

# Preferential Absorption of (Binary) Solvents by *p*-Hydroxyethyl Methacrylate Gels

## INTRODUCTION

Several reports have appeared on the properties of solutions of hydrophilic polymers. Tuzar and Bohdanecky<sup>1</sup> studied poly(hydroxyethyl methacrylate) in various binary solvents and found, by measuring intrinsic viscosities, that selective sorption occurred.

For these types of hydrogels, solvents with the greatest solvent power had an outstanding electron donor or electron acceptor character. These results are consistent with data reported by Wichterle and Chromecek.<sup>2</sup> Pouchly and Zivny<sup>3,4</sup> showed theoretically that sorption phenomena in systems (polymer–binary solvent) could be derived from osmotic equilibrium data. They explained the occurrence of so-called “inversion points,” concentrations at which preferential sorption switches from one solvent component to the other.

Thus, generally it is found<sup>3–5</sup> that sorption of binary solvents is not a simple additive process but a more complicated one, and that electron donor or acceptor properties play an important role. To our knowledge, these phenomena have not been studied with crosslinked hydrogels. Only Refojo<sup>6</sup> investigated binary solvents (water with up to a few per cent of certain salts and/or organic compounds), but he reported data on swelling properties of the gel rather than on selective sorption properties.

In this note, therefore, we shall present data on selective sorption studies in systems [crosslinked *p*-HEMA–binary solvents of mixtures of a good solvent for uncrosslinked *p*-HEMA (methanol, DMAC) and a nonsolvent (benzene)], with special emphasis on a possible analytic use of *p*-HEMA gel as purification agent.

## EXPERIMENTAL

### Materials

The monomer hydroxyethyl methacrylate (HEMA) was obtained from Hydro. Med. Sciences, Inc., U.S.A., and used without further purification. According to the manufacturer, the monomer contained about 0.3% crosslinker (ethylene glycol dimethacrylate, EGDMA). The initiator, methyl azobisisobutyrate, was obtained by esterification of azobisisobutyronitrile according to Thiele and Heuser.<sup>7</sup> All pure solvents used were obtained from Merck, Darmstadt, Germany.

The following binary solvents were used: (a) mixtures of benzene and methanol; (b) mixtures of benzene and dimethylacetamide; (c) mixtures of water and methanol. The solvents were analytic grade and were used without further purification.

### Methods

**Preparation of Gels.** Polymerization of HEMA was carried out at 35°–40°C during four days, with 0.2% initiator added to the monomer.

**Sorption Measurements.** Cylindrical pieces of *p*-HEMA (diameter,  $8.0 \pm 0.2$  mm; height,  $4.0 \pm 0.2$  mm) were incubated at 25°C in the solvent system to be investigated. Weight was measured until equilibrium was reached. The equilibrium concentration of the liquid phase above the swelling polymer gel was determined by gas chromatography, and equilibrium concentration of the liquid within the gel phase was determined by elemental analysis of the swollen gel phase.

## RESULTS AND DISCUSSION

In Figures 1, 2, and 3, the results of swelling experiments on *p*-HEMA gels in binary mixtures are presented. As can be seen, the vertical axis represents the swelling ( $S$ ), defined as total weight of swollen gel/weight of gel before incubation, while on the horizontal axis the concentration of both the supernatant (the liquid phase  $L$ ) and the solvent in the gel phase ( $G$ ) is displayed,  $X_L$  and  $X_G$ , respectively. It can be seen that these  $S$ - $X$  diagrams resemble familiar  $T$ - $X$  boiling diagrams of binary systems.

## ABSORPTION OF METHANOL/BENZENE IN polyHEMA GELS.

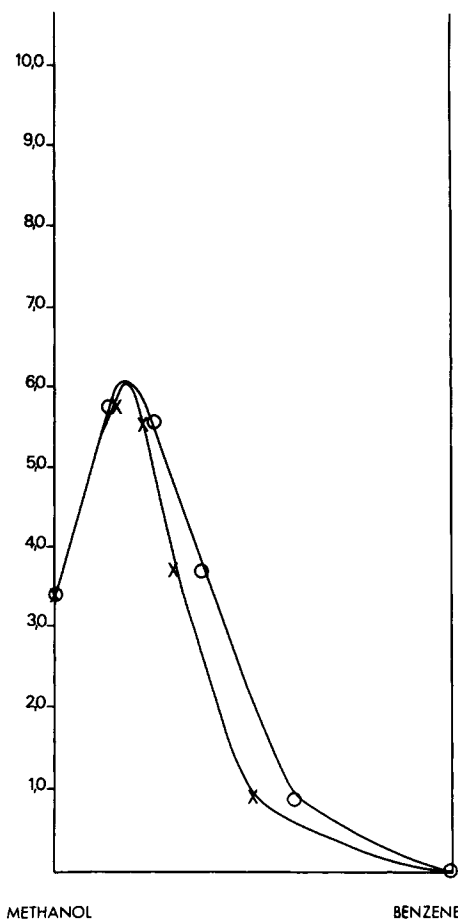


Fig. 1. Swelling  $S$  plotted as function of concentration (in weight) of liquid inside the gel ( $X_G$ ) and outside the gel ( $X_L$ ): (-O-O-O-)  $S(X_L)$ ; (-x-x-x-)  $S(X_G)$ .

The area below the  $S(X_G)$  curve represents  $S$ - $X$  combinations with no supernatant present but with only one phase, the gel phase  $G$ . Between the  $S(X_G)$  and  $S(X_L)$  curves, the gel phase  $G$  and the supernatant liquid phase  $L$  coexist, while above the  $S(X_L)$  curve no gel but only a liquid phase is present. The  $S(X_L)$  curve represents swelling as function of liquid phase concentration, while  $S(X_G)$  depicts swelling as a function of concentration in the gel phase.

### The Methanol-Benzene System

Mixtures of methanol-benzene containing up to about 20% benzene are not absorbed selectively by *p*-HEMA gels. Although benzene as a pure solvent is not absorbed at all, it is surprising that the swelling of the gel increases with increasing benzene content (up to 20%). Higher benzene ratios result in selective absorption, but still the gel absorbs benzene in mixtures up to near 100% benzene.

Thus, although pure methanol is absorbed readily and pure benzene not at all, the situation is quite different in mixtures of methanol and benzene: the gel does not "remove" only methanol, but it absorbs both constituents. In concentration of more than 20% benzene, methanol is absorbed preferentially.

ABSORPTION OF DMAC-BENZENE IN polyHEMA GELS;

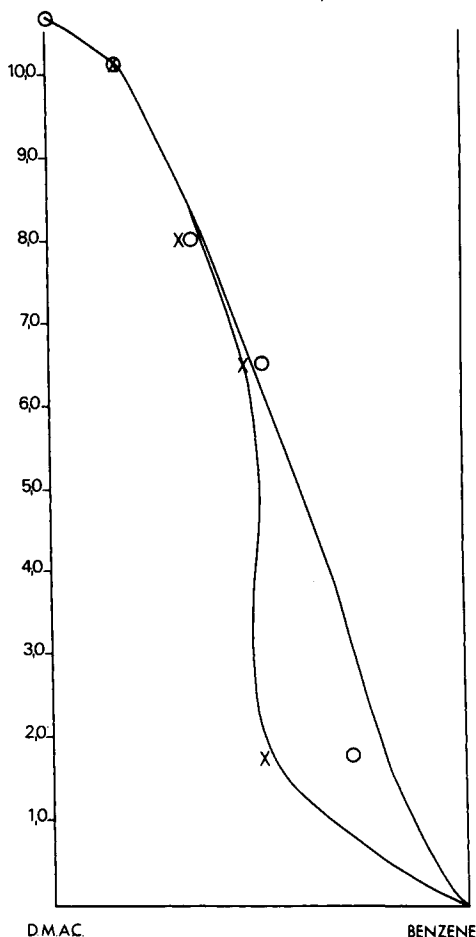


Fig. 2. Swelling  $S$  plotted as function of concentration (in weight) of liquid inside the gel ( $X_G$ ) and outside the gel ( $X_L$ ): (-O-O-O-)  $S(X_L)$ ; (-x-x-x-)  $S(X_G)$ .

### The Dimethylacetamide (DMAC)-Benzene System

Unlike the previously described system, no "azeotropic" point is present in the DMAC-benzene diagram. Only when more than about 50% benzene is present, the gel starts absorbing DMAC selectively; but again, at all concentrations except 100% benzene, the gel absorbs benzene.

### The Water-Methanol System

The maximum swelling occurs at a concentration of about 70% methanol and then reaches a degree of swelling of about 7, as compared with a degree of swelling of 0.4 for pure water and 3.7 for pure methanol. In water-rich mixtures some selective absorption occurs.

It is interesting to note that in two systems, Figures 1 and 3, the total absorption increases initially when a poor solvent is added. According to Tuzar and Bohcanecky,<sup>1</sup> a poor solvent can break up the associated structure of the good solvent, thus enhancing the sorption possibilities. In our cases, this means that benzene breaks up the associated structures of methanol and DMAC, while in mixtures of water and methanol a less associated structure would be present than in either solvent.

One would expect then, that selective absorption would occur by adding a poor solvent, but this is not found. Possibly, the explanation is that solvents protect the polar groups within the gel, thus allowing apolar solvents to be absorbed.

With regard to a possible use of *p*-HEMA as an analytic tool, the graphs of the benzene mixtures

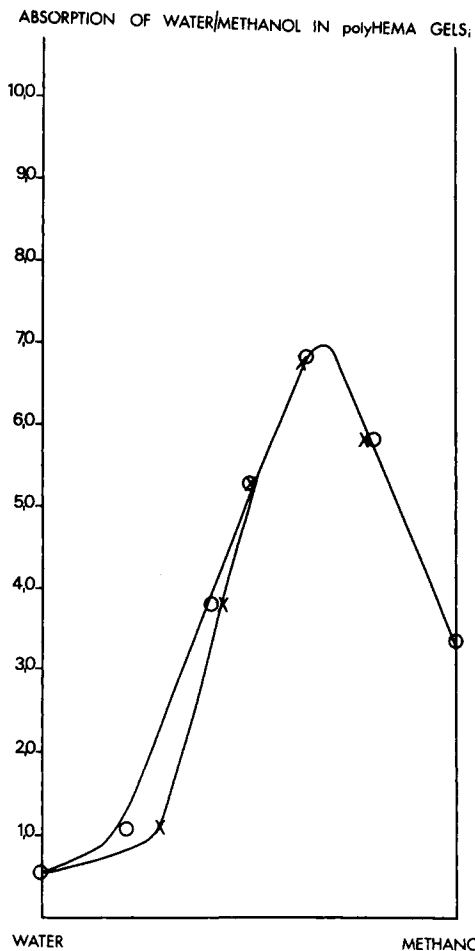


Fig. 3. Swelling  $S$  plotted as function of concentration (in weight) of liquid inside the gel ( $X_G$ ) and outside the gel ( $X_L$ ): (-O-O-O-)  $S(X_L)$ ; (-x-x-x-)  $S(X_G)$ .

show clearly that, although pure benzene is not absorbed at all, in mixtures the selective absorption is much less than suggested by the behavior of pure benzene. In our three cases, selective behavior occurs only to a small extent when the poorer solvent is in excess. We therefore do not foresee *p*-HEMA to be of much use in analytic purification procedures.

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### References

1. Z. Tuzar and M. Bohdanecky, *Coll. Czech. Chem. Comm.*, **34**, 289 (1969).
2. O. Wichterle and R. Chromecek, *J. Polym. Sci. C.*, **16**, 4677 (1969).
3. A. Zivny and J. Pouchly, *J. Polym. Sci. A2*, **10**, 1467 (1972).
4. J. Pouchly and A. Zivny, *J. Polym. Sci. A2*, **10**, 1481 (1972).
5. J. Pouchly, A. Zivny, and K. Solc, *Coll. Czech. Chem. Comm.*, **37**, 989 (1972).
6. M. F. Refojo, *J. Polym. Sci. A-1*, **5**, 3103 (1967).

7. J. Thiele and K. Heuserm, *Ann. Chem.*, **290**, 32 (1896).

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