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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · NOVEMBER 1999

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Sorption of Neutral Components in Ion-Exchange Resins. 1. Effect of Cross-Link Density and Counterion on Selective Sorption of Water–Ethanol Mixtures in Sulfonated PS–DVB Resins**Jari Tiihonen,* Markku Laatikainen, Ismo Markkanen, and Erkki Paatero***Laboratory of Industrial Chemistry, Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland*

Experimental data for the distribution of water–ethanol mixtures between a solid phase and a liquid phase at 298 K are reported. The solid phases studied were gel-type sulfonated poly(styrene-*co*-divinylbenzene) resins of different degrees of cross-linking (4–8% DVB) and carrying different counterions (Na^+ , Ca^{2+} , and La^{3+}). The shear moduli of the resin beads were also measured to characterize their elastic properties. All resins absorb water selectively, and the selectivity increases with increasing cross-link density. The low selectivity of the less densely cross-linked resins is shown to be mainly due to the mutual interaction of the solvents in the resin phase resulting in a pronounced maximum in the ethanol sorption isotherms. The influence of the counterion on the selectivity is more complex. At high water contents, the water selectivity of the Na^+ resin is higher than that of the Ca^{2+} and La^{3+} resins, whereas the selectivities are approximately equal at low water contents. The elastic properties of the resin beads remain unchanged from pure water to water mole fractions of around 0.4, where a sharp rise in the shear modulus occurs. The data are analyzed by means of a model based on the UNIQUAC equation and the affine network theory of elasticity. The effect of cross-link density on the selectivity and solvent content of the resins can be explained satisfactorily with the model. However, the calculated and experimental sorption isotherms for the La^{3+} resins deviate appreciably at low external water contents. The discrepancies are discussed on the basis of the elastic properties of the resins and the specific solvation interactions.

1. Introduction

The behavior of strongly acidic ion exchangers has been widely examined both in nonaqueous solvents and in aqueous–organic solvent mixtures.^{1–12} For instance, Samuelson and co-workers^{2,6} have studied the swelling and solvent distribution of water–ethanol mixtures in strong cation and anion exchangers. However, their data on cation exchangers are limited to monovalent counterions only. Sinegra and Carta¹¹ have examined the effect of counterion valence on the distribution of water and ethanol between the resin phase and the liquid phase at low water mole fractions. In these papers, the experimental data have been discussed in qualitative terms, and only empirical correlations have been used. In general, swelling of the strong cation exchangers, especially in salt forms, is strongest in water and decreases with increasing organic solvent content. This has been explained by the lower dielectric constant of solvent.^{1,5} Moreover, the resins are selective for water at all water–organic solvent compositions, and the selectivity is highest at low water contents.

A number of models have been introduced for the quantitative analysis of the equilibrium swelling of

nonionic and ionic polymer resins. Thermodynamic equilibrium conditions have been recently formulated by Maurer and Prausnitz.¹³ Their equilibrium equation of the resin phase is made up of the mixing term and the term due to the pressure difference between the resin phase and the external liquid. In model calculations for a dilute polyelectrolyte gel in water, the mixing contribution was evaluated from the Flory–Huggins equation and the elastic pressure term was written by means of the Flory affine network model.¹⁴ In addition to a classical thermodynamic approach, the swelling of polyelectrolyte gels has been described with scaling theories (e.g., Rubinstein et al.¹⁵), and Glueckauf¹⁶ has used a microscopic “reaction” model for sorption of water in cation exchangers.

In ionic systems, the mixing term includes the polymer–solvent, ion–solvent, and ion–ion effects, and they can be separated into dilute and semidilute systems. Typically, the Flory–Huggins equation is used for the polymer–solvent interactions and the ion–solvent effects are estimated from the ion concentration of the gel.^{14,17,18} On the other hand, in their studies on sorption of binary liquid mixtures in ion-exchange resins Mazzotti et al.¹² have used the Flory–Huggins expression to include all of the mixing effects. A more elaborate form of the mixing term based on the Guggenheim’s

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Table 1. Properties of the Resins

	CS08G	CS11G	CS16G	Dowex 50W X8	Dowex 50 ^a
cross-linkage, wt % of DVB	4.0	5.5	8.0	8.0	8.0
d_{av} , ^b mm	0.35	0.35	0.35	0.20–0.50	0.20–0.40
Q , ^c mequiv/g	5.05	5.12	5.22	5.16	4.50 ^d
V_{eq} , mL/equiv Na ⁺	129 ^e	129 ^e	125 ^e	127 ^f	127 ^f
V_{eq} , mL/equiv Ca ²⁺			123 ^e		
V_{eq} , mL/equiv La ³⁺	118 ^e		118 ^e		

^a Data from Rückert and Samuelson.⁶ ^b Average bead size in sodium form. ^c Hydrogen form. ^d Sodium form. ^e Calculated from the density data of the water-swollen resin. ^f From Boyd and Soldano.²⁴

quasi-chemical concept has been given by Hooper et al.¹⁹ and by Prange et al.²⁰

The classical Flory equation has been shown to explain the elasticity of many moderately swollen gels.^{13,20} As pointed out by Gusler and Cohen,²¹ the theory may not be valid in densely cross-linked networks. Their alternative expression derived for high degrees of cross-linking was subsequently used by Mazzotti et al.¹² for resins containing as much as 20% of the cross-linking agent. A different approach for the pressure effect was presented by Gregor^{22,23} in order to explain the swelling and water sorption of ion-exchange resins. Based on a mechanical analogy, the swelling pressure generated within the resin was assumed to be linearly dependent on the volume changes. This concept has been adopted also by Boyd and Soldano²⁴ and Nandan and Gupta¹⁰ in the analysis of the sorption of water and methanol vapors in various resins.

The studies referred to above deal almost exclusively with swelling in a single solvent, usually water, and only Mazzotti et al.¹² have considered sorption of binary solvent mixtures. Because Mazzotti et al.¹² investigated only a nonhomogeneous resin in acid form, it was considered appropriate to study the ternary sorption system with homogeneous gel-type resins in more detail. The present study is a part of a liquid chromatography project, and its main objective is to investigate the factors influencing sorption of binary solvent mixtures in ion-exchange resins and partitioning of various solutes between the solvent mixture and the resin. In this part 1, sorption of water–ethanol mixtures in sulfonated poly(styrene-*co*-divinylbenzene) resins having mono-, di-, and trivalent counterions and different degrees of cross-linking has been examined. The equilibrium solvent uptake and distribution in the resin phase have been measured, and the data are correlated with a sorption model based on a modified UNIQUAC equation²⁵ and the affine network model of Gusler and Cohen.²¹ In part 2,²⁶ the treatment is extended to analyze the sorption data of sugars from water–ethanol mixtures. The purpose of the work is to increase understanding of the phenomena involved in chromatographic separation with aqueous–organic solvent mixtures as the eluent.

2. Materials and Methods

Sulfonated poly(styrene-*co*-divinylbenzene) (PS–DVB) cation exchangers CS08G, CS11G, and CS16G were delivered by Finex Oy (Finland), and Dowex 50WX8 was obtained from Sigma. The nominal degree of cross-linking is given as the weight percentage of divinylbenzene (DVB) in the polymerization mixture, and the resins studied contained 4 (X4), 5.5 (X5.5), and 8 (X8) wt % of DVB, respectively. All of these are typical gel-type resins, and their properties are shown in Table 1.

CS16G was used in Na⁺, Ca²⁺, and La³⁺ forms and CS08G in Na⁺ and La³⁺ forms. Other resins were in Na⁺

form only. The resins were excessively washed in a column with water and exchanged into the desired ionic form. Na⁺ resins were obtained by treatment with 2 M aqueous sodium chloride, and the exchange into the calcium and lanthanum forms was done via the hydrogen form. After exchanging to the appropriate ionic forms, the resins were again washed with water.

The ion-exchange capacity of the resins in the hydrogen form was determined with the following procedure. The resin in the hydrogen form was eluted with 20 bed volumes (BV) of a 2 M NaCl solution. This solution was collected and titrated with 1 M NaOH. The resin was changed back to the hydrogen form with 20 BV of a 1.5 M HCl solution. After each alkali and acid treatment, the resin was washed with a great volume of water to remove the residual alkali or acid from the resin. Finally the 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. Equivalent volumes were calculated from the densities of the water-swollen resins measured pycnometrically at 298 K. A constant value of 18.1 mL/mol was assumed for the water molar volume. The values given in Table 1, therefore, correspond to the extrapolated volumes reported by Boyd and Soldano.²⁴

Ethanol (about 94 wt %, Primalco, Finland) was used as delivered. The exact composition of the ethanol solution was determined by density measurement (Anton Paar, DMA 55). The accuracy of the density measurement estimated from the duplicate test runs was ± 0.2 wt % at high ethanol concentrations and even better at low ethanol concentrations. Reagent-grade electrolytes were used to exchange the resins into the desired ionic form. All solutions were prepared in deionized water ($\kappa < 1 \mu\text{S cm}^{-1}$).

Equilibrium Measurements. Before the experiments the resins were stored in water or in 94 wt % aqueous ethanol. The initial solvent content was measured by centrifugating (2500 rpm, 10 min) the resin in a sintered tube in order to remove the nonabsorbed solvent around the particles and by weighing. The weighed resins were dried at 383 K overnight and weighed again. The composition of the equilibrated liquid was determined by density measurement.

The equilibrium distribution of water and ethanol between the resin and liquid phases was obtained as follows. A total of 4–6 g of the water-swollen resin or 3 g of the ethanol-swollen resin was weighed accurately in a test tube, and a known amount of the desired water–ethanol solution was added. The test tube was tightly sealed, and the sample was then agitated for 3 days at room temperature and finally equilibrated for 3 days at 298 ± 0.1 K. After equilibration, the solution was recovered and the resin was centrifugated and weighed. The solvent content in the resin and liquid phases was determined as described above. The devia-

tion between the duplicate measurements at high water mole fractions was ± 0.1 mol/equiv and somewhat greater at low water contents.

Elasticity Measurements. The elastic modulus was measured at room temperature for resin beads swollen in water and in various water–ethanol mixtures using a method adapted from Knaebel et al.²⁷ and Briscoe et al.²⁸ The spherical resin particle was put between two parallel glass plates. One of the plates was attached to a microload cell (Kyowa LTS-200GA) and the other to a micrometer screw. The resin bead and the glass plates were immersed in water or an appropriate water–ethanol solution, and the force corresponding to different degrees of deformation was measured. The deformation was increased stepwise, and the maximum deformation was 10–20% of the bead diameter. The equilibration time was kept very short in order to avoid volume changes of the bead. One cycle involving 10–20 points lasted only a few minutes. The diameter of the undeformed resin bead was measured separately using an optical microscope.

The shear modulus G of the swollen resins was calculated from the Hertz equation²⁷ (eq 1). Here Δd is

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

the deformation of the bead under load F and d is the undeformed bead diameter. The moduli calculated from duplicate cycles measured with the same bead differed by less than 5%. For resins equilibrated in concentrated ethanol solutions, the deviations were much larger because of the slow restoration of the spherical shape after compression. In such cases only the first cycle was used.

3. Theory

Sorption Model. In the present treatment, the resins are considered as homogeneous phases and the crosslinks are assumed to affect sorption only via the elastic properties of the resin. Consequently, the equilibrium conditions are written by combining suitable expressions for the mixing and elastic contributions to the free energy. As discussed by Oppermann,¹⁷ the mixing effect is predominantly due to the ions present in the resin phase, especially when the resin is immersed in non-electrolyte solutions. The ionic contribution can be evaluated with reasonable accuracy in dilute systems, but in the concentrated polyelectrolyte resins studied here, this is a formidable task even in binary systems. Therefore, no attempts are made to formulate explicitly the ion–solvent interactions, but all of the mixing effects are considered together.

In a study concerning a somewhat similar case, Pitzer²⁹ has reported the water activity data of some electrolyte systems from dilute solutions to fused salts. It was found that the data were well represented by the van Laar equation, except at the very dilute region, where the Debye–Hückel term became important. The same principle was later applied to aqueous and organic–aqueous solutions of simple electrolytes by combining the quasi-chemical UNIQUAC equation with the Debye–Hückel limiting law.³⁰ In the present model, the latter term is omitted, because the counterion molality in the resin phase is very high, ranging from about 2 mol/kg upward.

As a result, the equilibrium condition for the absorbate i is written as follows.¹³

$$\ln a_i(l) = \ln a_i(s) + \frac{V_{m,i}}{RT} \pi_{el} \quad (2)$$

$V_{m,i}$ is the partial molar volume of component i , and $a_i(l)$ and $a_i(s)$ are the activities of component i in the liquid and resin phases, respectively. The elastic pressure π_{el} is equal to the pressure difference between the resin and liquid phases. R and T have their usual meanings. In the derivation of eq 2, the standard chemical potentials are taken for the pure liquid i , and they are assumed equal for both phases. Consequently, the activity of component i is the product of the symmetric activity coefficient γ_i , and the mole fraction x_i .

The activity coefficients both in the liquid phase and in the resin phase were calculated from the modified UNIQUAC equation (eq 3)²⁵ where Φ_i is the molecular

$$\ln \gamma_i = \ln \left(\frac{\Phi_i}{x_i} \right) + 1 - \frac{\Phi_i}{x_i} + q_i \left(1 - \ln \sum_j \theta_j \tau_{ji} - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right) \quad (3)$$

$$\Phi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}}$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

$$\tau_{ij} = \exp \left(- \frac{a_{ij}}{T} \right)$$

volume fraction, θ_i is the molecular surface area fraction, r_i is the size parameter, q_i is the surface parameter, τ_{ij} is the Boltzmann factor, and a_{ij} is the interaction parameter. Equation 3 differs from the UNIQUAC equation presented originally by Abrams and Prausnitz³¹ in having a simplified expression for the combinatorial part of the activity coefficient and in using exponent $2/3$ instead of 1 in the definition of the molecular volume fraction.

Both the original and modified UNIQUAC equations were tested and shown to represent adequately the sorption data of water–ethanol mixtures. However, the modified equation was selected for this study, because it gave a much better representation for the sugar–mixed solvent systems reported in the second part of this paper.²⁶ Peres and Macedo^{32–34} have also used the modified UNIQUAC model to simulate and predict solid–liquid equilibria of sugars in mixed solvent systems.

The elastic pressure appearing in the last term of eq 2 can be calculated from the affine network model, and an expression (eq 4) from Gusler and Cohen²¹ is used here. It should be noted, however, that for resins experiencing only small volume changes the choice of

$$\pi_{\text{el}} = K_{\text{el}} \left(1 - \frac{2M_c}{M} \right) \left[\frac{5}{3} \phi_r^{1/3} - \frac{7}{6} \phi_r \right] \quad (4)$$

the expression is not critical. In fact, the term inside the square brackets of eq 4 remains nearly constant in the swelling range of this study. This contradicts, of course, the results of Boyd and Soldano,²⁴ who presented that the swelling pressure increases linearly with the volume of the resin. However, the affine swelling theory is used here, because its applicability in polyelectrolyte gel systems is well established. The number of dangling chains is assumed to be small for the moderately cross-linked and high molecular weight resins used in this work, and therefore $2M_c/M \ll 1$. The polymer volume fraction ϕ_r refers to the swollen state, and the reference state is taken as $\phi_r = 1$.

According to the classical theory of rubber elasticity,^{14,35} the elastic coefficient K_{el} in eq 4 is equal to the shear modulus of the unswollen cross-linked matrix. Here K_{el} is treated as a freely adjustable parameter, and its correlation with the shear modulus is tested by comparing with the values obtained experimentally. To obtain the modulus G_0 corresponding to the reference state, the modulus G measured at ϕ_r was rendered to $\phi_r = 1$ by means of eq 5. The exponent $1/3$ has been

$$G = G_0(\phi_r)^{1/3} \quad (5)$$

verified experimentally for weakly ionized polyelectrolyte gels swollen in water,^{17,27,36,37} but some deviations were observed at high degrees of ionization.³⁸ It is important to note that G_0 is here the modulus extrapolated to $\phi_r = 1$ and has no correlation with the actual modulus of the dry resin, as will be shown later.

Calculations. The phase equilibria of the ternary water (1)–ethanol (2)–resin (3) systems were calculated by means of eqs 2–4. The concentrations in the resin were obtained by solving the nonlinear equations with a Newton–Raphson procedure.³⁹ The volume fractions appearing in the elastic term (eq 4) were computed additively from the amounts and molar volumes of the components. For simplicity, constant values of 18.1 and 58.7 mL/mol (at 298 K) were used for the partial molar volumes of water and ethanol, even though it is known that the molar volumes vary considerably with the solvent composition.^{40,41} Data for partial molar volumes in multicomponent systems are not available, and these volumes are difficult to estimate.

The model parameters were obtained by minimizing the object function (eq 6) by a SIMPLEX parameter

$$\text{OF} = \sum_j \sum_i \left[w_{j,i} \left(\frac{n_{j,i,\text{exp}} - n_{j,i,\text{cal}}}{n_{j,i,\text{exp}}} \right)^2 \right] \quad (6)$$

estimation routine.³⁹ The summation goes over the data points j and the sorbed components i . The term $w_{j,i}$ is the weight coefficient of the j th data point of component i , and $n_{j,i,\text{exp}}$ and $n_{j,i,\text{cal}}$ are the experimental and calculated amounts of component i per equivalent of the resin. The values n_i were obtained from the mole fractions appearing in the equilibrium equations by noticing that for the polymer $n_3 = 1/\text{DP}$, where DP is the degree of polymerization of the un-cross-linked chains. This equality is based on the generally accepted assumption¹ that the conventional sulfonation process yields monosulfonation at every repeating unit of the polystyrene chain.

The validity of the fit was estimated by calculating from eq 7 the absolute average deviations (AAD) for each component having N data points.

$$\text{AAD}_i = \frac{\sum_j \left| \frac{n_{j,i,\text{exp}} - n_{j,i,\text{cal}}}{n_{j,i,\text{exp}}} \right|}{N} \times 100\% \quad (7)$$

The size and surface parameters r and q for water and ethanol were taken from Peres and Macedo.³² No data are available for the sulfonated PS resin, and the values $r = 6.0$ and $q = 5.0$ for the repeating unit were estimated from the molecular structure of a mono-sulfonated ethylbenzene unit. The same values were used for all counterions. The average degree of polymerization of the un-cross-linked chains was arbitrarily set as 1000.

Six interaction parameters a_{ij} are needed in order to define the ternary system water (1)–ethanol (2)–resin (3). The four parameters characterizing the interactions of the water–ethanol and water–resin pairs were determined using literature data. The values of a_{12} and a_{21} were estimated from the vapor–liquid equilibria (VLE) data measured for water–ethanol mixtures at a temperature range of 294–305 K.⁴² The number of data points was 11, and the AAD for the vapor phase mole fraction and the vapor pressure were 1.9% and 4.3%, respectively.

The parameters a_{13} and a_{31} of the water–resin pair were obtained from the osmotic and isopiestic data of aqueous solutions of poly(styrene sulfonates) and of lightly cross-linked PS–DVB resins at 298 K. In view of the discussion above, it is assumed that these parameters vary with the counterion but are not affected by the cross-links introduced in the resins. For the Na^+ resin, the data of the soluble sodium salt from Waxman et al.,⁴³ Reddy and Marinsky,⁴⁴ and Timmermann⁴⁵ as well as the data of the Na–Dowex 50 X0.5 resin⁴⁶ were used in parameter estimation. The AAD value for the 38 data points was 9.6%. The corresponding parameter values for the un-cross-linked calcium salt were estimated from the data of Reddy et al.⁴⁷ and Timmermann.⁴⁵ The AAD value of the 19 data points was 11%. No data seem to be available for the soluble lanthanum salt and, therefore, the interaction parameters were calculated using the data measured for a La–Dowex 50 X0.5 resin.⁴⁶ These values are only approximate, because no more than six experimental points were available, and because of the strong solvent–ion interactions of the La^{3+} salt the correlation was appreciably poorer than in the other salts. The size and surface parameters and the known interaction parameters are shown in Table 2.

The poly(styrene sulfonate) salts are insoluble in most organic solvents,⁴³ and the interaction parameters of the ethanol–resin pair cannot be determined independently. Therefore, the remaining parameters a_{23} and a_{32} and the elastic coefficient K_{el} were obtained by fitting the experimental sorption data to eqs 2–4. The data obtained for the Finex resins having the same counterion (Na^+ or La^{3+}) but different degrees of cross-linking were fitted simultaneously. The interaction parameters were the same for all resins, and each resin had its own elastic parameter.

The data points measured at external water mole fractions above 0.5 were weighed more than the rest of

Table 2. Size and Surface Parameters r_i and q_i and the Known UNIQUAC Interaction Parameters a_{ij} for the Water (1)–Ethanol (2)–Resin (3) System at 298 K

i	r_i	q_i	j for a_{ij} , K				
			water (1)	ethanol (2)	resin (3)		
water (1)	0.9200	1.400	0	56.36	Na ⁺	Ca ²⁺	La ³⁺
ethanol (2)	2.576	2.588	192.8	0	–429.9	–659.4	–1030
resin (3)	Na ⁺	6000	5000	61.50	0		
	Ca ²⁺	6000	5000	660.2		0	
	La ³⁺	6000	5000	1030			0

the data for three reasons. First, changes in the properties of the resins below a water mole fraction of 0.4 make the basic assumptions of the model untenable, as will be shown. Second, the experimental accuracy was best at high water contents and, finally, the composition range $1 < x_w < 0.5$ is most relevant for preparative chromatography applications because it avoids the complications due to a low degree of swelling.

4. Results and Discussion

Elastic and Volumetric Properties. To get an independent value for the elastic effects in the resins, the shear moduli of the water-swollen resins were determined. The applicability of the affine network model was tested by studying the elastic properties of some resins swollen in different water–ethanol mixtures. As an example, the dependence of the modulus on the external water content is illustrated in Figure 1 for the sodium and lanthanum X8 resins (CS16G). The dash–dotted lines represent the theoretical dependence on the degree of swelling given by eq 5. Figure 1 also shows the variation of the resin equivalent volume with the solvent composition. The continuous lines have been calculated additively from the sorption data. The validity of this procedure was checked by measuring the bead volumes of some resins microscopically, and these data are shown as discrete points.

As can be seen from Figure 1, the measured shear moduli of both resins are practically constant at water mole fractions over 0.4. Within the experimental accuracy, the data seem to conform with the assumption of affine swelling (eq 5). At low water contents, on the other hand, the behavior of the resin beads changes markedly. The apparent shear modulus increases very rapidly and finally attains a value of the essentially dry resin (not shown) which is about 2 orders of magnitude larger than the value of the water-swollen resin. It is interesting to compare the behavior of the modulus with the equivalent volume of the resins at different solvent compositions. The volume difference between the differently cross-linked Na⁺ resins (Figure 1A) decreases gradually, and for $0.3 < x_w < 0.4$ the effect of cross-link density disappears and the equivalent volumes become equal. It seems that in this region the driving force for swelling disappears and a transition from a gel to an unswollen polymer takes place. It is assumed that the transition is due to ion association induced by both the decrease in the dielectric constant and the growth of the counterion concentration with decreasing water content in the solvent mixture. Because of the transition, the material properties of the polymers at water mole fractions below 0.4 are completely different from those of the swollen resins and the model discussed above is, of course, no longer valid.

For the La³⁺ resins, the situation is qualitatively similar and the modulus starts to increase at about the

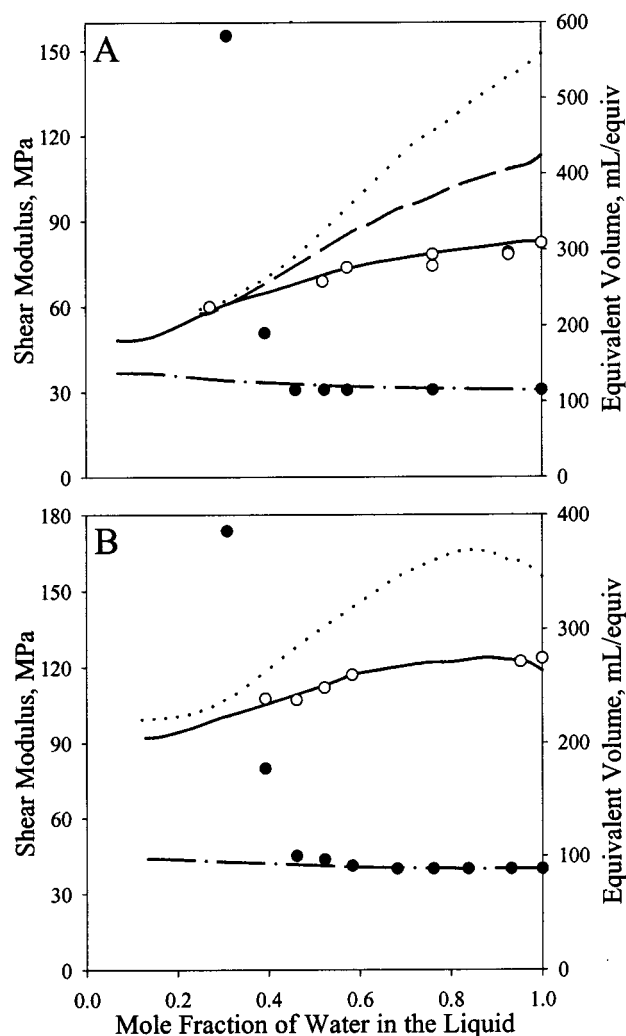


Figure 1. Effect of external solvent composition on the shear modulus of the X8 resin (CS16G) and on the equivalent volumes of CS resins of different cross-link densities A: Na⁺ resins. B: La³⁺ resins. (●) Experimental shear modulus; (○) experimental equivalent volume. The dash–dotted lines represent the moduli calculated from eq 5, and the calculated equivalent volumes at different cross-link densities are presented as follows: (···) X4; (– –) X5.5; (–) X8.

same solvent composition as for the Na⁺ resin. This seems to contradict the assumption of ion association because the multivalent ions should have a much higher association tendency.⁴⁸ It should be noted, however, that the comparison in Figure 1 is based only on the external solvent composition and that selective sorption of the solvent components also influences the conditions prevailing in the resin. The marked differences in the volumetric behavior (Figure 1) and in the sorption properties (see below) of the Na⁺ and La³⁺ resins imply, however, that the solvent structure in the latter is

Table 3. Estimated Interaction and Elastic Parameters a_{23} , a_{32} , and K_{el} for Sorption of Water–Ethanol Mixtures in the Sulfonated PS–DVB Resins at 298 K^a

resin	a_{23} , K	a_{32} , K	K_{el} , MPa		G_0 , MPa		AAD, %		<i>N</i>
			absolute	relative ^b	absolute	relative ^b	water	ethanol	
CS08G, Na ⁺	−237.1	229.6	3.2	0.29	4.9	0.12	8.9	9.0	25
CS11G, Na ⁺	−237.1	229.6	6.1	0.55	15	0.37	3.7	8.4	14
CS16G, Na ⁺	−237.1	229.6	11	1.00	41	1.00	9.6	12.6	26
CS16G, Ca ²⁺	−298.2	155.7	12	1.09	43	1.05	6.7	7.9	20
CS08G, La ³⁺	−602.0	138.7	7.7	0.70	4.5	0.11	17	18	18
CS16G, La ³⁺	−602.0	138.7	15	1.36	53	1.29	13	10	15

^a G_0 is the Extrapolated Shear Modulus. AAD is the absolute average deviation and *N* is the Number of Data Points. ^b Relative values compared to the CS16G sodium form.

rather complicated. For this reason a detailed discussion of the significance of ion association is not tried here.

Because of the discontinuous behavior shown in Figure 1, the resin matrixes were characterized with the moduli obtained by extrapolating the values of the water-swollen resins to $\phi_r = 1$ by means of eq 5. These values are given in Table 3 as G_0 . Obviously, the elastic parameters K_{el} calculated from the sorption data and the experimental shear moduli vary qualitatively a similar way with the degree of cross-linking and with the counterions. However, the growth in the cross-link density affects much more strongly the G_0 values and the difference is more prominent for the multivalent cations.

Effect of Cross-Linking on Sorption. The effect of cross-linking on sorption of water and ethanol is illustrated in Figures 2 and 3. For comparison, the data of Rückert and Samuelson⁶ for the Na–Dowex 50W X8 resin are included. It can be seen that these data coincide within experimental error with the values measured for the Na–CS16G resin. Therefore, only the CS resins are considered in the rest of this paper. The figures also show the fitted curves computed with the model. The parameter values calculated with eqs 2–4 and the AAD values are given in Table 3.

The amount of water in the resin decreases with increasing cross-linkage and, as shown in Figure 2, the effect is much stronger for the sodium resins than for the lanthanum resins. The difference between the resins is probably caused both by the lower osmotic activity of the trivalent ions and by the higher elastic modulus of the La³⁺ resins. The former contribution is evident from the osmotic coefficient data of Soldano and Larson,⁴⁶ and it is taken into account by the a_{31} values given in Table 2. The elastic parameters given in Table 3 are distinctly higher for the La³⁺ resins, especially for the less densely cross-linked resin. As discussed above, the same trend also was observed in the experimentally measured shear moduli but only for the densely cross-linked resins. The effect of cross-linking is greatest when the mole fraction of water in the liquid phase is high and, as already discussed in the preceding section, it vanishes at lower water contents.

In contrast to the monotonic isotherms of water, the amount of ethanol in the Na⁺ resin goes through a maximum and the maximum value increases with decreasing degree of cross-linking (Figure 3A). Moreover, the location of the maximum appears to be nearly independent of the degree of cross-linking. Obviously, sorption of ethanol in the resin depends strongly on its solubility in the water present in the resin phase, and in the resins of low cross-link density this effect is far more important than the interaction of the ethanol with the resin. The maximum is, of course, a result of two conflicting trends: increasing the external ethanol

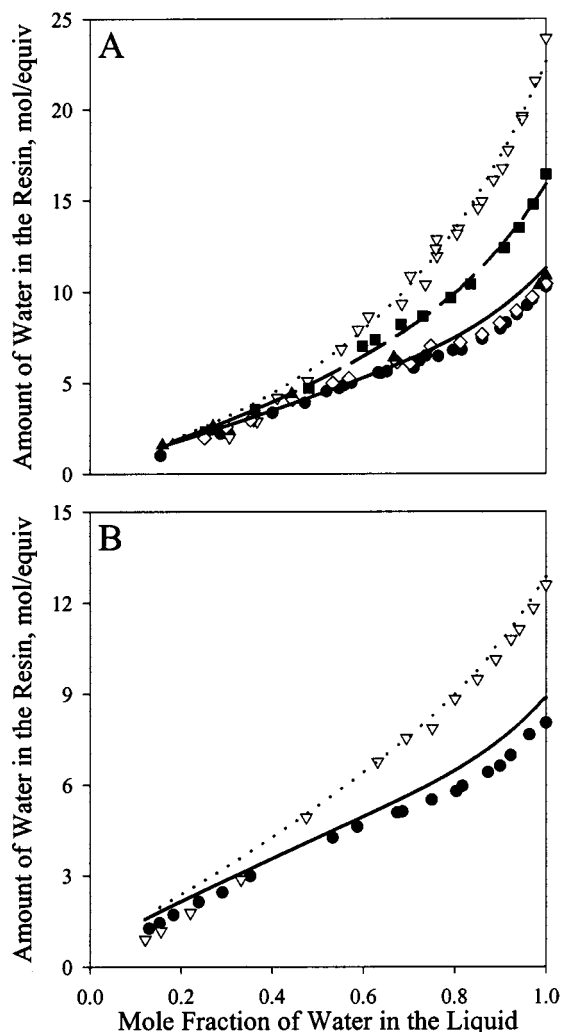


Figure 2. Effect of cross-linkage on water sorption from water–ethanol mixtures in sulfonated PS–DVB resins at 298 K. A: Na⁺ resins. B: La³⁺ resins. (●, —) X8 (CS16G); (■, —) X5.5 (CS11G); (▽, ...) X4 (CS08G); (◇) X8 (Dowex 50W X8). Data of Rückert and Samuelson (▲) X8 (Dowex 50).⁶ The lines were calculated from eqs 2–4 with the parameter values given in Tables 2 and 3.

concentration increases the ethanol content in the resin water, but at the same time the amount of the resin water decreases markedly (see Figure 2). Because of the smaller water content and the higher elastic modulus of the La³⁺ resins, the maximum is less prominent, although the behavior is qualitatively similar to that of the Na⁺ resins (Figure 3B).

Because of experimental difficulties, sorption could not be measured at very high ethanol concentrations and therefore sorption behavior in the region $x_w(l) < 0.2$ remains uncertain. However, the data seem to indicate that sorption of ethanol in isotherms of the Na⁺ and

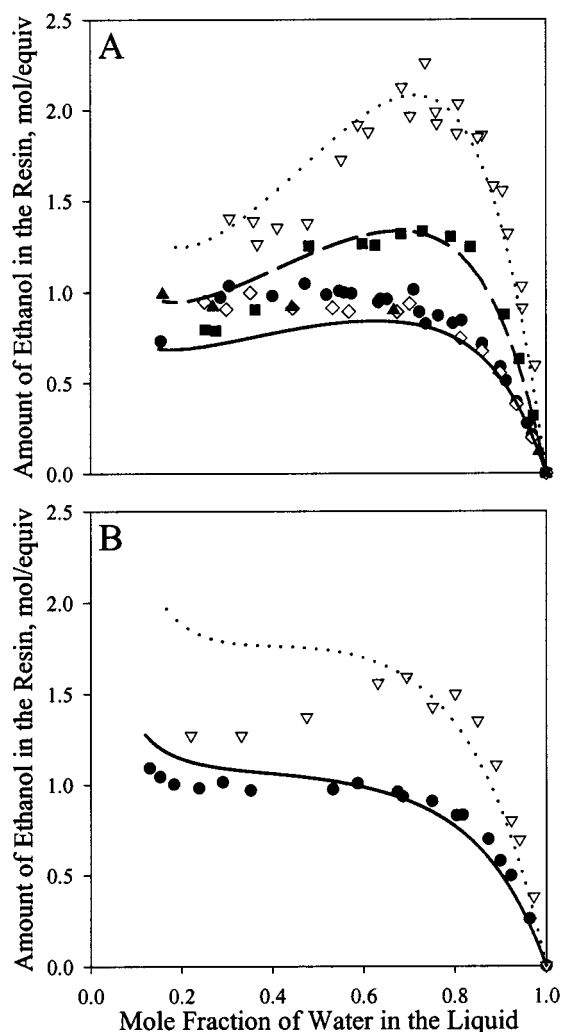


Figure 3. Effect of cross-linkage on ethanol sorption from water-ethanol mixtures in sulfonated PS-DVB resins at 298 K. A: Na^+ resins. B: La^{3+} resins. (●, —) X8 (CS16G); (■, - -) X5.5 (CS11G); (▽, ···) X4 (CS08G); (◇, - · -) X8 (Dowex 50W X8), data of Rückert and Samuelson; (▲) X8 (Dowex 50).⁶ The lines were calculated from eqs 2–4 with the parameter values given in Tables 2 and 3.

La^{3+} resins approaches a limiting value which depends only slightly on the cross-link density. This is in fact expected on the basis of the properties of the resins at low water contents (see Figure 1). The Na^+ forms of Dowex 50 X8 and Dowex 50 X4 have been reported to absorb 0.3 and 0.4 mol/equiv of anhydrous ethanol in 24 h, respectively.⁸ However, it is probable that these are not true equilibrium values. Long-term sorption tests carried out in this laboratory have shown that it takes about 10 days for the dry Na^+ resin containing 8 wt % DVB to reach an equilibrium in 95 mol % aqueous ethanol. The amount of ethanol in the resin was then 0.7 mol/equiv which seems to fit the values in Figure 3 better than the lower literature values.⁸

As shown by the calculated isotherms in Figure 2, the effect of the cross-link density in a given resin on water sorption can be reasonably well explained by differences in the elastic modulus and by assuming that the chemical interactions remain unchanged. Consequently, this basic assumption, frequently verified for moderately and highly swollen gels, seems justified for densely cross-linked resins, too. Moreover, the trend observed in the calculated elastic parameters was also found in the shear moduli measured experimentally, as already

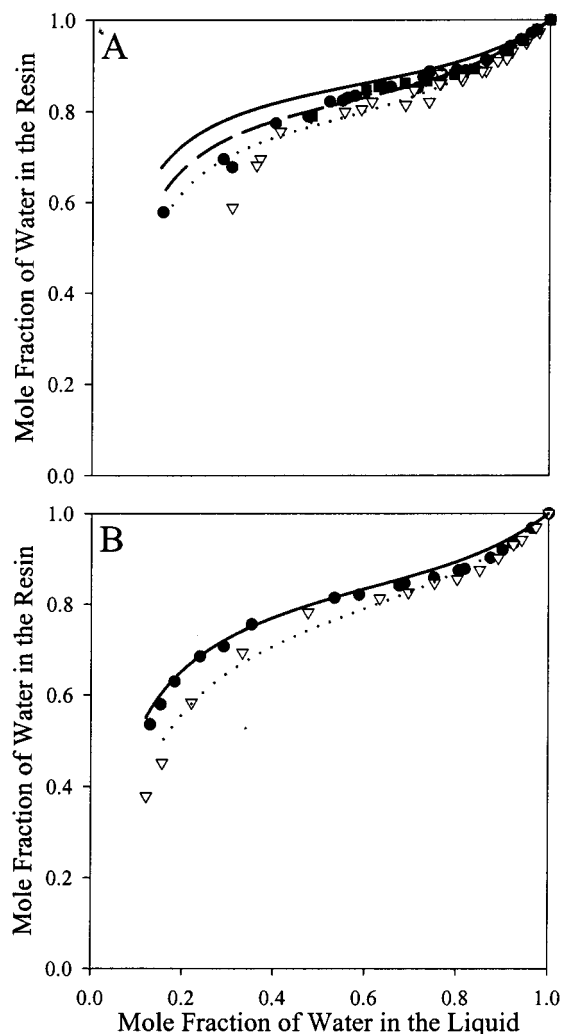


Figure 4. Effect of cross-linkage on water selectivity from water-ethanol mixtures in sulfonated PS-DVB resins at 298 K. A: Na^+ resins. B: La^{3+} resins. (●, —) X8 (CS16G); (■, - -) X5.5 (CS11G); (▽, ···) X4 (CS08G). The lines were calculated from eqs 2–4 with the parameter values given in Tables 2 and 3.

pointed out in the previous section. Another basic assumption of the model is the applicability of the liquid-phase interaction parameters a_{12} and a_{21} also for the resin phase. In contrast to this approach, Mazzotti et al.¹² have treated the binary Flory-Huggins interaction parameter in the resin as an adjustable parameter or fixed it to zero. The water-ethanol mixture is highly nonideal, and it is difficult to predict the changes of the solution structure caused by the charged polymer matrix. Despite the complexity of the system, the interaction parameters used in the model represent at least semiquantitatively the ethanol sorption data in Figure 3 and at high external water concentrations the agreement is satisfactory.

The sorption data of Figures 2 and 3 are replotted in Figure 4 as selectivity curves. The selectivity is illustrated here simply by comparing the water mole fractions in the absorbed liquid mixture and in the liquid phase. As expected, the hydrophilic resins studied here absorb preferentially the more polar water molecules from the water-ethanol solutions and the selectivity for water increases with increasing cross-linkage. It is close to unity at high mole fractions of water but increases rapidly with lowering of the water content in the external solution. Besides the polarity, selectivity

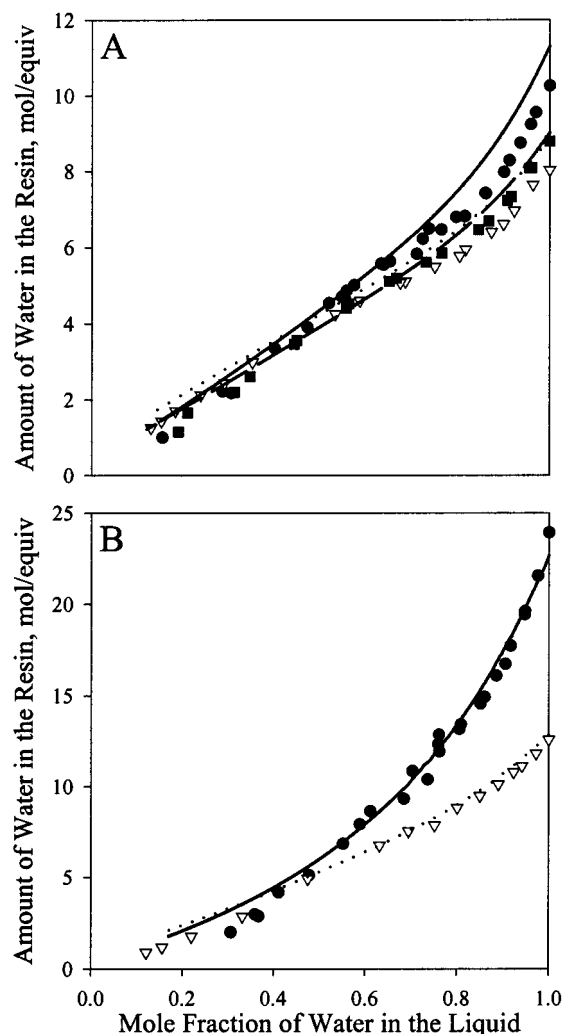


Figure 5. Effect of ionic form on water sorption from water–ethanol mixtures in sulfonated PS–DVB resins at 298 K. A: X8 (CS16G). B: X4 (CS08G). (●, —) Na^+ ; (■, - -) Ca^{2+} ; (▽, ···) La^{3+} . The lines were calculated from eqs 2–4 with the parameter values given in Tables 2 and 3.

is also affected by the difference in the molecular size of the absorbed components. The molar volume of pure ethanol is about 3 times as large as that of water and, consequently, the elastic pressure is experienced more strongly by ethanol (see eq 2). The importance of the volume effect can be illustrated by an example where the ethanol isotherms were recalculated with the parameter values of Table 3 and by using the molar volume of water for both water and ethanol. With these values the model predicts from 1.3 to 2.5 times as high ethanol contents in all resins at $x_w < 0.8$ compared to Figure 3. For example, the ethanol content of the Na^+ resin (X8) increases from 0.8 to 1.3 mol/equiv at water mole fraction 0.7. If correlated to the selectivity curves, this effect explains roughly 40% of the selectivity. The calculated selectivity curves follow the same sequence as the measured data, and the discrepancies at low external water contents are due to the failure of the model to correctly predict sorption of ethanol.

Effect of the Counterion on Sorption. The water isotherms for the resins having different counterions are compared in Figure 5, and the corresponding selectivity curves are given in Figure 6. In analogy with Figures 2–4, the lines indicate the curves calculated with the parameter values of Table 3.

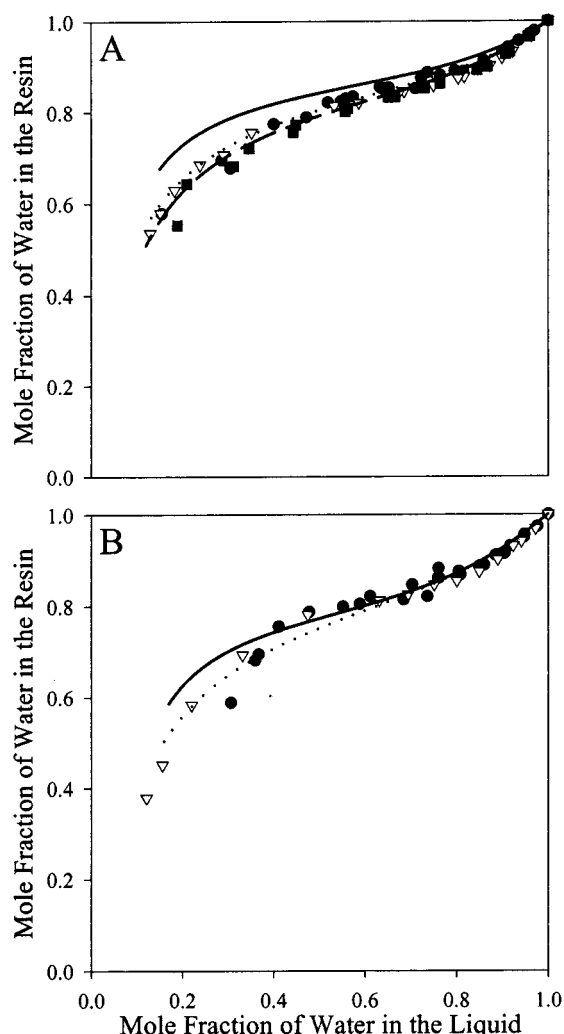


Figure 6. Effect of ionic form on water selectivity from water–ethanol mixtures in sulfonated PS–DVB resins at 298 K. A: X8 (CS16G). B: X4 (CS08G). (●, —) Na^+ ; (■, - -) Ca^{2+} ; (▽, ···) La^{3+} . The lines were calculated from eqs 2–4 with the parameter values given in Tables 2 and 3.

Figure 5 shows that increasing the counterion valence tends to reduce the amount of absorbed water, provided that the water mole fraction of the external solution is sufficiently high. In the concentration range of $x_w(l) < 0.4$, however, the order is reversed. It is also interesting to note that the isotherms of water absorbed from water–ethanol mixtures are clearly different from the isotherms of pure water vapor. As shown in Figures 2A and 5A, the typical sigmoidal shape of the water vapor isotherms⁴⁹ completely vanishes for the sodium resins and the amount of water in the resin phase decreases monotonically even to the lowest external water contents. Only the La^{3+} resin having a high cross-link density seems to retain partly the sigmoidal shape even in the presence of ethanol.

These findings can be explained only by considering solvation of the ionic species by the sorbed solvents. It is generally thought⁷ that, in analogy with concentrated electrolyte solutions, part of the sorbed water in the resin constitutes a hydration shell around the counterions of the resin, while the rest of it behaves more or less like bulk water. The reported vapor sorption isotherms of methanol¹⁰ and ethanol⁵⁰ show an analogous initial curvature as the water vapor isotherms, which seems to indicate a similar mechanism for alco-

holds, too. It is therefore plausible to assume that the flatness of the water isotherms in Figure 5 is due to the displacement of water by ethanol from the hydration shell. It is also possible, as discussed earlier, that the affinity for water at low concentrations diminishes because of association of the counterions with the fixed sulfonate groups in the environment of relatively low dielectric constant.^{5,8} The hydration water is more difficult to remove from the La^{3+} ion than the two other ions because of the high hydration tendency of the La^{3+} ion.⁴⁸ In aqueous solutions the hydration numbers of Na^+ , Ca^{2+} , and La^{3+} are 2.0, 4.3, and 7.5, respectively.⁴⁸

Although the size of the hydration shell of cations increases with increasing valence, at the same time the capacity of the resin to absorb free water may decrease because of the lower number of ions in the resin.⁷ As a result, if the decrease of the free water content exceeds the increase of hydration water due to higher valence, the total water content of the resins having di- and trivalent cations may be lower than that of the sodium resin. This idea is supported by the water sorption data measured for lightly cross-linked Dowex 50 X0.5 resins.⁴⁶ In qualitative agreement with Figure 5A, the isotherms intersect and the sigmoidal shape is more pronounced for the La^{3+} form. In terms of the model parameters used in this study, such effects should be reflected in the magnitude of the absorbate–resin interaction parameters. As shown in Table 2, the values of a_{13} become more negative when going from Na^+ to La^{3+} . This trend implies an enhanced solvent–resin interaction at low water contents and can be formally interpreted as stronger ion–solvent interactions of the multivalent cations. At the same time, the parameter a_{31} becomes increasingly positive, indicating lower affinity at high water contents. Comparison of the adjustable ethanol–resin interaction parameters is more difficult because their values are probably affected by the differences in the elastic parameters. The significance of K_{el} was estimated by recalculating the pure water sorption of the La^{3+} resins by using the elastic parameters of the Na^+ resins. Quite surprisingly, the difference in the water sorption capacity appears to be predominantly controlled by the elasticity of the resins. The experimental shear moduli given in Table 3 further support this result for the highly cross-linked resin, but conflicting results were obtained for the less densely cross-linked resins.

As can be seen from the selectivity curves in Figure 6, the selectivity of the sodium resin is slightly greater than that of the calcium and lanthanum resins at high water mole fractions, while within experimental error the selectivity difference vanishes at lower water contents. The shapes of the selectivity curves simply reflect the merging and crossing of the corresponding water isotherms discussed above and the merging of the ethanol isotherms at low external water contents (Figure 3).

Comparison of the calculated and measured values in Figure 5 shows that the model represents reasonably well the water sorption data of even the multivalent counterion resins. In view of the foregoing discussion, this is somewhat surprising because the model is based on the assumption of a homogeneous resin phase and the distinction between hydration water and free water cannot be taken into account. It seems that, in the presence of ethanol, the properties of the absorbed water can be expressed with average quantities and, except

for the La^{3+} resin at low water contents, the experimental data are correlated satisfactorily. On the other hand, the model is, of course, unable to explain the sigmoidal shape of the water vapor sorption isotherms. To remove this limitation, a more complete model including the solvation process can be constructed. However, more extensive experimental data are needed in order to evaluate the parameters involved, and therefore such a model is not attempted here. Moreover, the benefits of such a refinement can be questioned on the grounds of the complex behavior of the resin matrix at intermediate and low water contents.

5. Conclusions

In this paper, sorption of water–ethanol mixtures in strong cation-exchange resins has been studied. In particular, the effects of cross-link density (X4–X8) and the counterion (Na^+ , Ca^{2+} , and La^{3+}) on the amounts and ratio of the absorbed solvents have been investigated. In addition, the elastic properties of the resin beads have been characterized by measuring their shear moduli. The experimental sorption data have been analyzed in terms of a sorption model by taking into account the mixing effects and the elastic properties of the resins.

All of the studied resins are selective for water in water–ethanol solutions. However, the behavior of the resins depends on the external solvent composition, and it is possible to distinguish three composition ranges. At the highest external water contents, the water selectivity is low regardless of the cross-link density or counterion. In mixtures of $x_w > 0.9$, the compositions of the liquid in the resin and the external liquid are practically equal. In this composition range, the high water content of the resins allows unhindered partition of ethanol between the two phases, as indicated by the nearly linear sections in the ethanol sorption isotherms. Moreover, the slope of these linear sections increases substantially with decreasing cross-link density, implying that the water content of the resins is the key factor for ethanol partitioning. This dependence can be well explained in terms of the varying elastic moduli of the differently cross-linked resins.

At moderate water mole fractions ($0.5 < x_w < 0.9$), on the other hand, the decreasing polarity of the solvent mixture results in marked resin deswelling and the ethanol sorption becomes more difficult. This effect is clearly demonstrated by the maximum appearing in the ethanol isotherms and by the increased water selectivity of the resins. In this range, the selectivity depends on both the cross-link density and the counterion, thus indicating that the interactions between ethanol and the matrix become more dominant. The dependence on the cross-link density is again correctly predicted on the basis of the elastic moduli, but the effect of the counterion is more complex because of the differences in solvation properties. The water selectivity of the Na^+ resin is higher than that of the Ca^{2+} and La^{3+} resins down to $x_w = 0.5$, but below this point the selectivity curves intersect. The model correctly predicts the higher selectivity of the Na^+ resin but fails to predict the intersection.

This failure is partly due to the transition from a gellike structure to a slightly swollen polymer, which according to the elasticity and volumetric data takes place at $x_w = 0.4$ – 0.5 . Below this point, the effect of the cross-link density on sorption of both water and ethanol

nearly vanishes. The role of the counterion, on the contrary, becomes more important because of the dominance of the solvation interactions.

The water selectivity of the resins can be utilized in partition chromatography and, as will be shown in part 2 of this paper, the above results form the basis for explaining sorption of carbohydrate solutes in the cation-exchange resins. Moreover, the results discussed above clearly show that the moderate water contents in the external solvent mixture are most promising. The nonselective distribution at high water contents gives no advantage over pure water, and the phase transition at low contents diminishes the sorption capacity needed in preparative-scale applications.

Acknowledgment

The authors gratefully acknowledge financial support from TEKES (Technology Development Centre, Finland) and Cultor Oyj. The Finex CS resins were kindly supplied by Finex Oy (Finland).

Nomenclature

AAD = absolute average deviation

a = activity

a_{ij} = interaction parameter, K

d = diameter of the resin bead, m

d_{av} = average bead diameter in sodium form, m

F = load, N

G_0 = extrapolated shear modulus of the resin, Pa

G = shear modulus of the swollen resin, Pa

K_{el} = elastic parameter, Pa

M = molar mass of the resin, g/mol

M_c = molar mass of the chain between cross-links, g/mol

N = number of data points

n = amount of solvent in the resin, mol/equiv

OF = object function

Q = capacity of the resin, equiv/kg

q_j = surface parameter

R = gas constant, J/(mol K)

r_j = size parameter

T = temperature, K

V_{eq} = equivalent volume of the resin, L/equiv

$V_{m,j}$ = partial molar volume, L/mol

w_j = weight coefficient

x_j = mole fraction

Greek Letters

γ_i = symmetric activity coefficient

Δd = deformation of the bead, m

θ_j = molecular surface area fraction

τ_{ij} = Boltzmann factor

ϕ_r = volume fraction of the swollen resin matrix

ϕ_j = molecular volume fraction

π_{el} = elastic pressure, Pa

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Received for review June 7, 1999

Revised manuscript received September 22, 1999

Accepted September 22, 1999

IE990402J