Copolymers of Hydrophilic and Hydrophobic Monomers. Benzene and Water Vapor Sorption Equilibria by Random Copolymers of Styrene and Acrylamide[1,2]

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ABSTRACT: Random copolymers of styrene and acrylamide with compositions ranging from 15.6 to 82.8 mol % styrene were prepared by free-radical polymerization. Sorption of benzene vapor by polystyrene and the styrene–acrylamide copolymers was determined over a range of benzene vapor activities at 25°. Similarly, water vapor sorption isotherms by the copolymers and by polyacrylamide were determined at 25° and at 45°. When analyzing the results in terms of the Flory–Huggins theory of polymer solutions, the apparent value of the polymer–solvent interaction parameter (χ) was found to increase rapidly with the amount of vapor sorbed. The χ values for copolymers were lower than values obtained by linear interpolation between the χ values of the homopolymers, but the data did not fit Stockmayer's theory of the dependence of χ on copolymer composition. The initial slope of the sorption isotherm was also interpreted as defining a stoichiometric solvation equilibrium of acrylamide residues by water (K_w) and of styrene residues by benzene (K_b). The values of K_b were insensitive to copolymer composition, while K_w decreased rapidly with increasing styrene content, due to an increasingly unfavorable entropy of mixing of the water with the copolymer.

Polymer–solvent interactions involving random,[3] block,[4] and graft[5] copolymers have been investigated, for the dilute solution range, in a number of laboratories. The distinctive characteristics of copolymer behavior would be expected to become more pronounced as the solvation characteristics of the comonomers become more dissimilar. We have, therefore, chosen for our study the extreme case of copolymers containing hydrophilic and hydrophobic monomer residues.

The present report deals with styrene–acrylamide random copolymers and their interaction with water and benzene vapor. In this case, solvation is highly localized on the acrylamide and styrene residues, respectively. Apart from their intrinsic interest, it was hoped that principles clarified by such a study would have significant practical utility. The control of water sorption is important, for instance, in the use of synthetic polymers for textile applications and in the use of polymeric membranes for desalination by reverse osmosis.

Experimental Section

Polymers. Polystyrene, polyacrylamide, and styrene–acrylamide copolymers were prepared using a 40 wt % solution of the monomers in methanol, 0.5 wt % of azobis(isobutyronitrile) initiator based on the monomer weight, and a polymerization temperature of 60°. All polymerizations were stopped at low conversion to avoid a drift in the composition of copolymers. After purification by repeated reprecipitation from a suitable solvent–nonsolvent pair, the polymer samples were freeze-dried from a 10% solution using as the solvent water for polyacrylamide (PA), benzene for polystyrene (PS), and copolymer AS-1 and a mixture of benzene with glacial acetic acid (2:1, v/v) for the other copolymers. The polymers were then dried for several days in a vacuum oven at 60° and a pressure less than 10^{-2} Torr. The composition of copolymers was determined by uv spectroscopy, using dioxane as a solvent for copolymers AS-1, AS-2, and AS-3 and 2,2,2-trifluoroethanol (TFE) for copolymers AS-4, AS-5, and AS-6. All absorptions were measured on solutions containing 0.3 g of copolymers/l. using 1-cm silica cells and a Beckman DU-2 spectrophotometer at 25 ± 0.05°. The weight fraction w_s of styrene was obtained from $A = 0.009 + 0.522w_s$, where A was the absorbence at the peak lying at 269 nm in dioxane and at 267 nm in TFE. Table I lists the preparative procedure, composition, and intrinsic viscosities of the polymeric samples used in this study. The relation between the composition of the monomer feed and the copolymers was analyzed[6] to yield reactivity ratios $r_1 = 0.49$ and $r_2 = 1.37$, where acrylamide is monomer 1.

Measurement of Sorption Equilibrium. Quartz helical springs (cat. no. 100-75) and quartz helical balances (cat. no. 1-2020) from Misco Scientific Co. (Berkeley, Calif.) were used to follow the uptake of water or benzene vapor by the polymer samples. The assembled helical balances with samples of finely divided polymers were placed in a constant temperature air bath controlled to ±0.2°. Sulfuric acid–water and diphenyl ether–benzene solutions were used to control the water or benzene vapor pressure. Using the technique of Lindauer,[7] solutions containing 66.47, 58.61; 54.61, 48.90, 39.66, 30.39, and 19.79 wt % H_2SO_4 were found to have a relative aqueous vapor pressure $p/p°$ of 0.080, 0.192, 0.266, 0.380, 0.572, 0.745, and 0.882 at 25°, while at 45° the corresponding relative vapor pressures were 0.096, 0.211, 0.286, 0.400, 0.587, 0.753, and 0.874. Diphenyl ether solutions containing a benzene mol fraction of 0.078, 0.213, 0.301, 0.500, 0.673, and 0.856 had a relative benzene vapor pressure of 0.115, 0.296, 0.429, 0.633, 0.758, and 0.898 at 25°. A cathetometer equipped with a vernier scale allowing readings to 0.01 mm was used to follow the extension of the quartz helices. Calibration of two helices for ten loads ranging from 0.2 to 1.2 g yielded load:extension ratios of 25.03 ± 0.05 and 25.03 ± 0.01 mg per mm. Vapor sorption experiments were continued until equilibrium was reached. This was usually accomplished within a week.

Specific Volume of Polymer. Interpretation of the vapor sorption results required values for the specific volumes $\bar{v}_2$ of the polymers. Since the bulk polymers are in the glassy state at the temperatures used in this investigation, their specific volumes are

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(2) Abstracted from a Ph.D. thesis submitted by J.-C. Chuang to the Graduate School of the Polytechnic Institute of Brooklyn in June 1972.

(3) (a) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955); (b) T. Kotaka, T. Ohnuma, and Y. Murakami, *J. Phys. Chem.*, **70**, 4099 (1966); (c) T. Kotaka, Y. Murakami, and H. Inagaki, *ibid.*, **72**, 829 (1968); (d) T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami, and H. Inagaki, *Polym. J.*, **1**, 245 (1970); (e) Y. Shimura, *J. Polym. Sci., Part A-2*, **4**, 423 (1966); (f) J. Danon and R. Derai, *Eur. Polym. J.*, **5**, 659 (1969).

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(5) (a) F. M. Merrett, *Trans. Faraday Soc.*, **50**, 759 (1954); *J. Polym. Sci.*, **24**, 467 (1957); (b) S. Krause, *ibid.*, **35**, 558 (1969); (c) Y. Gallot, M. Leng, H. Benoit, and P. Rempp, *J. Chim. Phys.*, **59**, 1093 (1962).

(6) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

(7) M. W. Lindauer, *J. Chem. Educ.*, 37, 532 (1960).

Table I
Preparation Procedure and Characterization of Polymers

	PS	AS-1	AS-2	AS-3	AS-4	AS-5	AS-6	PA
Mol % styrene in monomer feed	100	76.9	64.9	46.5	30.0	19.9	10.0	0
Polymerization time (hr)	4	3	7	7	4	4.5	2	2
Conversion (%)	15	6	10	14	13	14	12	9
Mol % styrene in polymer	100	82.8	73.3	57.9	39.7	28.3	15.6	0
$[\eta]$ (dl/g)[a]	0.426	0.230	0.297	0.395	0.387	0.595	0.656	0.860

[a] All intrinsic viscosities are at 25° using dimethylformamide solutions except for PA which was determined in water.

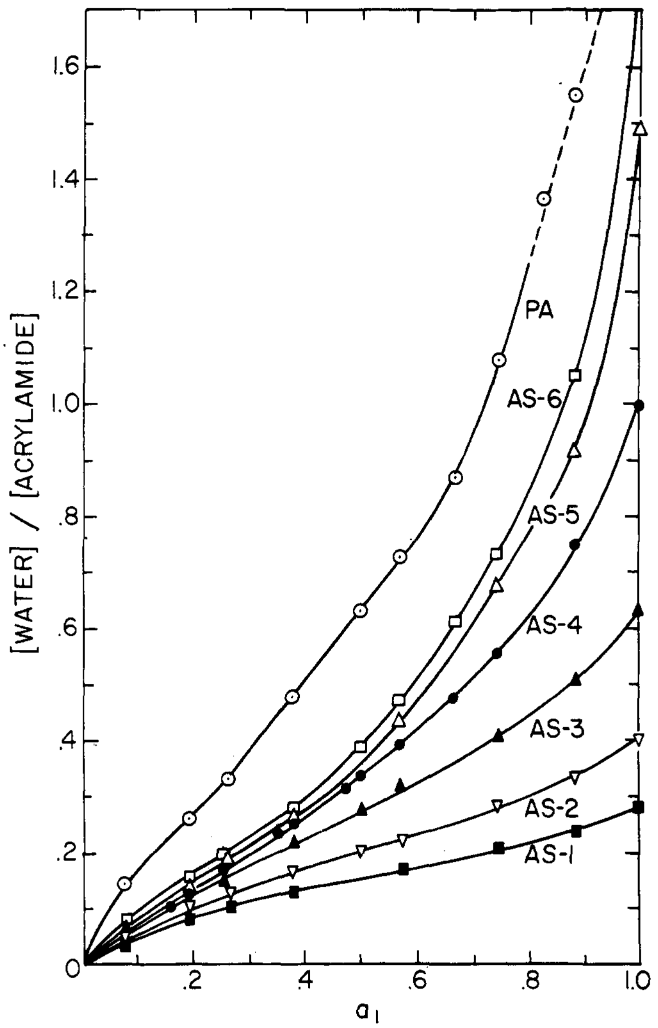

Figure 1. Stoichiometry of water sorption by acrylamide residues as a function of the relative aqueous vapor pressure at 25°.

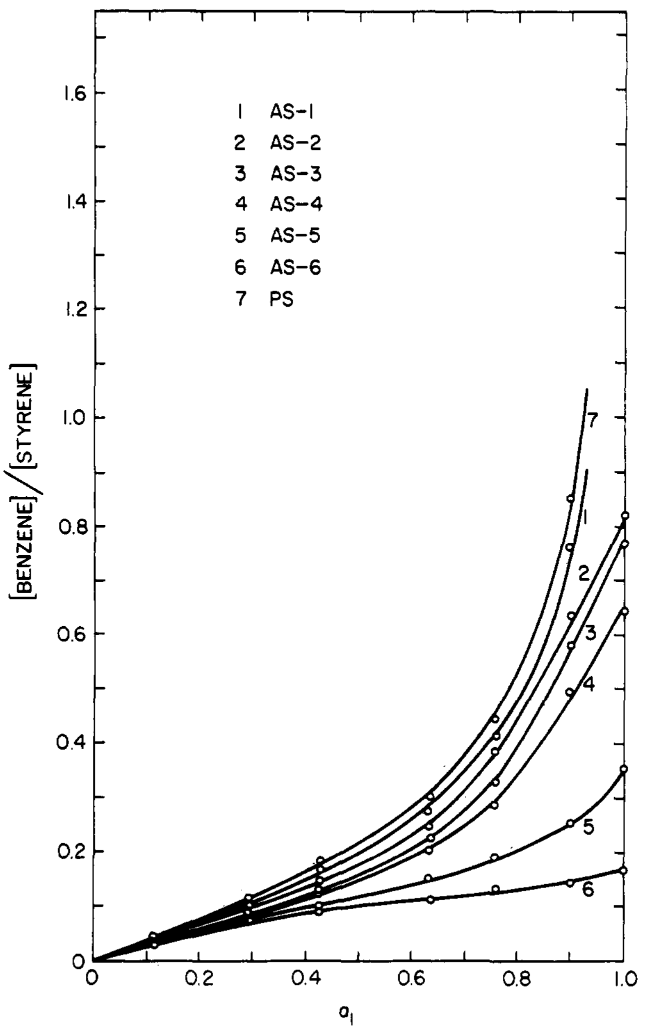

Figure 2. Stoichiometry of benzene sorption by styrene residues as a function of the relative benzene vapor pressure at 25°.

poorly defined. The following procedure was, therefore, arbitrarily adopted. The partial specific volume of PA in water and PS in benzene at infinite dilution was calculated from polymer solution density data.[8] These values (0.6890 and 0.9166 cm^3 per g, respectively) were used as $\bar{v}_2$ for the homopolymers and the specific volumes of copolymers were taken as linear in their composition.

Results and Discussion

It would be expected that the sorption of water by styrene-acrylamide copolymers is highly localized on the acrylamide residues and sorption isotherms are, therefore, most meaningfully represented as the dependence of the molar ratio of sorbed water and acrylamide residues on the thermodynamic activity a_1 of the vapor. Such a plot is shown in Figure 1 and an analogous plot for the sorption of benzene, which is expected to be localized on the styrene residues of the copolymer, is given in Figure 2. The dependence of the [water]:[acrylamide] and [benzene]:[styrene] ratios on copolymer composition at various solvent vapor activities is shown in Figures 3 and 4.

We have used two approaches to an analysis of the data. (1) According to the Flory-Huggins theory of polymer solutions,[9,10] which is applicable in the concentration range in which the polymer chains are heavily intertwined

$$\ln a_1 = \ln \phi_1 + [1 - (1/r)]\phi_2 + \chi\phi_2^2 \qquad (1)$$

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(8) T. Svedberg and K. O. Pederson, "The Ultracentrifuge," Oxford University Press, Oxford, 1940, p 58.

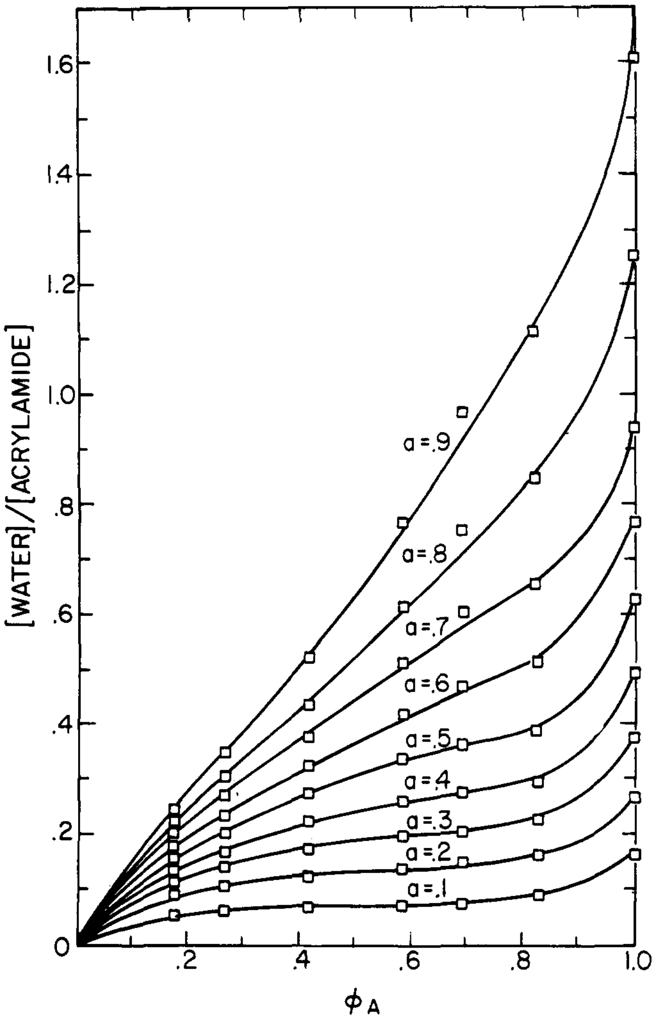

Figure 3. Dependence of the water sorption by acrylamide residues on the polymer composition.

where a_1 and ϕ_1 are the activity and the volume fraction of the solvent, r is the molar volume ratio of polymer and solvent, ϕ_2 is the volume fraction of the polymer, and χ is a characteristic polymer-solvent interaction parameter specifying, in units of kT, the excess free energy due to nearest-neighbor contact interactions when a molecule of the solvent is introduced into the pure polymer. Using the appropriate specific volume for the polymer, we obtain χ for $r \gg 1$, from

$$\chi = (1/\phi_2^2)[\ln(a_1/\phi_1) - \phi_2] \tag{2}$$

which reduces, for the case of a very poor swelling agent to

$$\lim(\phi \longrightarrow 0)\,(a_1/\phi_1) = \exp(1 + \chi) \tag{3}$$

Thus, the Flory-Huggins theory predicts that the sorption of very poor solvents is proportional to their activity. However, the theory on which this conclusion is based assumes that polymer-solvent interaction is uniform along the macromolecular chain. If this interaction is highly localized, vapor sorption will be analogous to surface sorption processes exhibiting saturation effects and this will lead to an increase in the apparent value of χ with an increasing concentration of sorbed vapor.[11] Figures 5 and 6 show that our systems behave in this manner, with the dependence of χ on the concentration of sorbed vapor becoming more pronounced as the concentration of the sorption sites in the copolymer is being reduced.

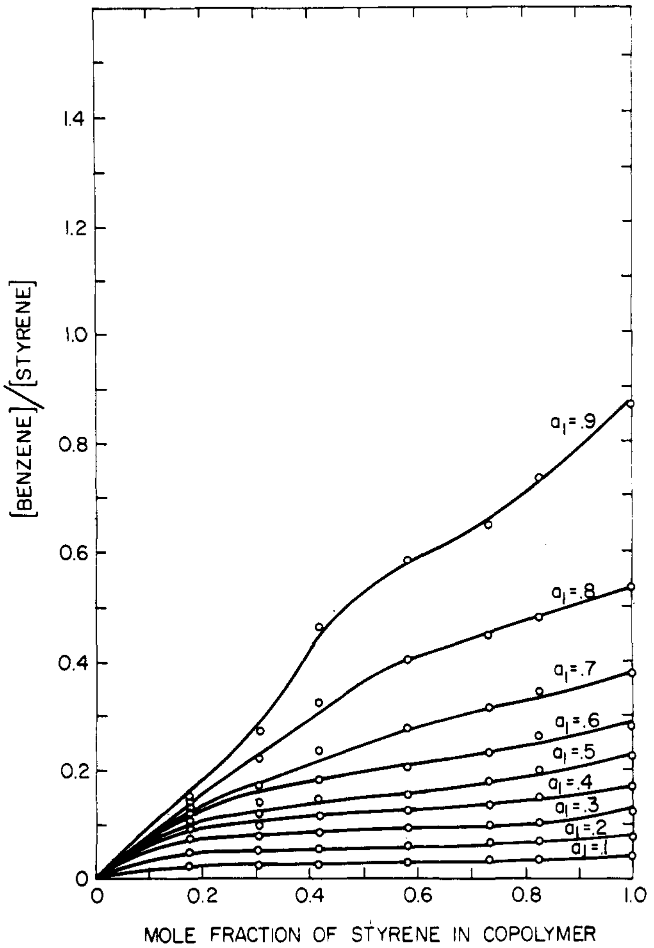

Figure 4. Dependence of the benzene sorption by styrene residues on the polymer composition.

We have extrapolated the data on Figures 5 and 6 to $\phi_1 = 0$ and designated the interaction parameter which characterizes the vapor affinity to the pure polymer by χ^*. On Figure 7 χ^* is plotted as a function of the volume fraction ϕ_A of acrylamide residues in the copolymer. The dependence of χ^* on copolymer composition is much more pronounced for the sorption of water than that of benzene. However, both lines shown on Figure 7 have a pronounced downward curvature, *i.e.*, they show that copolymers are, in general, better sorbents than would be expected from a linear interpolation of the behavior of the two homopolymers. This effect is analogous to the behavior of χ in dilute solutions[3a,f] and it arises because repulsive forces between dissimilar monomer residues in random copolymers contribute to the driving force for copolymer dilution. Stockmayer, *et al.*,[3a] have proposed that the dependence of χ on copolymer composition may be represented by

$$\chi = \chi_A\phi_A + \chi_B\phi_B - \chi_{AB}\phi_A\phi_B \tag{4}$$

where ϕ_A, ϕ_B are volume fractions of the comonomers in the copolymer, χ_A, χ_B are the interaction parameters of their homopolymers with the solvent, while χ_{AB} characterizes the interaction of the dissimilar monomer residues in the copolymer. Plots of $(\chi - \chi_A\phi_A)/\phi_B$ against ϕ_A or of $(\chi - \chi_B\phi_B)/\phi_A$ against ϕ_B should then be linear with the same slope $-\chi_{AB}$. We have tried to use such a plot of the χ^* data not only for the characterization of χ_{AB}^* but also for the

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(9) P. J. Flory, *J. Chem. Phys.*, 9, 660 (1941).
(10) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, 41, 1 (1941).
(11) J. W. Rowen and R. Simha, *J. Phys. Chem.*, 53, 921 (1949).

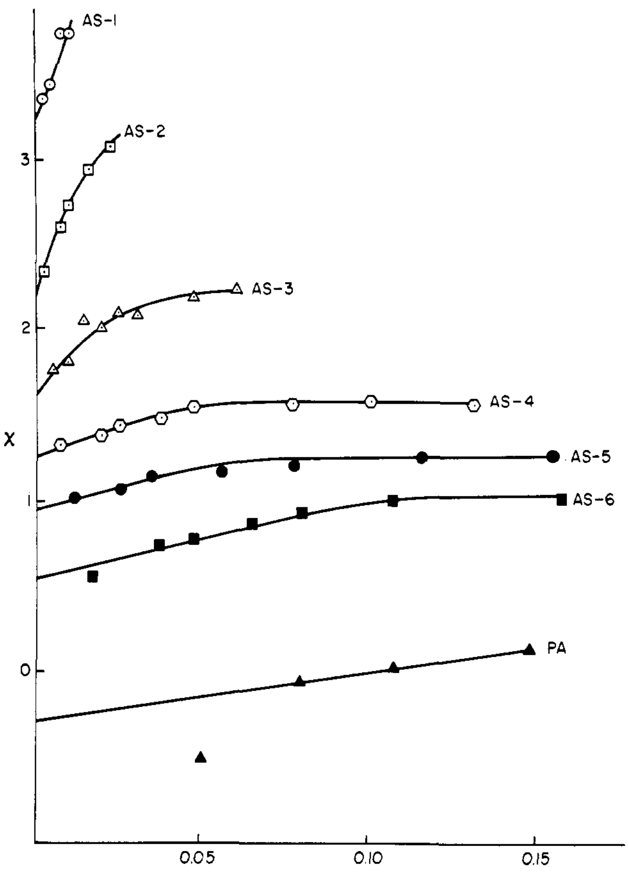

Figure 5. Dependence of the apparent interaction parameter χ on the volume fraction of water sorbed by the polymer.

estimation of the χ^* value characterizing the sorption of water by polystyrene and of benzene by polyacrylamide which are not accessible to direct measurement. Although the extrapolation of χ to χ^* is subject to appreciable error, Figure 8 shows clearly that the data do not yield the linear plot suggested by eq 4. This is not surprising, since this relation is based on the assumption that χ_{AB} is relatively small, so that the distribution of the two monomer residues may be considered to be essentially random. This would certainly not be expected in the case of styrene–acrylamide copolymers with the strong hydrogen-bonding forces operating between the acrylamide residues.

(2) A second approach to the analysis of our data used a procedure analogous to that employed in the treatment of adsorption isotherms. It represented the initial sorption of water by acrylamide residues (Am) or of benzene by styrene residues (St) formally by the equilibria

$$\mathrm{Am} + \mathrm{H_2O} \rightleftharpoons \mathrm{Am{\cdot}H_2O} \qquad (5a)$$

$$\mathrm{St} + \mathrm{C_6H_6} \rightleftharpoons \mathrm{St{\cdot}C_6H_6} \qquad (5b)$$

which define the apparent equilibrium constants

$$K_w = [\mathrm{Am{\cdot}H_2O}]/[\mathrm{Am}]a(\mathrm{H_2O}) \qquad (6a)$$

$$K_b = [\mathrm{St{\cdot}C_6H_6}]/[\mathrm{St}]a(\mathrm{C_6H_6}) \qquad (6b)$$

These equilibrium constants were estimated from the initial slopes of Figures 3 and 4 and a similar plot for the water sorption by the various polymers at 45°. Although the estimate of the initial slopes has some measure of uncertainty, the values of the equilibrium constants obtained, plotted in Figure 9, are highly consistent. The following points may be made. (a) K_b depends very little on the composition of the copolymer. This is not surprising; it suggests that styrene residues and benzene molecules are characterized by a similar contact energy with acrylamide residues. (b) K_w increases rather sharply with the concentration of acrylamide residues in the polymer. This means that contacts of styrene residues with $\mathrm{Am{\cdot}H_2O}$ are thermodynamically much more unfavorable than contacts with Am. The plot of log K_w against the copolymer composition is linear over most of the composition range, but a sharp drop of log K_w characterizes the introduction of the first styrene residue into PA. (c) The sorption of water decreases with increasing temperature at constant water vapor activity. Although we have data for only two temperatures differing only by 20°, the heats of mixing

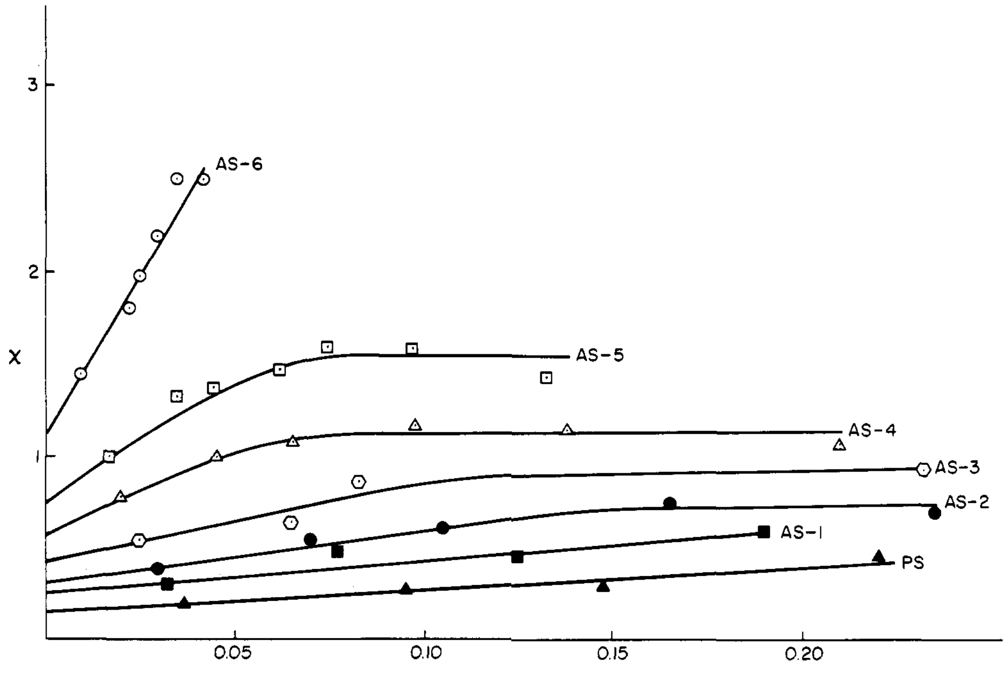

Figure 6. Dependence of the apparent interaction parameter χ on the volume fraction of benzene sorbed by the polymer.

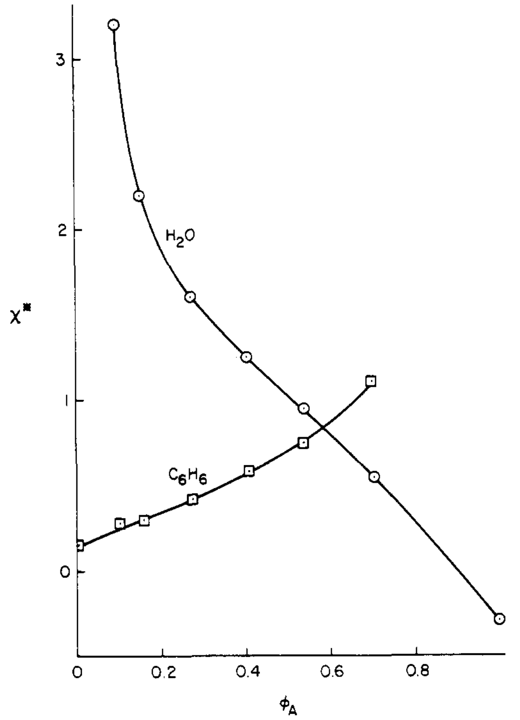

Figure 7. Dependence of χ^* on the volume fraction ϕ_A of acrylamide residues in styrene-acrylamide copolymers.

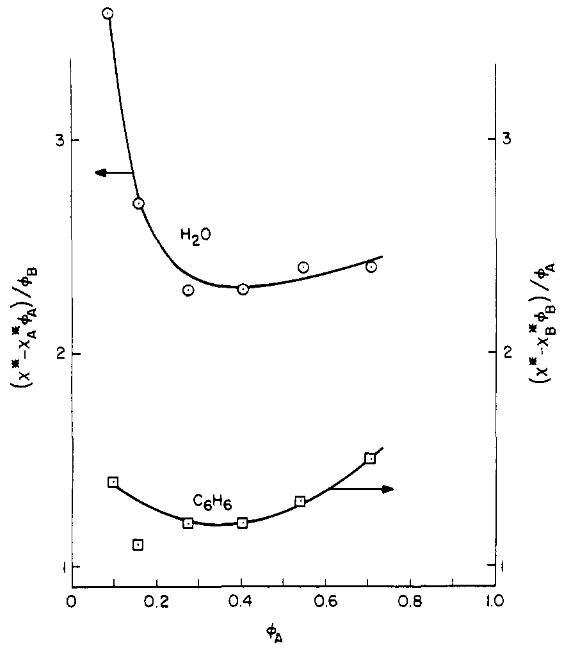

Figure 8. Treatment of χ^* data according to eq 4. The χ^* values of polyacrylamide and polystyrene are denoted by χ_A^* and χ_B^*, respectively, while ϕ_A and ϕ_B give the volume fractions of acrylamide and styrene residues in the copolymers.

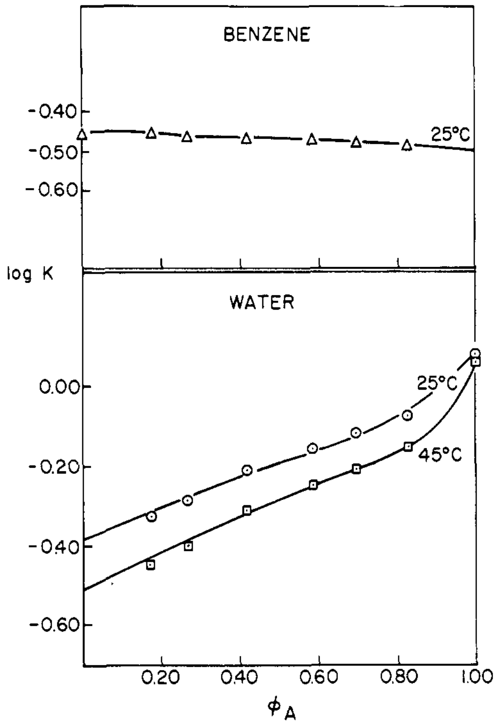

Figure 9. Dependence of the apparent equilibrium constants for water sorption by acrylamide residues and for benzene sorption by styrene residues on the composition of styrene-acrylamide copolymers.

calculated from the temperature dependence of K_w yield consistent values with ΔH becoming more negative with decreasing acrylamide content. For polyacrylamide, $\Delta H = -0.6$ kcal/mol; it is -1.6 kcal/mol for AS-6 and -2.6 kcal/mol for AS-1. Since the water affinity for the acrylamide residues of the copolymers decreases with increasing styrene content in spite of a more favorable heat of mixing, the behavior must be due to a loss of entropy associated with contacts between water and styrene residues.

The high solvent affinity of the copolymers, as compared with what might have been expected by interpolation between the behavior of the homopolymers, was also reflected in their solubility in organic solvents. Most striking was the observation that copolymer AS-3 dissolved in methanol, a strong precipitant for both polystyrene and polyacrylamide.

Copolymers AS-4 and AS-5 took up 12 and 23% of water when equilibrated with saturated water vapor. This degree of water swelling is similar to that characterizing membranes used for desalination by reverse osmosis. Maconochie, *et al.*,[12] have previously shown that suitable membranes for this application may be obtained by copolymerization of hydrophilic and hydrophobic vinyl monomers, but they employed a rather costly material for the hydrophilic component which would be unlikely to be used on an industrial scale. We plan to extend the present study to determine the salt rejection and water permeation characteristics of membranes prepared from styrene-acrylamide copolymers, so as to evaluate the utility of these materials for desalination applications.

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(12) G. Maconochie, A. Sharples, and G. Thomson, *Eur. Polym. J.*, 7, 499 (1971); G. Maconochie and G. Thomson, *ibid.*, 7, 513 (1971).