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Hysteresis-like Behavior in the Swelling/Deswelling of Polystyrene Cross-Linked Resins Using Binary Solvent Mixtures

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ABSTRACT: A polystyrene resin prepared from 40 vol % commercial divinylbenzene (i.e., ~20% cross-linked) with toluene as a diluent (2/1 v/v relative to monomer) shows apparent hysteresis in its swelling/deswelling behavior when treated with a "good" solvent, A, followed by a "poor" solvent, B either water or methanol. The effect decreases for solvent A in the order acetic acid ≈ ethylenediamine > acetone > pyridine > dioxane > tetrahydrofuran (THF). This order suggests a model in which the initially solvent-swollen matrix becomes desolvated, and if the desolvation is sufficiently rapid, porosity can be "locked in" to the matrix via complex chain entanglement and pseudo phase separation, similar to the situation that arises in the preparation of macroreticular resins using precipitant diluents. In the case of THF, essentially no hysteresis occurs because the deswelling is a slow equilibrium process in which the polymer chains can adjust their conformation progressively as the overall character of the medium changes. The phenomenon is discussed in terms of known solubility parameters, δ, and speculation is made concerning the scope of the effect and its potential use.

Introduction

Cross-linked polystyrene-based resins have been widely exploited as supports for catalysts, reagents, protecting groups, etc.,[1] and increasingly other macromolecular backbones and structures are being used similarly when particular applications demand these.[2] Polystyrene-based resins with essentially no additional functional groups, but with controlled surface area and porosity, have also been used to sorb organic molecules from aqueous solutions.[3,4] Many of these applications give rise to situations, whether by design or default, where mixtures of solvents make contact with the resin support. As a result of this we have for a number of years routinely monitored the solvent uptake, or imbibition, of our resin-bound species in order to try and optimize the performance of resin-bound functionalities. Recently, we reported the discovery of the hysteresis-like swelling/deswelling behavior of a cross-linked polystyrene resin in contact with acetone/water mixtures.[5] At that time we showed that tetrahydrofuran/water mixtures did not show a similar behavior, and we concluded that the acetone/water system was the "anomaly". We have now taken these investigations much further to include other water/organic solvent and methanol/organic solvent binary mixtures and, to our surprise, have found that the hysteresis-like behavior, in contrast to our orginal view, represents by far the most common response of our polystyrene resins to swelling/deswelling in binary solvent mixtures.

Experimental Section

Materials. Acetone, acetic acid, dioxane, ethylenediamine, and tetrahydrofuran (THF) were AnalaR reagents and were used as supplied. Methanol, hexane, and pyridine were general purpose grade solvents and were used as supplied.

Polystyrene Resins. Two spherical resins of particle size 500–1180 μm designated 20X21T and 20X11T were employed in this work. Each was prepared by a standard suspension polymerization methodology that we have reported before.[5,6] 20X21T was prepared from a comonomer mixture of commercial divinylbenzene (40 mL) and styrene (60 mL) (i.e., ~20% cross-linked) with toluene present as a porogen or diluent (200 mL). 20X11T was prepared similarly but the level of toluene used was halved (i.e., 100 mL). In the dry state 20X21T had a surface area of 16.2 m^2 g^{-1} (N_2, BET; Micromeritics Accusorb 2100) and a porosity of 0.092 mL g^{-1} (Hg intrusion; Micromeritics Autopore II 9220), while 20X11T had a surface area also of 16.2 m^2 g^{-1} and a porosity of 0.074 mL g^{-1}. In the dry state, therefore, both resins had little internal structure.

Swelling Measurements. Rather than use the somewhat time-consuming centrifugation procedure that we normally use to quantify resin solvent imbibition[7] (in grams of solvent per gram of resin), in this work we continued with the use of a simple calibrated glass tube in which swelling is monitored as a percentage increase in height of a known weight (and height) of dry resin as follows. A known weight of dry resin (usually 0.5 g) was introduced into a calibrated (cm/mm) glass tube at room temperature, and the initial dry settled volume was recorded as an equivalent height (mm). Excess of the solvent in question was then added to the tube and the mixture shaken by hand. The resin was then allowed to settle under gravity and equilibrate with the solvent for 3 h. The new height was then read off, and the swelling (%) was expressed as a percentage increase on the original height. For each resin the experiment was performed in three modifications using 20, 40, 60, and 80 vol % of solvent A in solvent B (usually water or methanol). The first way involved contacting the resin with pure A and then adjusting the overall liquid composition to the required value by appropriate addition of solvent B. The second way was similar, but solvent B was added first. In the third procedure mixtures of solvent A and B were made up with the required compositions, and the resin was contacted directly with these mixtures. With the consecutive addition of solvents resins were left for an additional 24 h to equilibrate. Note in general terms solvent B was always the poorer solvent for polystyrene, and so these procedures essentially generate data for a swelling/deswelling cycle in which the resin is expanded in solvent A and then contracted by addition of B (cycle time ~24 h).

Clearly, this is not an absolute swelling technique, but it does allow a very convenient and rapid comparison of the behavior of a large matrix of resins to be made. We have not carried out additional measurements to confirm an exact proportionality between the increase in height of a resin on swelling and the actual degree of swelling; nor do we necessarily imply that such a strict proportionality exists throughout the range in volume expansion we observe. The changes we report, however, are very large, are readily observable, are reproducible, and are quantitative according to the procedure we have described.

Results and Discussion

To provide correlation with our earlier data, THF/water and acetone/water mixtures were examined first with

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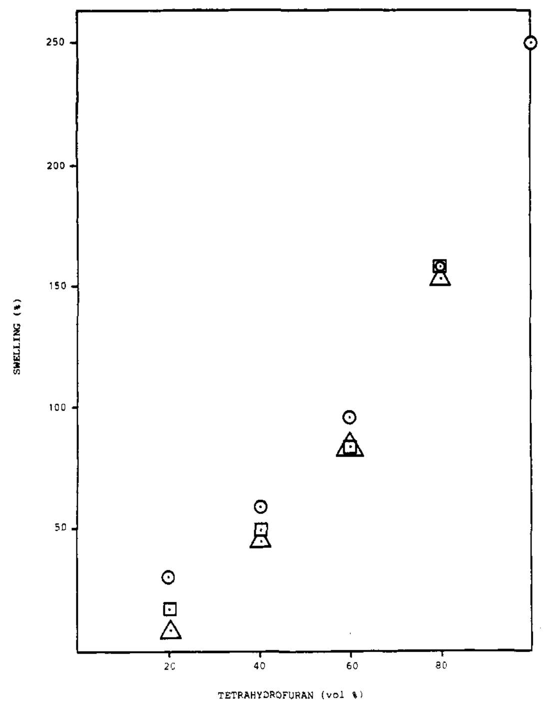

Figure 1. Swelling (%) of poly(styrene-divinylbenzene) resin 20X21T as a function of tetrahydrofuran (vol %) in water: (⊙) THF added first: (▲) water added first; (⊡) premixed solutions.

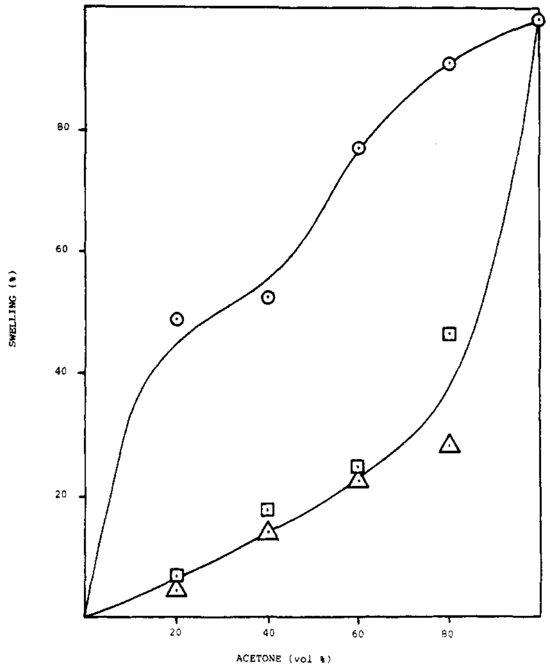

Figure 2. Swelling (%) of poly(styrene-divinylbenzene) resin 20X21T as a function of acetone (vol %) in water: (⊙) acetone added first; (▲) water added first; (⊡) premixed solutions.

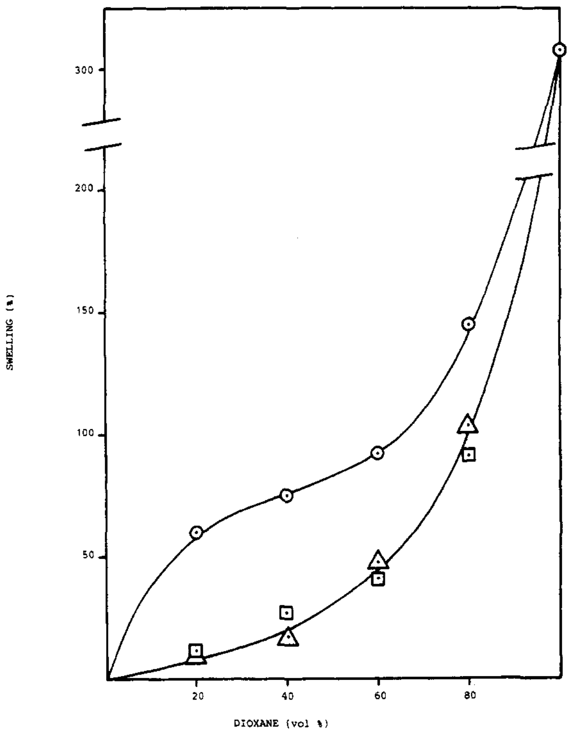

Figure 3. Swelling (%) of poly(styrene-divinylbenzene) resin 20X21T as a function of dioxane (vol %) in water: (⊙) dioxane added first; (▲) water added first; (⊡) premixed solutions.

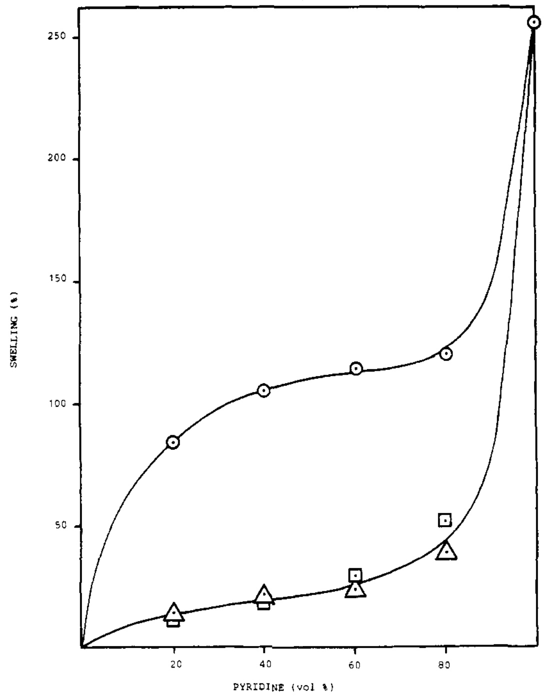

Figure 4. Swelling (%) of poly(styrene-divinylbenzene) resin 20X21T as a function of pyridine (vol %) in water: (⊙) pyridine added first; (▲) water added first; (⊡) premixed solutions.

resin 20X21T. Figures 1 and 2 show graphically the results obtained. Though there are some minor variations, these agree substantially with our previous findings and show that the swelling (%) is essentially independent of the order of addition of solvents in the case of THF and water, but with acetone and water there is a strong dependence. When the resin is swollen initially in acetone, addition of water does *not* cause deswelling to the level anticipated from direct use of preformed acetone/water mixtures, or the use of water first, followed by acetone; i.e., the cycle of swelling in acetone followed by deswelling by addition of water is characterized by a hysteresis-like loop. One resin sample on the top of the hysteresis loop was left for many weeks to see if some slower secondary deswelling process occurred. None was observed over this time period.

Similar experiments carried out with other water-miscible solvents, somewhat to our surprise, yielded similar hysteresis-like behavior. Figure 3 shows the data for dioxane, Figure 4 those for pyridine, Figure 5 those for acetic acid, and Figure 6 those for ethylenediamine. The remarkable feature of these results is that the effect is manifest irrespective of the initial degree of swelling, ranging from ~300% for dioxane down to only ~25% for ethylenediamine. Furthermore, closer inspection of Figure

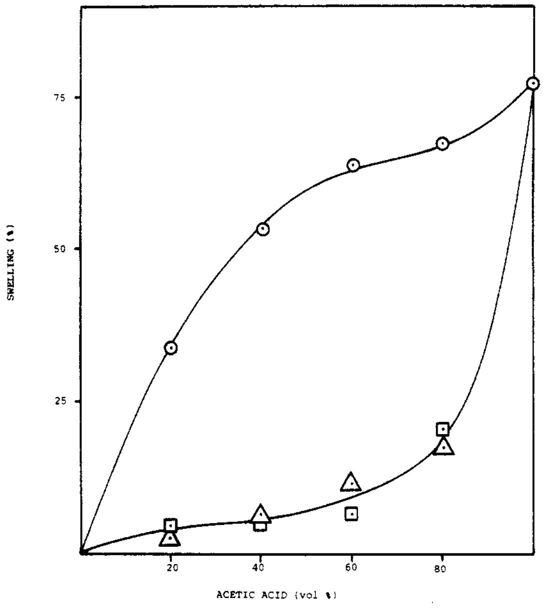

Figure 5. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of acetic acid (vol %) in water: (⊙) acetic acid added first; (△) water added first; (⊡) premixed solutions.

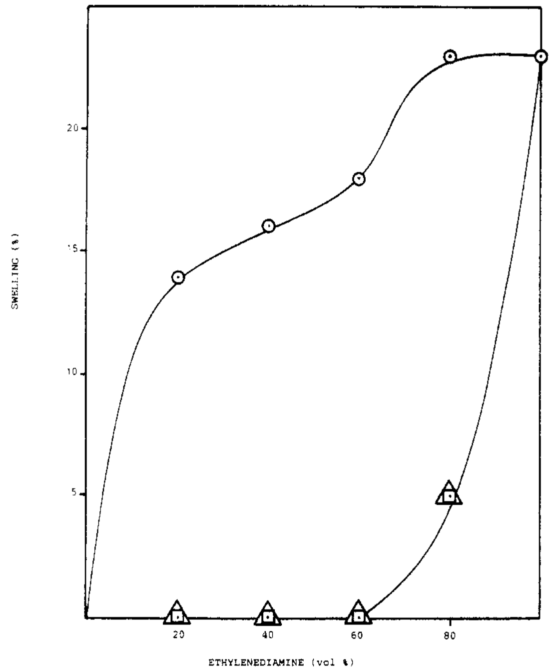

Figure 6. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of ethylenediamine (vol %) in water: (⊙) ethylenediamine added first; (△) water added first; (⊡) premixed solutions.

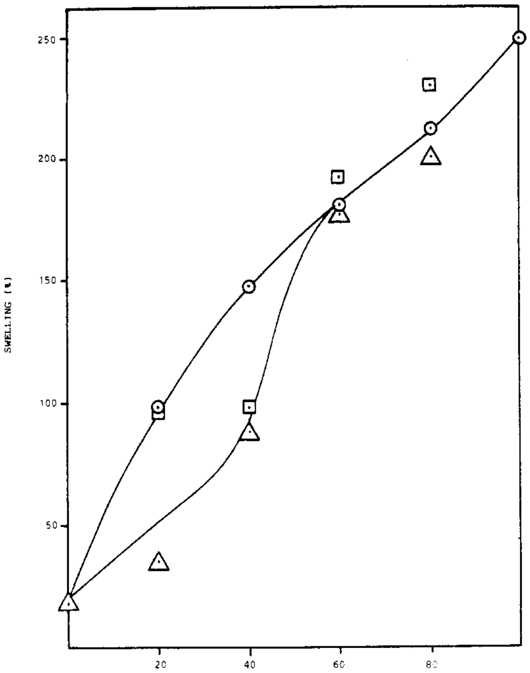

Figure 7. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of tetrahydrofuran (vol %) in methanol: (⊙) THF added first; (△) methanol added first; (⊡) premixed solutions.

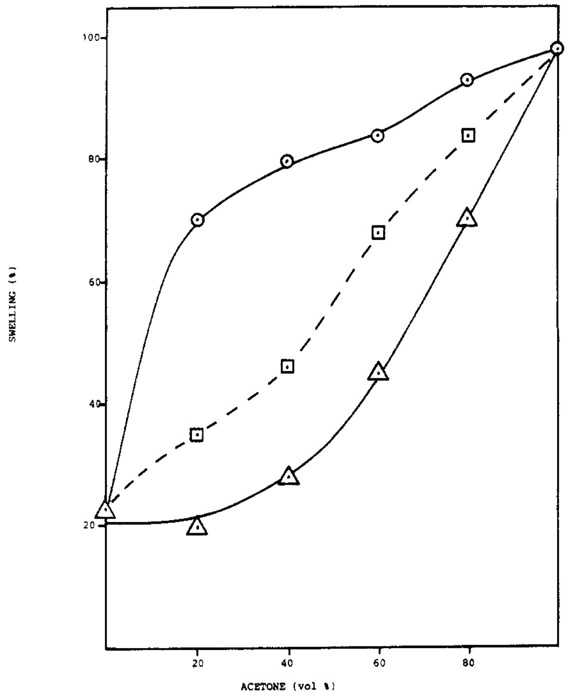

Figure 8. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of acetone (vol %) in methanol: (⊙) acetone added first; (△) methanol added first; (⊡) premixed solutions.

1 and previous data for THF/water mixtures[5] suggests that there might also be a small effect with this mixture as well at low THF contents in the mixture (0–40%).

Nor indeed is the effect peculiar to aqueous binary mixtures. Replacement of water with methanol yielded similar behavior for THF (Figure 7), acetone (Figure 8), and dioxane (Figure 9) mixtures. Overall the effect is attenuated a little, and again in the case of THF the size of the effect is small, and more accurate data are really required in this case. Also, it may be of significance that pure methanol itself shows a small swelling effect, whereas with water none is detectable by the experimental method used here.

Both water and methanol are, of course, poor solvents for polystyrene in terms of having high solubility parameters (Table I). Hexane on the other hand is a poor solvent with a very low solubility parameter. Examination of acetone/hexane mixtures therefore was thought to be of interest to see if similar hysteresis-like swelling/deswelling occurred with this complementary mixture. Figure 10 shows the data obtained. Again, to our initial surprise, not only was such an effect *not* manifest but indeed maximum swelling did *not* occur with 100 vol % acetone but with ~60 vol %. Overall, however, swelling varied very little in the range 20–100 vol % acetone, and again pure hexane displayed a finite swelling itself (~20%).

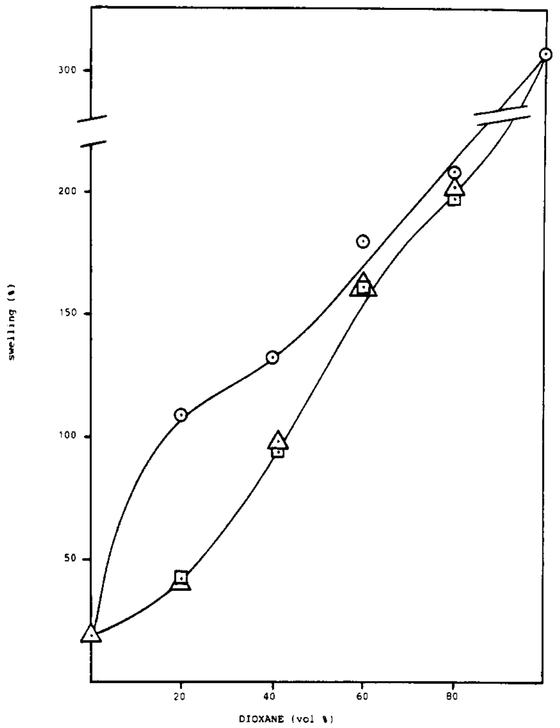

Figure 9. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of dioxane (vol %) in methanol: (⊙) dioxane added first: (▲) methanol added first; (⊡) premixed solutions.

Table I
Hansen Solubility Parameters of Solvents at 25 °C[a]

solvent	solubility parameters,[b] (MPa)$^{1/2}$				order of tendency to show hysteresis effect[c]
	δ	δ_d	δ_p	δ_h	
hexane	14.9	14.9	0	0	NA
THF	19.4	16.8	5.7	8.0	6
acetone	20.1	15.5	10.4	7.0	3
dioxane	20.5	19.0	1.8	7.4	5
acetic acid	21.3	14.5	11.9	16.6	1–2
pyridine	21.7	19.0	8.8	5.9	4
ethylenediamine	25.4	16.6	8.8	17.0	1–2
methanol	29.7	15.1	12.3	22.3	NA
water	47.9	15.5	16.0	42.4	NA

[a] References 8 and 9. δ[Poly(styrene–divinylbenzene)] = 18.6 (MPa)$^{1/2}$.[15,16] [b] $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$; δ = overall parameter, δ_d = dispersive term, δ_p = polar term, and δ_h = hydrogen-bonding term. [c] With water mixtures.

It is clear, therefore, that at least two "solvent-expanded" or "solvent-induced" states exist for polystyrene resin 20X21T in contact with aqueous, or methanolic, binary solvent mixtures. Furthermore, these states have significant long-term stability; i.e., they seem to correspond to significant thermodynamic free energy minima. In a recent series of definitive papers Errede and his collaborators[10–14] have described their detailed work on polymer swelling and drying using single solvents. Evidence from the latter studies in particular[13] suggests that in the case of a pure solvent two types of sorbed molecule arise. A mobile nonadsorbed species that is easily and quickly lost on drying, and a more strongly adsorbed species that is lost much more slowly and at a rate that is determined by the relative force of association between the solvent and the monomer unit of the polymer in the gel state. A similar explanation might therefore be advanced here. Two types of sorbed molecule arise when the swelling solvent A is introduced into resin 20X21T. When the deswelling solvent B is added, the mobile nonadsorbed species (of A) are desorbed from the resin into the bulk liquid phase, but the strongly adsorbed species (of A) remain associated with the monomer units of the polymer chains. Some collapse of the solvent-expanded network is thus observed, but this is not a full collapse to an nonsolvated state, but a partial collapse to a state retaining the tightly bound A component. The top curve of each hysteresis loop corresponds to this state. In the cases where the resin is exposed to the non-swelling solvent B first, or the performed mixtures of A and B, the highly expanded state arising from solvation by A alone, along with strong adsorption of A, is never achieved, and the lower curve of each hysteresis loop is followed. This explanation has three important shortcomings. First, it would be expected that the tightly bound A component would be exchanged slowly in an analogous fashion to the secondary drying process reported by Errede.[13] Hence a resin that finds itself on the top of a hysteresis loop would be expected to deswell slowly to the corresponding point on the lower curve of the loop. This is not observed in practice. Second, the solubility parameter δ for poly(styrene–divinylbenzene) is 18.6 (MPa)$^{1/2}$,[15,16] and the solvent with the closest δ value in this work is THF (Table I). Hence it might be expected that the strongest interaction between A solvents and resin 20X21T would be in the case of THF, and hence that aqueous mixtures of THF should present the best opportunity for manifestation of a hysteresis effect. In practice the effect is almost completely absent with THF mixtures (Figure 1). Third, the magnitude of the observed effect is in practice in the order acetic acid ≈ ethylenediamine > acetone > pyridine > dioxane > THF for their aqueous mixtures. This represents to a good approximation the order of the strength of interaction of each of these with water (and indeed methanol). In the case of acetic acid and ethylenediamine the interaction with water is hydrogen-bonding dominated (δ_h in Table I), while with acetone the major contribution is a dipolar interaction (δ_p in Table I). Hence the loss of any potentially tightly bound solvent A on addition of water (B) would be expected to be most rapid for acetic acid and ethylenediamine, and these would be expected to offer the worst prospect for manifestation of any hysteresis-like swelling behavior rather than the best, as observed in practice.

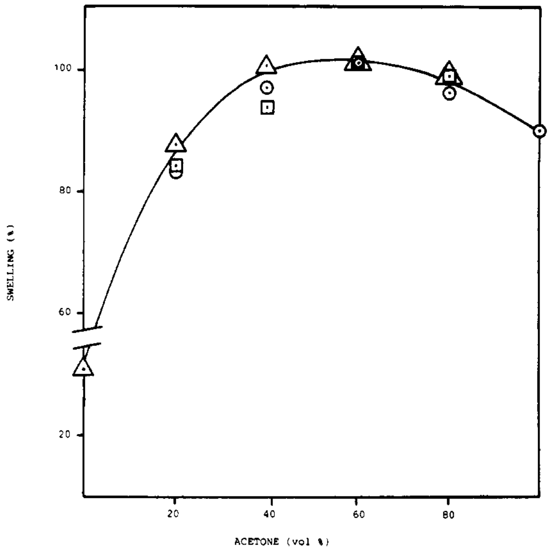

Figure 10. Swelling (%) of poly(styrene–divinylbenzene) resin 20X21T as a function of acetone (vol %) in n-hexane: (⊙) acetone added first; (▲) hexane added first; (⊡) premixed solutions.

In fact we believe the solvent order specified above is the real clue to the overriding mechanism of this effect. Initially the polystyrene resin is swollen to a state controlled by the level of interaction of solvent A with the polymer, and this correlates very well with the solubility parameter data, δ, in Table I. Addition of the deswelling solvent B (water or methanol) causes desolvation of the polymer chains. The stronger the interaction between A and B, the faster is this desolvation process. In the extreme, a situation approaching precipitation of the polymer chains within resin beads occurs. Since the resin is cross-linked, rapid collapse and precipitation to a rigid, permanently entangled glasslike structure lead to formation of voids within the resin and within which the solvent mixture resides. The situation parallels very closely that which prevails in the synthesis of cross-linked resins using precipitating diluents or porogens,[17,18] giving rise to macroreticular materials with a permanent internal porous structure. The upper curve of the various hysteresis loops does not thereore reflect the residual degree of *swelling* of the matrix in a given mixture, but rather it reflects the level of porosity trapped within each matrix during rapid deswelling. The effect is maximized with acetic acid and ethylenediamine and is minimal with THF. In the latter case the interaction between the polymer chains and the swelling solvent is maximized, and between the latter and water, minimized. Hence the desolvation in the case of THF is a slow equilibrium process in which polymer chains can adjust their conformation slowly with the changing solvation conditions they experience. Overall therefore the resin matrix settles back slowly to the state associated with the lower curve of each hysteresis loop. The dual-sorption mechanism proposed by Errede[13] may well be superimposed upon the changes described above, but almost certainly it is of second-order importance in these experiments.

When methanol is used in place of water as the deswelling solvent B, almost certainly the same mechanism operates, although the order of magnitude of the effect would be expected to be lower, and indeed is so experimentally. This is because methanol itself interacts to some extent with polystyrene resins, certainly more so than does water; hence the desolvation process would be expected to be slower. In addition the "pull" on the swelling solvent by methanol might also be less than that by water (especially in the case of acetic acid and ethylenediamine).

In the case of hexane as the supposed deswelling solvent B, then again the proposed mechanism remains consistent. Only acetone/hexane mixtures have been studied (Figure 10). Hexane alone shows a significant swelling with 20X21T and is clearly less likely to achieve the rapid deswelling required to "freeze in" porosity and give rise to hysteresis. In general, the levels of interaction of poly(styrene–divinylbenzene) with the group of solvents—hexane, THF, acetone, and dioxane (as indicated by δ values, Table I)—do not vary too much, and so the likelihood of achieving porosity by such a swelling/deswelling procedure is very low. Indeed it is clear from the data in Figure 10, where the degree of swelling over the range 20–100 vol % acetone changes very little, that the interactions in the ternary system acetone–hexane–poly(styrene–divinylbenzene) are remarkably uniform. The small but definitive maximum swelling around 60 vol % acetone came as a surprise to us, but the literature confirmed that acetone/*n*-alkane mixtures display a "classic cosolvency" effect in which mixtures of two "nonsolvents" can actually dissolve a linear polymer, in this case polystyrene.[19,20] The cooperative action of two "nonsolvents" in this manner might be attributed to interaction of one component (*n*-alkane) specifically with the polymer backbone, and the other (acetone) specifically with the side-chain groups. In reality, however, the effect can be explained totally on strict thermodynamic grounds and has been done so very elegantly.[20]

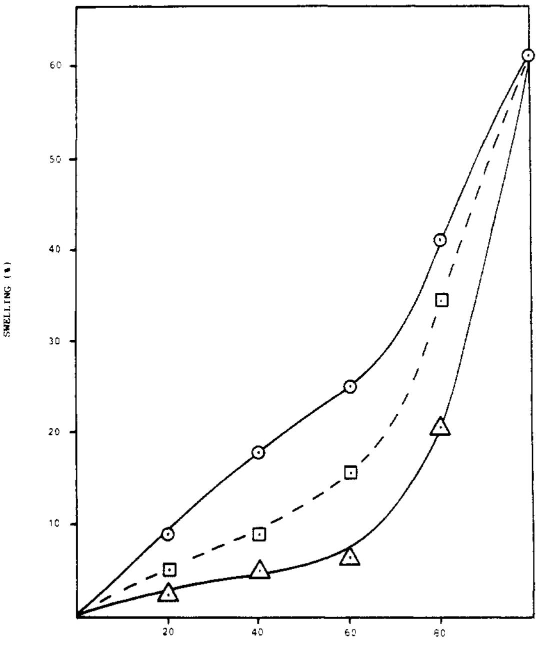

Figure 11. Swelling (%) of poly(styrene–divinylbenzene) resin 20X11T as a function of acetone (vol %) in water: (⊙) acetone added first; (△) water added first; (⊡) premixed solutions.

The question now arises as to whether the hysteresis-like effect characterized for resin 20X21T is peculiar to this resin or is an example of a more general phenomenon. The model proposed suggests it should be general and will be manifest providing the deswelling process is rapid and providing the resin structure is capable of "locking in" permanent porosity as result of complex chain entanglement. Figure 11 shows the data for acetone/water mixtures with resin 20X11T. The latter is similar to 20X12T except the toluene diluent used in its preparation was present at a level 1/1 v/v with respect to the monomers, instead of 2/1 v/v. Clearly, the same hysteresis-like behavior is manifest, though the effect is reduced to some extent. Further work is required, but this suggests that, providing the above two criteria are met, the phenomenon will be observed. What is not clear, however, is what factors in the resin construction are required to allow porosity to be "locked in" on deswelling, i.e., what level of cross-linking (if any), what diluents in the resin manufacture, etc. Since macroreticular resins can be prepared with a fairly broad resin composition,[17] this suggests that the scope for generating the hysteresis-like effects described here is quite large. Our intention is to investigate this further.

A second question that arises is, can different levels of porosity be "locked in" by the swelling/deswelling procedure using the same solvent A–solvent B mixture? For example, if the resin is first swollen to a level below its maximum level (with pure A) by an initial A–B mixture, and then additional B added, can a second (and of course lower) degree of porosity be "locked in". Again we plan to investigate this possibility further, but it is interesting to note that with acetone/methanol mixtures with 20X21T (Figure 8) and acetone/water mixtures with 20X11T (Figure 11) there is clear evidence for a discrete third state (dashed line) arising when premixtures of these solvents are used.

Finally of course if the model presented is correct, the effect could be a useful one in terms of generating novel porous polymer structures. Such morphologies might be fragile in terms of destruction or modification by contact with particular solvents or solvent mixtures. However, they could be robust in terms of applications involving nonsolvents or in terms of gas-phase use, and this manipulative technique could provide a simple and versatile procedure for adjusting the porosity of *one* resin to produce a range of resins. We now intend to evaluate the porosity of resins that have been passed through a hysteresis swelling/deswelling cycle using N_2 adsorption and Hg porosimetry. Data from these techniques will not only confirm or deny our model but also indicate whether the porous structures obtained have a different range of parameters (surface area, pore size, and pore size distribution) than conventionally produced resins and hence whether they may be usefully exploited.

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Registry No. THF, 109-99-9; (divinylbenzene)(styrene) (copolymer), 9003-70-7; acetone, 67-64-1; dioxane, 123-91-1; acetic acid, 64-19-7; pyridine, 110-86-1; ethylenediamine, 107-15-3; methanol, 67-56-1; water, 7732-18-5.