

Elasticity of Ion-Exchange Resin Beads in Solvent Mixtures

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ABSTRACT: The effect of the solvent composition on the elasticity of strong and weak cation- and anion-exchange resin beads was studied. Poly(styrene-*co*-divinylbenzene) resins containing sulfonic acid or quaternary ammonium groups and an acrylic acid resin crosslinked with divinylbenzene were immersed in water, NaCl solutions, or aqueous alcohol solutions and the shear modulus was measured with a uniaxial compression method. The elastic data were compared with the swelling properties. In pure water the shear moduli increased when the crosslink density, counterion valence, counterion size, and functional group size increased. Two additional phenomena in the elastic behavior were observed when the swelling degree of the resins was changed by the addition of alcohol or salt. A decrease of the modulus was observed when moving from the fully swollen state to a less swollen state, and a steep upturn of the modulus took place at a characteristic swelling region. The depth of the minimum and the location of the transition from the rubbery to the glassy state depended on the characteristics of the resins. The finite expansibility of the polymer chains and the glass transition explained these findings. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1256–1264, 2001

Key words: shear modulus; ion exchanger; ethanol; 2-propanol; glass transition

INTRODUCTION

The elastic properties of ion-exchange resins are intimately linked to their other properties, such as swelling and selective sorption. The study of the elastic characteristics of the resins can thus help to understand their behavior, for example, as a chromatographic stationary phase, as a membrane material, or in catalytic applications. The knowledge of the elastic behavior of the resins in water or in the actual solvent composition is also necessary when modeling the sorption properties of these polyelectrolytes. However, literature data on the elastic properties of ion-exchange resin

beads are very limited.¹ On the other hand, the elasticity of strongly swellable hydrogels has been extensively studied; for instance, slightly crosslinked homopolymer and copolymer gels of acrylic acid, methacrylic acid, and acrylamide have been quite thoroughly surveyed.^{2–8}

The elastic modulus in the swollen state is at least one decade smaller for the hydrogels than for the more heavily crosslinked ion-exchange resins. On the other hand, elastic moduli comparable in magnitude to the ion-exchange resins have been reported, for example, for swollen poly(styrene-*co*-divinylbenzene) (PS-DVB) copolymers,⁹ a swollen crosslinked polysaccharide,¹⁰ and swollen gels containing $-\text{SO}_3^-$ or $-\text{CH}_2\text{SO}_3^-$ functional groups.¹¹ Moreover, some bulk modulus data calculated from sorption isotherms have been reported for strong cation and anion exchangers.¹²

The mechanical measurements of hydrophilic materials like polyelectrolyte gels have been performed mainly in water or in aqueous salt solu-

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Table I Properties of Resins

Resin Name	Resin Type	Ionic Form	Crosslinkage (wt % DVB)	d_{av} (mm)	Effective Capacity (mequiv/g)	Water Retention (wt %)	$q = V_{water}/V_{dry}$ (mL/mL)
CS16G	SCE X8	H ⁺	8	0.35	5.1	52	2.2
	SCE X8	Na ⁺	8		4.7	46	2.1
	SCE X8	Ca ²⁺	8		4.7	44	1.8
	SCE X8	La ³⁺	8		4.2	40	1.7
CS11G	SCE X5.5	Na ⁺	5.5	0.35	4.6	56	2.7
	SCE X5.5	Ca ²⁺	5.5		4.6	50	2.2
	SCE X5.5	La ³⁺	5.5		3.9	44	2.1
	SCE X5.5	(CH ₃) ₄ N ⁺	5.5		3.7	50	2.0
CS08G	SCE X4	Na ⁺	4	0.35	4.5	65	3.6
	SCE X4	Ca ²⁺	4		4.6	57	2.9
	SCE X4	La ³⁺	4		4.1	48	2.3
AS511G	SAE X5.5	Cl ⁻	5.5	0.35	3.6	49	1.7
IRC86	WCE NA	Na ⁺	NA	0.58–0.78	9.3	67	4.0
	WCE NA	(CH ₃) ₄ N ⁺	NA		6.3	64	3.0
	WCE NA	H ⁺	NA		11.6	50	2.2

SCE, strong cation exchanger; SAE, strong anion exchanger; WCE, weak cation exchanger; NA, crosslink density not available; d_{av} , the average bead diameter in water.

tions. The elastic behavior of polyelectrolytes in solvent mixtures or partially swollen with water has received less attention. Furthermore, the existing data are limited to univalent counterions. The shear moduli of some sulfonic acid gels have been studied in water–acetonitrile mixtures, and the elasticity in water–ethanol or water–acetonitrile solutions has been reported in an article concerning the shear moduli of the anionic and cationic gels.^{11,13} Moreover, Tong and Liu¹⁴ used water–acetone mixtures to study the dynamic mechanical properties of acrylic gels containing sulfonic or carboxylic acid groups.

The scarcity of the reported data on the elastic behavior of ion-exchange resins in water and in solvent mixtures encouraged us to report the results of the elasticity of the ion-exchange resins. Elastic data are used to confirm the elastic parameters of equilibrium sorption models.¹ In this work the elastic moduli of several ion-exchange resins in water, water–NaCl, water–ethanol, and water–2-propanol solutions were measured. The effect of the crosslinkage, counterion, functional group, and resin matrix on the elasticity of the resins was investigated.

EXPERIMENTAL

Resin Pretreatment and Characterization

The sulfonated PS-DVB strong cation exchangers (SCE) CS16G, CS11G, CS08G, and the aminated

PS-DVB strong anion exchanger (SAE) AS511G were delivered by Finex Oy. The weak acrylic cation exchanger (WCE) IRC86 was obtained from Rohm & Haas. The characteristics and the ionic forms of the resins are shown in Table I. The sulfonated PS-DVB cation exchangers were functionalized with sulfonic acid groups, the strong anion exchangers with quaternary ammonium groups, and the acrylic cation exchanger with carboxylic acid groups. The nominal degree of crosslinking was given as a weight percentage of DVB in the polymerization mixture.

The strong cation-exchange resins were pretreated and exchanged into the desired ionic form, and their ion-exchange capacity was determined according to the method presented in earlier work.¹ The capacity of the strong anion exchanger was determined by eluting the Cl⁻ form resin with 20 resin bed volumes (BV) of 1M NaOH in a column. The unreacted NaOH was titrated with 1M HCl and the OH⁻ form resin was dried at 383 K overnight and weighed. The capacity of the weak cation exchanger was determined as follows. The weak cation exchange resin in the hydrogen form was stirred with 6 BV of 1M NaOH and then with 20 BV of water for 4 h. The unreacted NaOH was quantitatively collected and titrated with 1M HCl. The sodium form resin was dried at 383 K overnight and weighed. The effective capacities of other ionic forms were calculated by taking into account the change of the equivalent weight of the resin.

The resins were stored in the appropriate water–NaCl, water–ethanol, or water–2-propanol solutions several days before the mechanical measurements. The ethanol (about 94 or 99.5 wt %, Primalco) and 2-propanol (>99.7 wt %, Baker Analyzed HPLC reagent, J. T. Baker) were used as received. The exact composition of the alcohol solutions was determined by density measurements (DMA 4500, Anton Paar) with high accuracy (± 0.2 wt %). Reagent-grade electrolytes were used to change the resins into the desired ionic form and for the water–NaCl solutions.

Mechanical Measurements

The shear modulus of the resin beads was measured by using the static compression method presented earlier.¹ All measurements were done at room temperature ($22 \pm 1^\circ\text{C}$). A resin bead immersed in the equilibration solution was placed between two parallel plates that were attached to a micrometer screw and a microload cell (Kyowa LTS-200GA or Kyowa LVS-20GA). The resin beads swollen with a predetermined amount of water were immersed in *n*-heptane during the measurement. The deformation was increased stepwise up to about 10% of the bead diameter. The volume changes of the bead were avoided by keeping the measurement cycle time as short as possible. One cycle took only a few minutes involving 30–150 points. The diameter of the undeformed resin bead was measured visually.

The shear modulus (G) of the swollen resins was calculated from the Hertz equation, which under constant volume conditions can be written as eq. (1).^{15,16}

$$\Delta d = \left[\frac{3F}{4G\sqrt{d}} \right]^{2/3} \quad (1)$$

Here Δd is the deformation of the bead under load F and d is the undeformed bead diameter.

The method was tested by measuring the shear modulus for crosslinked dextran particles (Sephadex G50, Pharmacia) and comparing the results with the value reported in Briscoe et al.¹⁰ The measured shear moduli of three beads were 0.09, 0.09, and 0.11 MPa whereas the value of Briscoe et al.¹⁰ was 0.06 MPa at 25°C .

For all the resins at least three beads were measured and at least two compression cycles were recorded for each bead. The moduli calculated from duplicate cycles differed less than 5%. The data corresponding to deformations of 1–3% were neglected because of uncertainties due to

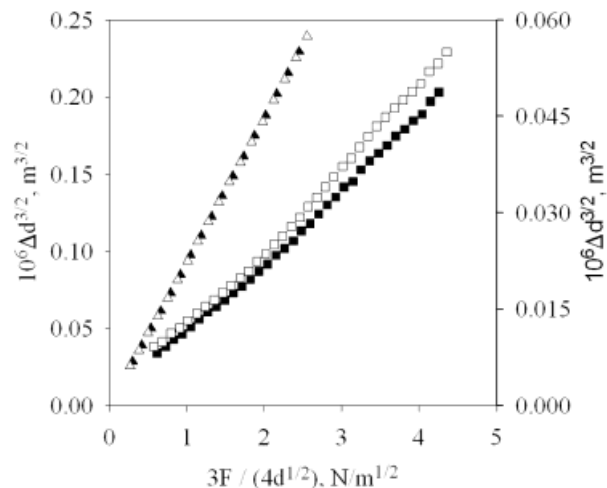


Figure 1 Typical compression cycles of the ion-exchange resin beads plotted in the form of eq. (1). (Δ , \blacktriangle) water (left y axis), (\square , \blacksquare) concentrated ethanol solution (right y axis), (\blacktriangle , \blacksquare) first cycle, and (Δ , \square) second cycle.

very small compressive forces.¹⁷ Typical data plotted in the form of eq. (1) are presented in Figure 1 where the shear modulus is obtained as the inverse of the slope. In water and dilute NaCl or alcohol solutions the linear dependence was excellent. For the resins equilibrated in concentrated NaCl or alcohol solutions, on the other hand, the differences between duplicate cycles were larger because of slow restoration of the spherical shape after compression. In such cases only the first cycle was used. Moreover, marked deviations from linearity were observed in concentrated alcohol solutions (Fig. 1) and therefore the values at the transition region were only approximate. It may be noted that the linear dependence was again observed in the dry or nearly dry state, where the moduli were 2–4 GPa. However, this region was not studied systematically.

The difference between the moduli of different beads was also tested by measuring 40 SCE X8 Na^+ beads, 17 SCE X5.5 Na^+ beads, and 14 WCE NA Na^+ beads. The moduli of different beads of the same resin deviated in most cases by less than 10%. The deviation was smaller for the less densely crosslinked resins.

In order to eliminate the swelling differences between resins, the moduli of the water-swollen resins were extrapolated to an unswollen state ($q = 1$) by means of eq. (2).

$$G = G_0 q^{-1/3} \quad (2)$$

Here $q = V/V_0$ is the degree of swelling and V and V_0 are the bead volumes in the swollen and dry

state, respectively. Equation (2) is based on the assumption of affine swelling and it was verified experimentally for weakly ionized polyelectrolyte gels swollen in water,^{4,8,15} but some deviations were observed at high degrees of ionization.² In eq. (2) the G_0 corresponds to the modulus at a hypothetical reference state and it has no correlation with the real modulus of the dry resin, as shown later.

For the WCE sodium resin and the SCE X4 sodium resins, for which the shear modulus reached a clear minimum at a certain solvent composition (see Fig. 2), the G_0 was also calculated from that minimum value in order to get more reasonable estimates for the G_0 of these resins (see Table II). For other resins the minimum was small or not observed at all and only the modulus in water was used.

RESULTS AND DISCUSSION

Moduli of Resins Equilibrated in Water

The crosslink density is known to affect the elastic modulus of hydrogels.^{3,4,7} In this respect, ion-exchange resins are not exceptions. Furthermore, the ionic form of the ion-exchange resin also has an influence on the modulus.¹ These effects can be seen from the G and G_0 values calculated with eq. (2) for the water-swollen resins (Table II). The effect of the crosslink density is straightforward: the increasing amount of crosslinker shortens the length of the polymer chains between the crosslinks (M_c) and according to the classical theory of rubber elasticity the elasticity is inversely proportional to M_c .¹⁸ On a quantitative level, however, the agreement failed and the measured dependence on the crosslink density was much more pronounced than predicted by the theory.

The effect of the counterion appeared to be more complicated. A comparison of the monovalent ions indicated that the modulus of the acid form of the strong resin was significantly higher than that of the sodium form resin. On the other hand, the modulus of the weak resin in the acid form was considerably smaller than in the sodium form. For the weak acrylic cation exchange resin the difference of the modulus between H^+ and Na^+ resin could be explained by the strained polymer matrix in the Na^+ form. A more detailed explanation is given later in this article.

For counterions having similar crystal radii (Na^+ , Ca^{2+} , La^{3+}), increasing ion valence increased the modulus, especially at the highest

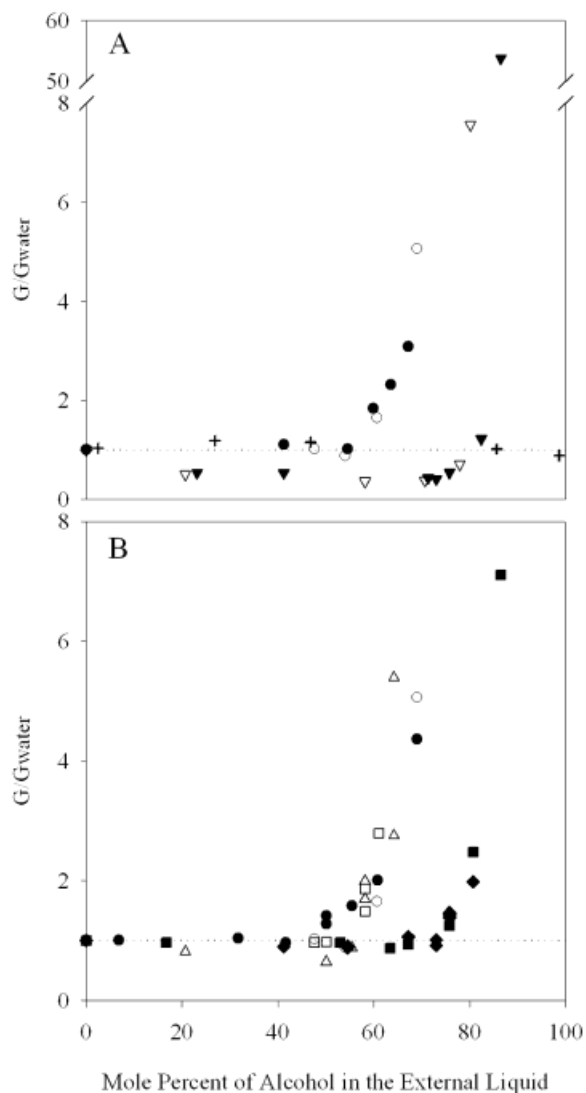


Figure 2 The relative shear modulus of the ion-exchange resins in different binary aqueous solutions. (A) strong H^+ cation exchanger: (+) X8, ethanol; strong Na^+ cation exchanger: (○) X8, ethanol and (●) X8, 2-propanol; weak Na^+ cation exchanger: (▽) ethanol and (▼) 2-propanol. (B) Strong cation exchanger: (○) Na^+ , X8, ethanol; (●) La^{3+} , X8, ethanol; (□) Na^+ , X5.5, ethanol; (■) $(CH_3)_4N^+$, X5.5, ethanol; (△) Na^+ , X4, ethanol; strong anion exchanger: (◆) Cl^- , X5.5, 2-propanol. The relative shear modulus is equal to one in water for each resin.

crosslink density (X8). At lower crosslink degrees the effect seemed to vanish or even become the opposite. The increasing modulus for multivalent ions can be possibly explained by the fact that counterions with higher valences bind more than one functional group and form "ionic crosslinks." On the other hand, at lower crosslinkage the distance between adjacent chains increases because

Table II Measured Shear Moduli (G) and Extrapolated Moduli (G_0) of Resins Equilibrated in Pure Water. All Values are in MPa

Resin Type	H^+		Na^+		Ca^{2+}		La^{3+}		$(CH_3)_4N^+$		Cl^-	
	G	G_0	G	G_0	G	G_0	G	G_0	G	G_0	G	G_0
SCE X8	27	35	21	27	29	37	37	44				
SCE X5.5			9.6	13	10.5	14	8.2	11	14	17		
SCE X4			3.8/3.0 ^a	5.8/4.0 ^b	3.3	4.7	2.8	3.8				
SAE X5.5											12	14
WCE NA	2.5	3.2	8.9/3.4 ^a	14/4.4 ^b					16.8	24		

SCE, strong cation exchanger; SAE, strong anion exchanger; WCE, weak cation exchanger; NA, crosslink density not available.

^a Minimum value of the shear modulus.

^b Calculated from the minimum of the shear modulus.

of the higher water contents of the resin so that the ionic interactions diminish and the stiffening effect is no longer observed. Of course, the considerably larger hydrated radius of multivalent counterions¹⁹ can also restrict the movement of the adjacent chains and strain the chains. At the same time, however, the number of the multivalent ions is smaller.

The data in Table II also indicate that increasing counterion size increased the shear modulus: the modulus of the $(CH_3)_4N^+$ resin was greater than that of the Na^+ resin. A bulky organic counterion can hinder the movement of the adjacent chains and strain the chains, resulting in a clear increment in the moduli of the otherwise similar resins. The same phenomenon was seen, although not as clearly, when the size of the functional group was increased. The modulus of the strong anion exchanger in the Cl^- form was only slightly higher than the modulus of the sulfonated strong cation exchanger in the Na^+ form. The matrices of the strong anion and the strong cation exchangers were identical but the substitution degree of the strong cation exchanger was higher. Therefore, the weaker size effect in the anion exchanger was at least partly due to the lower substitution degree. Moreover, there was a covalent bond between the functional group and the anion-exchanger matrix, whereas the ionic interactions dominated between the sulfonic acid group and the $(CH_3)_4N^+$ counterion.

Moduli of Resins Equilibrated in Solvent Mixtures

The external solution composition is known to affect the elastic properties of polymer gels. Especially, the effect of salt concentration on the modulus of the hydrogels has been extensively studied.^{3-5,8} Another way to influence the degree

of swelling and the elastic properties of the polyelectrolytes is to add an organic solvent to water.¹ The effect of the solvent composition on the shear modulus of the ion-exchanger resins is shown in Figure 2. In order to elucidate the differences, the values are given as ratios of the moduli in the solvent mixture to the respective moduli in water.

Two phenomena in the elastic modulus of the salt form resins were observed when changing the external solvent composition. The shear modulus went through a minimum when moving toward concentrated alcohol solutions (less swollen resin) and a steep upward curvature was seen at a certain composition range. The minimum in the modulus curve was most pronounced for the weak cation exchanger and the value was only about 40% of the value measured in water [Fig. 2(A)]. For other resins the minimum was weaker or not observed at all. Similar behavior was also found for hydrogels in brine solutions, although there the minimum occurred at swelling degrees that were at least 10 times higher.^{3-5,8} The minimum in the modulus of hydrogels at higher swelling degrees than that of the resins can be explained by the much stronger swelling ability of hydrogels. The hydrogels can swell from 100 to over 1000 times from the dry volume whereas the maximum swelling degree of the resins is typically less than 10 (Table I). The finite expansibility of the hydrogel chains is influenced at high swelling degrees, and therefore in water the chains are strained and the modulus is large. At lower swelling degrees the chains become less strained and the modulus decreases. The same explanation can also be used for the elastic behavior of the more densely crosslinked and much stiffer ion-exchange resins. This explanation was supported by the fact that increasing crosslinkage moved the

minimum of the modulus of the hydrogels toward smaller swelling degrees.³ For instance, when the crosslink density of an polyacrylamide-acrylic acid gel was 0.18 wt %, the minimum was at $q = 1000$, and when it was 0.59 wt % the minimum shifted to $q = 100$.³ Therefore, for the ion-exchange resins containing between 4 and 8 wt % DVB, the minimum can be expected to move to much lower swelling degrees. This proved to be the case as shown in Figure 3 where the relative shear moduli are plotted at different swelling degrees.

Moreover, the above explanation is supported by the following finding. Preliminary data on the weak acrylic cation exchanger resin in the H^+ form showed that its modulus in water was comparable with the minimum modulus of the weak acrylic cation-exchanger Na^+ resin (Table II) and no minimum was observed. At the same time the degree of swelling in water was 2.2, which was close to the location of the minimum in the curve of the Na^+ form [Fig. 3(A)]. Therefore, the further expansion of the matrix induced by neutralization seemed to be the primary cause for the increasing modulus.

The rapid upturn of the modulus at a certain external solvent composition or at a certain swelling degree is evident in Figures 2 and 3. The upturn most probably indicated the onset of the glass transition at the temperature of the measurement. All salt form resins had the transition point at a characteristic swelling range (Fig. 3). This meant that the glass-transition temperature (T_g) of the dry resin was above room temperature and its modulus was substantially higher than that of the water-swollen resin. In fact, the T_g of the dry ion exchangers used in this study was markedly above room temperature. Linear PS has a T_g of about 100°C and the crosslinking and the ionic functionalization increase it.^{20–23} The crosslinking with 8 wt % DVB increased the T_g about 40°C above that of the linear polymer and at a moderate degree of substitution the sulfonation was affected 2–3°C per mole percentage point.^{20,22–23} Accordingly, the monosulfonated resins used in this work had significantly higher T_g values than only partly sulfonated polymers. For the linear poly(acrylic acid) salts with a chemical structure similar to the weak cation exchanger, the glass-transition temperature was also substantially above room temperature and the value depended on the counterion.²⁴ On the other hand, the swelling agent was found to radically drop the T_g of the polymers, neutral or ionic.^{10,20,25} The water or the solvent mixture ab-

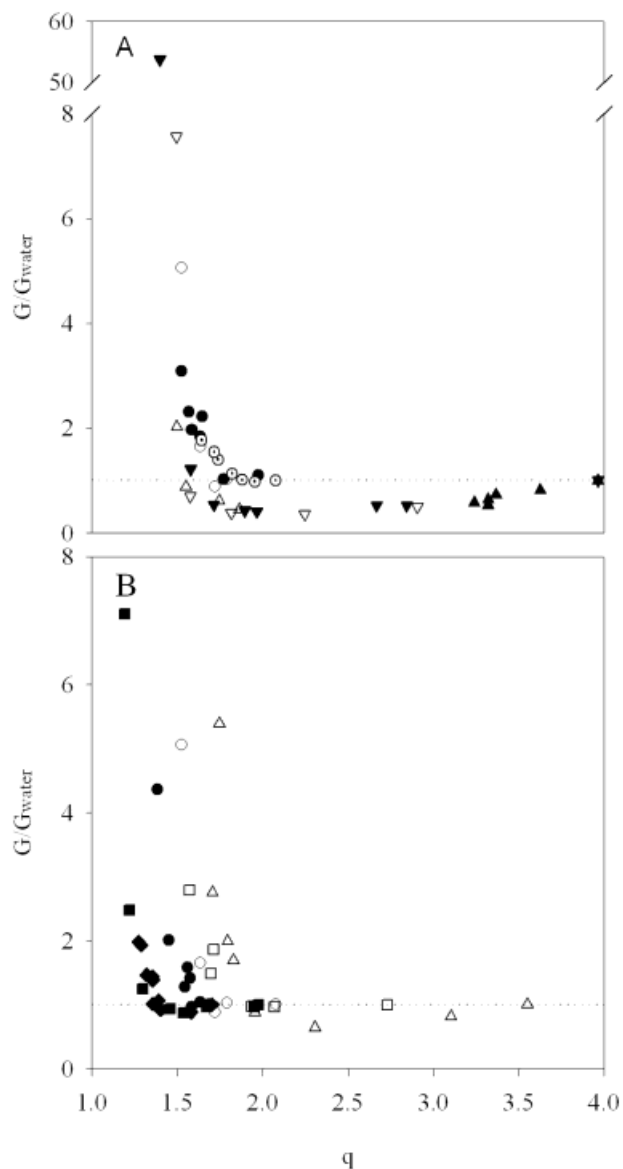


Figure 3 The relative shear modulus of the ion-exchange resins at different swelling degrees of the resins in water or in binary water–alcohol solutions. (A) Strong Na^+ cation exchanger (X8): (○) NaCl solution, (○) ethanol, (●) 2-propanol; weak Na^+ cation exchanger: (△) water, (▲) NaCl solution, (▽) ethanol, (▼) 2-propanol. (B) Strong cation exchanger: (○) Na^+ , X8, ethanol; (●) La^{3+} , X8, ethanol; (□) Na^+ , X5.5, ethanol; (■) $(CH_3)_4N^+$, X5.5, ethanol; (△) Na^+ , X4, ethanol; strong anion exchanger: (◆) Cl^- , X5.5, 2-propanol.

sorbing into the ion exchanger acted as a plasticizer, and the T_g of the exchanger dropped dramatically and remained below room temperature between the water-swollen state and the transition region.

Further evidence for the glassy behavior of the strong cation exchangers at low swelling degrees

was given by the ethanol vapor sorption studies of Mattisson and Samuelson.²⁶ Ethanol vapor sorption and desorption behavior in the Na⁺ strong cation-exchanger resins showed significant hysteresis originating from the nonequilibrium state of the sorption system.²⁶ Furthermore, the excessively slow diffusion rates observed in concentrated ethanol solutions¹ were also indicative of the glassy structure.

Quite interestingly, no glass transition was observed for the H⁺ strong cation-exchanger resin, even in the most concentrated ethanol solutions [Fig. 2(A)]. However, this result is easily explained by the small volume changes of the H⁺ resin bead. The bead volume decreased only a few percent from water to aqueous ethanol within the whole composition range. Thus, the deswelling was too small for the H⁺ resin bead to reach the characteristic swelling degree where the transition starts at room temperature.

In Figures 2 and 3 several variables affecting the transition from the rubbery to the glassy state were considered. The crosslink density was one of the factors that most affected the properties of the ion exchangers. According to Figure 2(B), the glass-transition temperature of the strong cation exchangers (Na⁺) with different crosslink densities seemed to be independent of the external solvent composition. On the other hand, Figure 3(B) shows the same data as a function of the volume swelling and a shift of the transition point with the crosslinkage is observed. In fact, Figure 2 shows only the situation outside of the exchanger and does not really tell anything about the solvent composition or content inside the exchanger, as is the case in Figure 3.

According to Figure 3(B) the transition point moved toward the lower swelling degrees with increasing crosslinkage. This meant that the exchanger needed less plasticizing solvent to become a rubberlike state when its crosslink density increased. In other words, smaller crosslink density meant higher T_g at the same swelling degree. This observation was contradictory to the data reported for the dry PS-DVB polymers, for which the T_g increased with increasing crosslinkage.^{20,23} On the other hand, according to Gutierrez and Ford²⁰ the slope of the decreasing T_g values of the PS-DVB polymer at different toluene contents was steeper when the crosslink density increased. Assuming that this is valid also for the sulfonated matrix and for the solvents used in this study and that the decreasing T_g values at different crosslink densities intersect at a higher temperature than the measurement temperature,

the transition regions of the exchangers with different crosslinkages are in a logical order in Figure 3(B).

Figure 2 and Figure 3 also illustrate how the counterion valence and size, the functional group, and the resin matrix influence the transition from the rubbery to the glassy state. The increasing counterion valence shifts the transition to a smaller swelling degree in Figure 3(B). Mark et al.²⁷ observed the opposite effect for the dry ionic polymers, where the glass-transition temperature increased with increasing ion charge. It was also claimed that the T_g value rose with decreasing cation size.²⁷ Although the size of the unhydrated La³⁺ ion is quite near the size of the unhydrated Na⁺ ion, the hydrated size of La³⁺ is much larger as already mentioned and a shift to a lower T_g value with increasing ion charge seems to be justified in this case.¹⁹ However, the solvent structure in the La³⁺ resin seems to be rather complicated¹ and the result should be interpreted with caution.

The large organic counterion [i.e., (CH₃)₄N⁺] in the sulfonated resin and the functional group [—N⁺(CH₃)₃] of the strong anion exchanger had similar effects on the transition. The transition moved toward the less swollen state as compared with the sulfonated Na⁺ resin [Fig. 3(B)]. Thus, the sulfonated (CH₃)₄N⁺ resin and the strong anion-exchange resin had a lower T_g value than the T_g value of the sulfonated Na⁺ resin at the swelling degree where the sulfonated Na⁺ resin had the transition point. The decreasing T_g value with increasing counterion size was reported earlier for partially sulfonated PSs in different alkyl ammonium forms, although the effect was not observed until in the tributylammonium form.²⁸ The decreasing T_g value with increasing counterion size was also supported by the data of Mark et al.²⁷ as already mentioned. Finally, the effect of the functional group was connected to the flexibility of the group. The increasing number of alkyl groups in the side chain of the polymer is known to decrease its glass-transition temperature.²⁷

The weak exchanger had a transition point at a swelling range, which implied lower q values than that of the strong cation exchangers, as can be seen from Figure 3(A). The exact crosslink density of the weak acrylic cation exchanger is not available but from the data measured in our laboratory it can be estimated to be between 6 and 8 wt % DVB. This corresponds to 4.7–6.3 mol % DVB crosslinkage. For the strong cation exchangers the crosslink degree between 5.5 and 8 wt % DVB corresponded to 4.4–6.5 mol % DVB. In this

respect, the weak Na^+ cation exchanger had the transition point at a lower swelling degree than the equally crosslinked strong Na^+ cation exchanger. It was likely that the sulfonated PS-DVB resin with very high aromatic ring contents of the side chains was more rigid than the acrylic acid resin with quite low aromatic ring contents (crosslinks only).²⁷

Concerning the role of the external solution components, Figures 2 and 3 show that the two solvents (ethanol and 2-propanol) resulted in similar shear modulus curves. The upward curvature of the modulus appeared at the same solvent contents and at the same swelling degree, irrespective of the organic solvent used. On the other hand, it was found that for the strong cation exchangers the transition point moved to a higher swelling degree when NaCl was used instead of organic solvent. The effect was very small for the X8 resin [Fig. 3(A)] but clearer for the resins of lower crosslink density. Thus, the similar behavior in the organic solvents seemed to be more or less coincidence and due to the similarity of the solvents.

In the case of the weak cation exchanger similar behavior was observed in pure water, NaCl solutions, water-ethanol, and water-2-propanol [Fig. 3(A)]. However, this was as expected, because according to sorption measurements (not shown here), the weak resin contained almost pure water, irrespective of the external water-alcohol composition. Furthermore, the change of the swelling degree of the weak acrylic cation exchanger Na^+ resin in the electrolyte solutions was far too small to reach the transition point. Nevertheless, the decrement of the modulus followed the same trend as in the other solutions.

Volume Changes in Solvent Mixtures

The influence of the glass transition on the swelling properties can be further clarified by comparing the elastic data given in Figure 2 with the corresponding volume change data depicted in Figure 4. The data of the strong Na^+ cation-exchanger beads (Fig. 4) indicated a close correlation between the glass transition (Fig. 2) and the swelling behavior. The glass transition occurred at the same external liquid composition range (around 60 mol % of ethanol) where the crosslinking effect on the volume swelling disappeared. Therefore, it seemed that within a relatively narrow composition range the PS-DVB matrix underwent a direct change from the glassy state to a swollen gel.

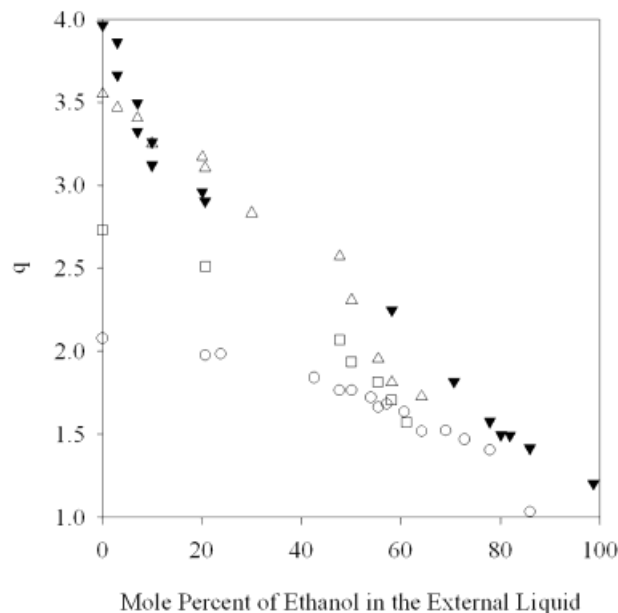


Figure 4 The swelling of the ion-exchange resins in different water-ethanol mixtures. Strong Na^+ cation exchanger: (○) X8, (□) X5.5, (△) X4. (▼) Weak Na^+ cation exchanger.

The situation appeared to be somewhat different for the weak acrylic cation exchanger resin. According to Figure 2, the glass transition of this polymer matrix started at about 75 mol % of ethanol and this was reflected in the swelling curve as a bend (Fig. 4). The rapid volume increase occurred however at much more dilute ethanol solutions and the transition to a true gel started at 20 mol % of ethanol. This interpretation was supported by our preliminary sorption data on resins having a polymer matrix similar to the weak acrylic cation exchanger resin: the influence of the crosslink density on the isotherms vanished at around 20 mol % of ethanol and at higher ethanol concentrations all values laid on a single curve.

The fact that the glass transition and the gel transition were widely separated in the weak acrylic cation exchanger resin while they practically coincided in the strong cation exchanger resin can be explained by stronger interchain interactions in the former material. However, the exact interaction mechanisms are unknown.

CONCLUSIONS

In this work several variables affecting the elasticity of ion-exchange resins in water and in sol-

vent mixtures were studied. The glass-transition region of the salt form ion-exchange resins was clearly seen from the elastic data. Moreover, the minimum of the elastic modulus, which normally occurs in a much higher swelling region for the hydrogels, was also seen in the ion exchangers with moderate degrees of crosslinking.

A comparison of the elastic data with volume changes of the resin beads implied that at a given temperature the resins could be in three different states, depending on the degree of swelling. Besides the transition from the glassy to the rubbery state, a point appeared to exist beyond which the resin became a true gel. These two transitions more or less coincided in the strong cation exchanger resins, but for the weak cation exchanger containing carboxylic groups there was a relatively wide region between the glassy state and the true gel. The different behavior of the two materials was probably attributable to stronger interactions between the polymer chains and/or the functional groups of the weak acrylic cation exchanger resin.

The knowledge gathered in this work combined with the other characteristics of the resins can be utilized when constructing models to predict sorption phenomena in the ion-exchange resins when used, for instance, as a chromatographic stationary phase. In particular, the results indicate a useful operation range for the gel-like resins as partition stationary phases. The highly swollen gel state provides the most favorable separation conditions, whereas the glassy state should be avoided because of slow diffusion rates and hysteresis problems.

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