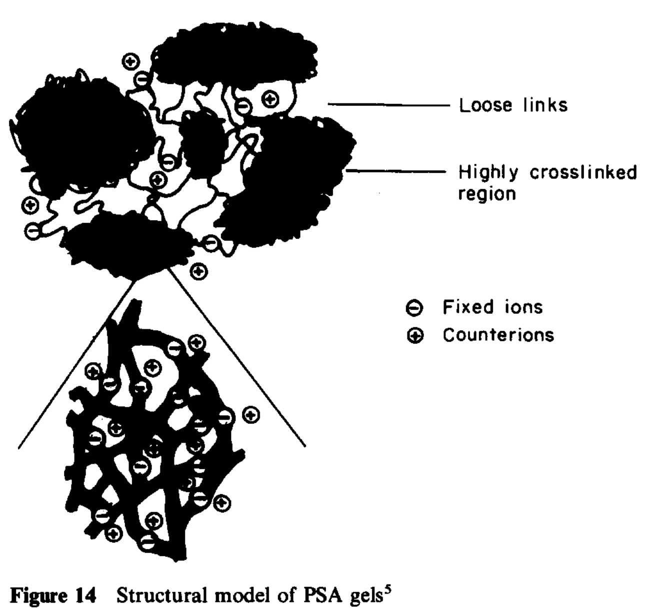

Figure 14 Structural model of PSA gels[5]

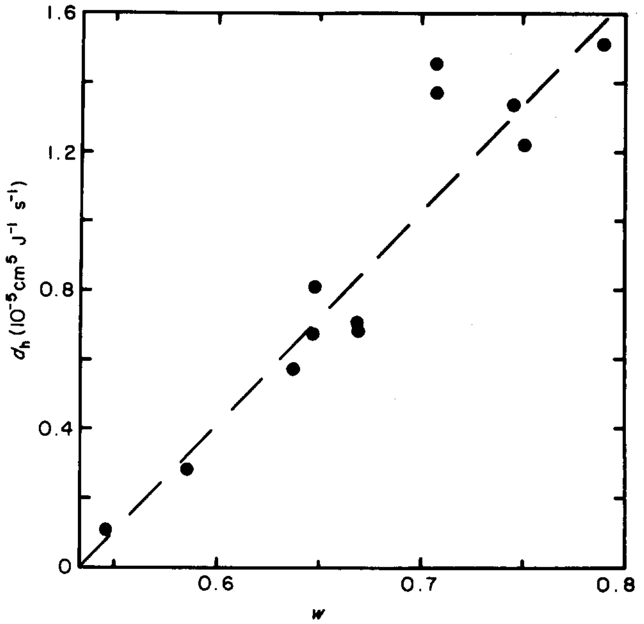

Figure 15 Mechanical permeability d_h of PSA gels loaded with K^+ ions in swelling equilibrium with water as a function of water content of the gels. $d_h = J_V\delta/(a\,\Delta P)$; J_V = volume flow; a = area; δ = thickness of the gel; P = externally applied pressure difference

minutes) is assumed to be connected with viscoelastic deformations of the short chain segments within the highly crosslinked regions and the relaxation time τ_2 (about 50 min) with viscoelastic deformation of the loose links.

This structural model, which can explain qualitatively the static viscoelastic properties of PSA gels reported in this study, is supported by different independent lines of evidence: (a) small-angle X-ray scattering experiments with PSA gels[14]; (b) measurements of streaming potential of PAA membranes leading to the concept of a 'static' and 'dynamic' fixed ion concentration[4,15,16] (this is the experimental basis of the assumption stated above that the number of charges per unit length of the loose links is smaller than that of the chain segments in the highly crosslinked regions); (c) studies of the hydrolytic activity of PSA membranes loaded with H^+ ions as a function of the molar mass of the substrate to be hydrolysed[17]; (d) measurements of the temperature dependence of the self-diffusion coefficient of radioactive counterions in frozen gels as a function of temperature[18]; (e) hyperfiltration experiments of acetonitrile water mixtures using PSA membranes[19]. However the structural analysis of PSA gels is not complete enough as yet to estimate the volume fraction of the highly crosslinked region or the volume fraction of the space formed by the loose links.

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REFERENCES

1 Schlögl, R. 'Stofftransport durch Membranen', Steinkopff Verlag, Darmstadt, 1964
2 Drumm, M. F. and LeBlanc, J. R. in 'Step Growth Polymerization' (Ed. D. H. Salomon), Marcel Dekker, New

York, 1972, p. 157
3 Knap, A. and Scheib, W. 'Chemistry and Application of Phenolic Resins', Springer-Verlag, Berlin, Heidelberg, New York, 1979
4 Wiedner, G. and Woermann, D. *Ber. Bunsenges. Phys. Chem.* 1975, **79**, 868
5 Koschel, D. and Schlögl, R. *Z. Phys. Chem.* (N.F.) 1957, **11**, 137
6 Manecke, G. *Z. Phys. Chem.* 1952, **201**, 193
7 Schlögl, R. and Schödel, U. *Z. Phys. Chem.* (N.F.) 1964, **5**, 372
8 Pfenning, D., private communication
9 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953, Ch. 11
10 Hasa, J., Ilavsky, M. and Dušek, K. *J. Polym. Sci.* 1975, **13**, 253
11 Hasa, J. and Ilavsky, M. *J. Polym. Sci.* 1975, **13**, 263
12 Oppermann, W., Rose, S. and Rehage, G. *Br. Polym. J.* 1985, **17**, 175
13 'BMDP, Derivative-Free Nonlinear Regression', Computing Center, Northwestern University, Evanston, Illinois, 1983
14 Würz, U., Belkoura, L. and Woermann, D. *Ber. Bunsenges. Phys. Chem.* 1977, **81**, 1201
15 Franck, U. F. *Ber. Bunsenges. Phys. Chem.* 1963, **67**, 657
16 Toyoshima, Y. and Nozaki, H. *J. Phys. Chem.* 1969, **73**, 2134
17 Woermann, D. *Ber. Bunsenges. Phys. Chem.* 1970, **74**, 441
18 Schlögl, R. and Schurig, H. *Z. Electrochem., Ber. Bunsenges. Phys. Chem.* 1961, **65**, 863
19 Pfenning, D. and Woermann, D. *J. Membrane Sci.* submitted for publication