

point of view.<sup>45</sup> The phase equilibria with different bases and the acyl-sulfonated ion-exchange polymers have been investigated, and a number of chromatographic separations involving a number of different amines, including alkaloids of biological origin, will be described.<sup>46</sup> Cation-exchange processes involving sulfonic acid polymers and metal chelate complexes dissolved in nonaqueous solvents were also investigated.

(45) M. Shida and H. P. Gregor, *J. Polymer Sci.*, in press.

(46) A. G. Tsuk and H. P. Gregor, *J. Am. Chem. Soc.*, **87**, 5538 (1965).

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## Oleophilic Ion-Exchange Polymers. II. Swelling of Cross-Linked Networks with Multiple Hetero Side Chains

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*Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York. Received April 2, 1965*

The theory of swelling of a cross-linked network with a large number of flexible side chains of a different kind (heterograft) was developed along the lines of Flory's statistical-mechanical treatment. The partial molar free energy of mixing of the multibranched polymer with solvent is

$$\frac{\overline{\Delta G_1}}{RT} = \ln(1 - v_2) + v_2 + \frac{X_\beta + gX_\sigma}{1 + g} v_2^2 + \frac{V_1 v_e}{Q_\beta} \left[ \left( \frac{v_2}{1 + g} \right)^{1/3} - \frac{1}{2} \left( \frac{v_2}{1 + g} \right) \right]$$

where the subscript  $\beta$  refers to the backbone and  $\sigma$  to side chains,  $g$  is the volume ratio of side chains to backbone,  $Q_\beta$  is the total volume of the unbranched polymer, and other symbols have the same meaning as in Flory's derivation. Upon subtracting from this expression the partial molar free energy of mixing of the unbranched polymer with solvent,  $(\Delta G_1/RT)$ , we obtained the difference  $\Delta$  due to the introduction of side chains

$$\Delta = \frac{g}{1 + g} (X_\sigma - X_\beta) v_2^2 - \frac{V_1 v_e}{Q_\beta} \left[ v_2^{1/3} - \left( \frac{v_2}{1 + g} \right)^{1/3} - \frac{v_2 g}{2(1 + g)} \right]$$

If, at the  $v_2$  value corresponding to maximum swelling of the unbranched network  $\Delta < 0$ , then the introduction of side chains will increase swelling. If  $\Delta > 0$ , a decrease in swelling will result. By neglecting the numerically small second term in the  $\Delta$  expression, and by expressing  $X$  in terms of cohesive energy densities, the arithmetic mean of the cohesive energy densities of the backbone and side chains emerges as a dividing line. For lauroylated polystyrene this value was  $8.5 \text{ (cal. ml.}^{-1}\text{)}^{1/2}$ , and theory predicts that swelling of polystyrene will be increased by the introduction of lauroyl side chains for all

solvents whose cohesive energy density ( $\delta_1$ ) is lower than 8.5, and decreased for solvents with  $\delta_1 > 8.5$ . Measurements of the swelling of lauroylated polystyrene largely confirmed these predictions. The introduction of polar (acetate or sulfonate) groups into polystyrene or lauroylated polystyrene reduced swelling in nonpolar solvents. Lauroylated and partially sulfonated cross-linked polystyrene was found to swell considerably in a number of solvents tested, including hydrocarbons.

The problem in extending the use of ion-exchange resins towards nonaqueous solvents, especially hydrocarbons, arises primarily because of the insufficient swelling of ordinary ion exchangers in these solvents. Several attempts were made in this laboratory to increase the swelling of ion exchangers in nonpolar solvents by chemical modification of the resin matrix. The results of this work are given in the accompanying paper.<sup>2</sup> Among the most promising of these modifications was the grafting of lauroyl side chains onto cross-linked polystyrene by means of a Friedel-Crafts condensation. The resulting resin was then sulfonated to give a cation exchanger.

This paper reports the changes in swelling in various solvents that occur when flexible side chains and/or polar groups are introduced into cross-linked and sulfonated polystyrene, and correlates these changes with the thermodynamic theory of swelling.

### Theoretical

Flory<sup>3</sup> has developed a theory for the swelling of cross-linked polymer networks. Our derivation of the free energy of mixing for lauroylated polystyrene is analogous to Flory's, except that the flexibility of the multiple side chains as well as the chemical dissimilarity between

(1) Taken from the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

(2) H. P. Gregor, *et al.*, *J. Am. Chem. Soc.*, **87**, 5525 (1965).

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

side chain and backbone is taken into account. In order to find an expression for the partial molar free energy of mixing, we first evaluate the entropy of mixing, the heat of mixing, and the entropy of elastic stretching.

Throughout this derivation, subscript  $\beta$  refers to the backbone,  $\sigma$  to the side chain, 2 to the polymer as a whole, and 1 to the solvent.

*Partial Molar Entropy of Mixing ( $\overline{\Delta S}_1$ ).* The derivation of  $\overline{\Delta S}_1$  for a multibranched polymer is done analogously to Flory's<sup>3</sup> derivation of  $\overline{\Delta S}_1$  for linear polymers. Polymer and solvent are placed in a lattice, where each polymer segment and solvent molecule occupies one lattice site. Each lattice site has  $z$  other sites immediately adjacent to it. The polymer backbone is  $\beta$  segments long, and attached to each segment is a side chain  $\sigma$  segments long. The total number of lattice sites is  $n_0$ .

Suppose that  $i$  polymer molecules have been inserted previously at random into the lattice. The task is to evaluate the number of different ways of placing the  $(i + 1)$ th molecule. For the first segment of the backbone there are  $n_0 - (\sigma + 1)\beta i$  available sites. The next backbone segment can be placed into any of  $z(1 - f_i)$  sites, where  $f_i$  is the probability that any site is already occupied. The next backbone segment and all the other backbone segments will have  $(z - 1)(1 - f_i)$  sites available to them. The total number of ways the backbone can be placed is

$$\Omega_\beta = [n_0 - (\sigma + 1)\beta i]z(z - 1)^{\beta-2}(1 - f_i)^{\beta-1}$$

Let us now place the  $j$ th side chain. The first segment, adjacent to the backbone, has  $(z - 2)(1 - f_i)$  sites available to it; all the others have  $(z - 1)(1 - f_i)$ . The number of ways to place the side chain is

$$\Omega_\sigma = (z - 2)(z - 1)^{\sigma-1}(1 - f_i)^\sigma$$

There are  $\sigma$  side chains, and all of them are distinguishable by virtue of their being linked to the backbone. The total number of possible spatial arrangements for the  $(i + 1)$ th molecule is thus

$$\Omega_{i+1} = \Omega_\beta(\Omega_\sigma)^\beta =$$

$$[n_0 - (\sigma + 1)\beta i]z(z - 1)^{\beta\sigma-2}(z - 2)^\beta(1 - f_i)^{(\sigma+1)\beta-1} = \\ [n_0 - (\sigma + 1)\beta i]z(z - 1)^{(\sigma+1)\beta-2} \times \\ \left(\frac{z - 2}{z - 1}\right)^\beta (1 - f_i)^{(\sigma+1)\beta-1}$$

If we compare this expression with the corresponding one in Flory's derivation and bear in mind that  $(\sigma + 1)\beta$ , the total number of segments in the polymer, corresponds to  $x$  in Flory's notation, we see that the only difference is the factor  $[(z - 2)/(z - 1)]^\beta$  that appears in the expression for the multibranched polymer. In proceeding further with Flory's derivation, this factor gives rise to terms that are independent of  $n_1$ , the number of solvent molecules. Thus, in the evaluation of the entropy of mixing, this factor, like all the other  $z$ -dependent factors, cancels out entirely, and the entropy of mixing for multibranched polymers is the same as for linear polymers, namely

$$\Delta S = -R(n_1 \ln v_1 + n_2 \ln v_2)$$

where  $n$  denotes the number of moles and  $v$  the volume

fraction of polymer or solvent. The partial molar entropy of mixing is

$$\overline{\Delta S}_1 \equiv \frac{\partial(\Delta S)}{\partial n_1} = -R \left\{ \ln(1 - v_2) + \left[ 1 - \frac{1}{(\sigma + 1)\beta} \right] v_2 \right\}$$

In the majority of cases, the term  $1/(\sigma + 1)\beta \ll 1$  and can be neglected and thus  $\overline{\Delta S}_1 = -R[\ln(1 - v_2) + v_2]$ .

*Partial Molar Heat of Mixing ( $\Delta H_1$ ).* Since the backbone and the side chains are chemically dissimilar, their heat of mixing with solvent is also different. We assume that both heats of mixing are of the van Laar type, and that they are independent and additive. The total heat of mixing will then be

$$\Delta H = RT(n_1 X_\beta v_\beta + n_1 X_\sigma v_\sigma)$$

where  $X_\beta$  and  $X_\sigma$  are Flory's interaction parameters between solvent and backbone and between solvent and side chain, respectively.

We introduce  $g$  as the ratio of the total volume of the side chains to that of the backbone. Then

$$\Delta H = RTn_1 \left( X_\beta \frac{v_2}{1 + g} + X_\sigma \frac{g v_2}{1 + g} \right) = RTn_1 \overline{X}_1 v_2$$

where  $\overline{X}_1$  is a volume-average interaction parameter defined  $\overline{X}_1 = (X_\beta + g X_\sigma)/(1 + g)$ . The partial molar heat of mixing is then  $\overline{\Delta H}_1 = \partial(\Delta H)/\partial n_1 = RT\overline{X}_1 v_2^2$ .

*Partial Molar Entropy of Stretching ( $\overline{\Delta S}_{el}$ ).* According to Flory's<sup>3</sup> the elastic stretching entropy of a cross-linked network is  $\Delta S = -Rv_e 2^{-1}(3\alpha^2 - 3 - \ln \alpha^3)$ , where  $v_e$  is the number of moles of elastically effective chains and  $\alpha$  is the linear deformation factor. If the network is relaxed in the dry state of the original (unbranched) polymer,  $\alpha^3 = v_\beta^{-1} = (1 + g)/v_2$ .

$$\Delta S_{el} = -\frac{Rv_e}{2} \left[ \frac{3(1 + g)^{2/3}}{v_2^{2/3}} - 3 + \ln \frac{v_2}{1 + g} \right]$$

The partial molar stretching entropy is

$$\overline{\Delta S}_{el} = \frac{\partial(\Delta S_{el})}{\partial n_1} = -\frac{RV_e V_1}{Q_2} \left[ (1 + g)^{2/3} v_2^{1/3} - \frac{v_2}{2} \right]$$

where  $V_1$  is the molar volume of the solvent and  $Q_2$  is the total volume of the polymer.

We can also express the elastic stretching entropy in a slightly different manner. Recognizing that the volume of the backbone only is  $Q_\beta = Q_2/(1 + g)$

$$\overline{\Delta S}_{el} = -\frac{RV_1 v_e}{Q_\beta} \left[ \left( \frac{v_2}{1 + g} \right)^{1/3} - \frac{1}{2} \left( \frac{v_2}{1 + g} \right) \right]$$

*Partial Molar Free Energy of Mixing ( $\overline{\Delta G}_1$ ).* Assuming the heat of elastic stretching is zero, we can formulate the partial molar free energy of mixing for the multibranched polymer from the foregoing.

$$\frac{\overline{\Delta G}_1}{RT} = \ln(1 - v_2) + v_2 + \overline{X}_1 v_2^2 + \\ \frac{V_1 v_e}{Q_\beta} \left[ \left( \frac{v_2}{1 + g} \right)^{1/3} - \frac{1}{2} \left( \frac{v_2}{1 + g} \right) \right]$$

Let us compare this expression with the one that is applicable to the original (unbranched) network. There  $\overline{X}_1$  will be replaced by  $X_\beta$ , and

$$\left(\frac{\overline{\Delta G_1}}{RT}\right)_\beta = \ln(1 - v_2) + v_2 + X_\beta v_2^2 + \frac{V_1 v_e}{Q_\beta} \left[ v_2^{1/3} - \frac{v_2}{2} \right]$$

Changes in swelling due to the introduction of branches can be evaluated by taking the difference between these two expressions

$$\Delta \equiv \left(\frac{\overline{\Delta G_1}}{RT}\right) - \left(\frac{\overline{\Delta G_1}}{RT}\right)_\beta$$

$$\Delta = \frac{g}{1+g} (X_\sigma - X_\beta) v_2^2 - \frac{V_1 v_e}{Q_\beta} \left[ v_2^{1/3} - \left( \frac{v_2}{1+g} \right)^{1/3} - \frac{v_2 g}{2(1+g)} \right]$$

If, at the  $v_2$  value representing the maximum swelling of the unbranched polymer,  $\Delta < 0$ , then further swelling will result; *i.e.*, the introduction of side chains increases swelling. The opposite will be true for  $\Delta > 0$ . The expression for  $\Delta$  is composed of two terms, a heat of mixing and an elastic entropy term. Examination of the latter reveals that its numerical value is usually small. For typical values of  $v_2 = 0.5$ ,  $g = 2$  (lauroylated polystyrene),  $V_1 = 100$  ml., and  $v_e/Q_\beta = 10^{-4}$  mole ml.<sup>-1</sup>, the second term amounts to about  $-0.0008$ . This value is negligible when compared to the heat term, unless  $X_\beta \approx X_\sigma$ . Consequently, it is largely the sign and magnitude of the factor  $(X_\sigma - X_\beta)$  that determines whether the introduction of side chains increases or decreases swelling in a given solvent.

If we express the interaction parameters in terms of cohesive energy densities<sup>4</sup>

$$(X_\sigma - X_\beta) = \frac{V_1}{RT} [(\delta_\sigma - \delta_1)^2 - (\delta_\beta - \delta_1)^2] = \frac{V_1}{RT} (\delta_\sigma - \delta_\beta) (\delta_\beta + \delta_\sigma - 2\delta_1) = \frac{2V_1}{RT} (\delta_\sigma - \delta_\beta) \left( \frac{\delta_\beta + \delta_\sigma}{2} - \delta_1 \right)$$

where  $\delta_1$  is the cohesive energy density of the solvent, defined as the square root of its latent heat of vaporization per unit volume. The cohesive energy densities of the backbone and the side chains cannot be obtained directly. From the literature we use the value for polystyrene<sup>4,5</sup> and set  $\delta_\beta = 9.2$  (cal./ml.)<sup>1/2</sup> and we estimate  $\delta_\sigma = 7.8$  (cal./ml.)<sup>1/2</sup> from the corresponding value for *n*-dodecane.<sup>6</sup> Thus, the term  $(\delta_\sigma - \delta_\beta)$  of the last equation is negative. The other term represents the difference between the cohesive energy density of the solvent and the arithmetic mean of the cohesive energy densities of the backbone and side chains, 8.5 (cal./ml.)<sup>1/2</sup> in this case.

In conclusion, in the case of lauroylated polystyrene, the theory predicts that  $\Delta$  will be negative (*i.e.*, the introduction of side chains increases swelling) for all solvents whose cohesive energy density is less than 8.5 (cal./ml.)<sup>1/2</sup>, and the reverse is true for solvents where  $\delta_1 > 8.5$  (cal./ml.)<sup>1/2</sup>. This relation cannot be expected to apply if there are specific interactions between polymer

and solvent. Hydrogen bonding, solvation, or acid-base reactions between polymer and solvent can give rise to negative  $X$  values and to greatly increased swelling.

The introduction of polar groups into the polymer alters its heat of mixing. Yamakawa, *et al.*,<sup>7</sup> evaluated the Flory interaction parameter  $X$  for polar polymers in polar and nonpolar solvents. They found that except in the case where the dipole moments of the polymer segments and solvent molecules were identical, the value of  $X$  was increased by polarity in polymer and/or solvent, and that the effect of polar polymer was greater than that of polar solvent. The increase in  $X$  became smaller if the dielectric constant of the solvent was large. Since a larger  $X$  means reduced swelling, we can expect the sulfonated polymers to swell less than their precursors in any solvent which does not solvate the sulfonate group.

## Experimental Section

All resins were prepared from cross-linked polystyrene beads, obtained from the Rohm and Haas Co., which contained 1% divinylbenzene. The diameter of these beads ranged from 0.1 to 0.6 mm., with the bulk at 0.4 mm. Acetyl or lauroyl groups were introduced by a Friedel-Crafts reaction, and sulfur trioxide was used as sulfonating agent. The details of the preparations of the resins are reported elsewhere, with the same symbols for the different resins.<sup>2</sup> Capacities of the sulfonated resins in the hydrogen form were determined by equilibration with aqueous sodium or potassium chloride (1–2 *M*) and titration of the liberated acid.

Swelling was measured after the beads had been equilibrated with solvent for at least 24 hr.; swelling equilibrium was usually attained within 2 hr. The swollen resin was rapidly filtered under suction on a small crucible, which was equipped with a small circular filter paper to avoid clogging, and weighed. Reproducibility was about  $\pm 5\%$ . All the results are expressed as grams of imbibed solvent per gram of dry resin.

Table I. Swelling of Polystyrene and Acylated Polystyrenes

Solvent	Cohesive energy density, (cal./ml.) <sup>1/2</sup>	Resin symbol		
		Poly-styrene 1'	A1'	L1'-7
Water	23.8 <sup>a</sup>	<0.05	0.18	<0.05
Methanol	14.5 <sup>a,4</sup>	0.12	0.24	<0.05
1-Butanol	11.5 <sup>b</sup>	0.12	0.23	0.58
1,2-Dichloroethane	9.91 <sup>6</sup>	4.80	4.73	4.18
1-Decanol	9.8	0.24	0.21	1.25
Acetone	9.71 <sup>6</sup>	0.84	1.16	0.41
Benzene	9.15 <sup>4,6</sup>	4.92	1.20	2.85
Cyclohexane	8.18 <sup>6</sup>	1.12	0.05	1.76
Diethyl ether	7.74 <sup>6</sup>	1.12	0.10	1.34
<i>n</i> -Heptane	7.42 <sup>6</sup>	<0.05	<0.05	1.27
Acyl substituent on resin	None	Acetyl	Lauroyl	
% substitution based on styrene			86	98

<sup>a</sup> E. E. Walker, *J. Appl. Chem.*, **2**, 470 (1952). <sup>b</sup> Estimated value based on extrapolation of cohesive energy density values of the homologous series of alcohols.

(4) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes" Reinhold Publishing Corp., New York, N. Y., 1950.

(5) R. F. Boyer and R. S. Spencer, *J. Polymer Sci.*, **3**, 97 (1948).

(6) G. M. Bristow and W. F. Watson, *Trans. Faraday Soc.*, **54**, 1731 (1958).

(7) H. Yamakawa, S. A. Rice, R. Corneliussen, and L. Kotin, *J. Chem. Phys.*, **38**, 1759 (1963).

Table II. Swelling of Sulfonated Resins

Solvent	S1'	Resin symbol					
		AS1'	LS1'-1	LS1'-7	LS1'-3	LS1'-2	L1'-7
Water	6.44	0.51	4.21	0.83	0.44	0.29	<0.05
Methanol	6.23	0.60	3.16	2.96	2.41	1.53	<0.05
Ethanol			2.95	2.66			
<i>n</i> -Propyl alcohol			2.90	2.65			
Isopropyl alcohol			2.69	2.42			
<i>n</i> -Butyl alcohol	4.40	0.92	2.80	2.89	2.70	2.65	0.58
Isobutyl alcohol			2.58	2.72			
<i>t</i> -Butyl alcohol			2.13	2.33			
Amyl alcohol			2.63	2.65			
Isoamyl alcohol			2.56	2.58			
1-Decanol	5.39	0.38	2.87	2.71	2.94	2.78	1.25
Acetone	1.42	0.72	1.37	1.75	1.82	1.36	0.41
1,2-Dichloroethane	0.62	1.67	0.30	0.94	1.35	2.33	4.18
Benzene	0.35	0.27	0.19	0.64	1.07	1.96	2.85
Cyclohexane	0.24	0.18	0.14	0.13	0.66	1.18	1.76
Diethyl ether	0.41	0.17	0.25	0.51	1.27	1.30	1.34
<i>n</i> -Heptane	0.14	0.14	<0.05	0.06	0.29	0.67	1.27
Acyl substituent	None	Acetyl	Lauroyl	Lauroyl	Lauroyl	Lauroyl	Lauroyl
% acyl substitution	0	86	42	98	88	88	98
% sulfonation	51	23	78	84	42	24	0
Capacity, mequiv./g.	3.52	1.43	3.17	2.57	1.40	0.83	0

Table I compares the swelling of acetylated and lauroylated polystyrene with that of polystyrene. Acetylation increases the polarity of polystyrene with little or no increase in configurational entropy; therefore a decrease in swelling is expected. Indeed, there is a drastic decrease in swelling in ether and hydrocarbons. Also, there is an increased swelling in acetone, water, and the lower alcohols, which can be explained by solvation and hydrogen bonding to the carbonyl group. The swelling of lauroylated polystyrene largely confirms the theory of swelling of multibranch networks given above. The prediction that lauroylation should increase the swelling of polystyrene in solvents whose cohesive energy density is less than 8.5 (cal./ml.)<sup>1/2</sup> is fully observed. The corollary prediction, namely that lauroylation should depress swelling in solvents with  $\delta > 8.5$ , is also largely observed. With the exception of 1-butanol and 1-decanol, lauroylation depressed or maintained a low level of swelling in the higher cohesive energy density solvents. Lauroylation increased the swelling of polystyrene in long chain alcohols probably because of the combined effect of hydrogen bonding to the carbonyl group and London attraction between the two aligned paraffin chains.

Although the theory is fairly successful in predicting the *direction* of the change in swelling due to lauroylation, the magnitude of the change seems to be unrelated to the cohesive energy densities. From a practical viewpoint, lauroylated polystyrene offers a fairly even swelling spectrum in a great variety of nonaqueous solvents.

Table II summarizes the swelling of sulfonated resins. The swelling of a lauroylated, but unsulfonated, resin (L1'-7) is included for comparison. We can see that sulfonation increases swelling in water and alcohols, and decreases (or maintains a low level of) swelling in most other solvents. The swelling in acetone appears ambiguous. The decrease in swelling in nonpolar solvents is not unexpected, in view of the polarity of the sulfonate groups. Solvation of the sulfonate group probably accounts for the increased swelling in hydrogen-bonding solvents. Resin AS1', which has two kinds

of polar substituents, acetyl and sulfonic acid groups, shows a generally poor swelling. The last four columns in Table II show the effect of gradually increasing degrees of sulfonation on the swelling of lauroylated polystyrene.

It is surprising that swelling of lauroylated and sulfonated polystyrenes is virtually identical for the homologous series of alcohols from ethanol to decanol. This points to the combined effect of hydrogen bonding to the sulfonate or carbonyl group and the subsequent alignment of the paraffinic part of the alcohol with that of the lauroyl side chain. The effect of this alignment is demonstrated by the fact that swelling in branched-chain alcohols was consistently less than in their straight-chain isomers, and that the lowest swelling among alcohols occurred with *t*-butyl alcohol, which was also the most branched.

Swelling of sulfonated resins in water seems to depend primarily on the number and position of the sulfonate groups. The swelling of sulfonated resins in water, expressed as gram of water imbibed per mequiv. capacity were as follows: S1', 1.83; AS1', 0.36; LS1'-1, 1.37; LS1'-7, 0.32; LS1'-3, 0.32; LS1'-2, 0.35. Resins AS1' and LS1'-7, -3, and -2 were essentially fully acylated prior to sulfonation. With the acyl group occupying the *para* position with respect to the polymer chain, the sulfonate group could go only to the *ortho*, or perhaps *meta* position. The sulfonate group in this position caused swelling of 0.32–0.36 g./mequiv. capacity in water. Sulfonated polystyrene (S1'), on the other hand, where the sulfonate group presumably occupies a *para* position, swells in water to more than fivefold this value. Resin LS1'-1, which was only partially lauroylated before sulfonation, shows a degree of swelling intermediary between those corresponding to *para* or *ortho-meta* positions. The difference in swelling in water of resins sulfonated in different positions is probably due to the large steric hindrance of the *ortho* position and also to the markedly lower polarity of this form.

The swelling of lauroylated and partially sulfonated resins is considerable in all the solvents tested. They

are thus suitable for cation exchange in nonaqueous media. For any solvent to be employed, it is possible to tailor-make a resin with optimal cation-exchange properties as far as capacity and swelling are concerned, since it is evident that an increase in swelling in nonpolar solvents can be attained only at the cost of

lowered capacity. The properties of these resins as cation exchangers will be the subject of a forthcoming paper.

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## Oleophilic Ion-Exchange Polymers. III. Equilibria and Chromatographic Separation of Organic Bases by Sulfonic Acid Resins in Nonaqueous Media<sup>1</sup>

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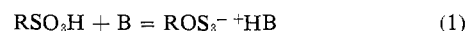
*The reactions between organic bases and an oleophilic sulfonic acid were investigated in polar and nonpolar media. The neutralization of the resin in the hydrogen form by the bases was regarded as an association-dissociation equilibrium whose constant is a measure of the strength of the base toward the resin sulfonate group. A measurable equilibrium of this type was found for diphenylamine. Assuming that base strengths toward the resin parallel their strengths in water, the selectivity coefficients, as a first approximation, may be set equal to the ratio of the respective base dissociation constants in water. The measured selectivities confirmed this qualitatively for bases of widely differing strengths. For bases of nearly equal strength, secondary binding between resin and base influenced the selectivity strongly. The effect on these equilibria of different solvents or temperatures was only minor. On the basis of selectivities, some chromatographic separations of organic bases were performed in nonpolar media. Aniline was separated from pyridine, nicotine from aniline, renoxidine from reserpine, rescinnamine, and deserpidine, and leurosine from vincleukoblastine. In each case a chromatographic separation, at least comparable to those encountered with ordinary exchangers in water, was obtained.*

### Introduction

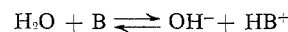
The principal deterrent to extending the techniques of ion-exchange chromatography to nonpolar solvents has been the insufficient swelling of conventional exchangers in these solvents with a resultant low capacity and extremely low rate of exchange. We have succeeded in preparing cation exchangers whose structure was modified to increase their swelling in nonaqueous solvents.<sup>2</sup> This paper describes ion-exchange equilibria of lauroylated and sulfonated polystyrene with different organic bases in nonaqueous media. These exchangers were prepared from polystyrene beads cross linked with 1% divinylbenzene. Lauroyl groups were attached to the styrene residues by a Friedel-Crafts reaction with

lauroyl chloride. Acylation was followed by partial or total sulfonation with sulfur trioxide. Details of the preparation are reported elsewhere.<sup>2</sup> Fully lauroylated and partially (25–50%) sulfonated resins showed considerable swelling in all solvents tested, including saturated hydrocarbons.<sup>2,3</sup> Their capacities ranged from 0.8 to 1.6 mequiv./dry g.

We can represent the neutralization of a sulfonic acid resin by a base in a nonpolar medium as an association-dissociation process of the following type



where R signifies resin and B an organic base. The resin sulfonate group or the base are not assumed to be ionized in this medium. Equation 1 bears an analogy to the dissociation equilibrium of bases in water.

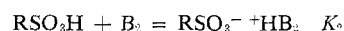
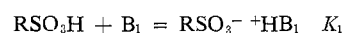


The constant of this latter equilibrium is taken as a measure of the strength of the base in water. Similarly, the equilibrium constant  $K$  of eq. 1 is a measure of the strength of the base towards the resin sulfonate group. Since this group is a much stronger acid than water, we can expect the position of equilibrium to be far to the right for bases which show only partial dissociation in water. In order to evaluate  $K$  we substitute concentrations for activities

$$K = \frac{[\text{RSO}_3^- + \text{HB}]}{[\text{RSO}_3\text{H}][\text{B}]} = \frac{\bar{X}}{(1 - \bar{X})[\text{B}]}$$

where  $\bar{X} = [\text{RSO}_3^- + \text{HB}]/([\text{RSO}_3^- + \text{HB}] + [\text{RSO}_3\text{H}])$  is the fraction of exchange sites occupied by the base. The concentration of free base in the resin phase  $[\text{B}]$  is taken, as a first approximation, to be equal to the concentration ( $c$ ) of base in the solution outside of the resin. Thus  $K = \bar{X}/(1 - \bar{X})c$ .

If we expose two bases  $\text{B}_1$  and  $\text{B}_2$  to the resin, the following simultaneous equilibria will result.



(1) Taken from the dissertation submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1964.

(2) H. P. Gregor, *et al.*, *J. Am. Chem. Soc.*, **87**, 5525 (1965).

(3) A. G. Tsuk and H. P. Gregor, *ibid.*, **87**, 5534 (1965).