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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Rudzinski, Walter E. and Aminabhavi, Tejraj M.(1983) 'Preferential Interactions on Polystyrene Divinylbenzene Copolymeric Sorbents', *Journal of Macromolecular Science, Part A*, 19: 8, 1247 – 1253

To link to this Article: DOI: 10.1080/00222338308081099

URL: <http://dx.doi.org/10.1080/00222338308081099>

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Preferential Interactions on Polystyrene Divinylbenzene Copolymeric Sorbents

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ABSTRACT

The adsorption of picric acid, naphthalene-sulfonic acid, and toluenesulfonic acid onto a polystyrene divinylbenzene copolymeric sorbent in methanol-water systems at 25°C was studied by reverse-phase high performance liquid chromatography. The observed peak asymmetry and increase in capacity factor at high methanol concentrations in the mixture was attributed to preferential interactions of the solutes at the surface. The phenomena were not as pronounced for octadecyl silane bonded phases.

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INTRODUCTION

It has been well established that when a polymer is dissolved in a binary solvent mixture, usually one of the solvents preferentially solvates the polymer [1, 2]. From the extent of preferential binding, thermodynamic interaction parameters have been calculated [3]. Using batch extraction methods, the preferential adsorption of a solvent onto a polymer can be determined. When hydro-organic solvent mixtures are employed, the polymer exhibits limited solubility in the solvent mixture and this makes the data more difficult to reproduce.

Reverse-phase liquid chromatography (RP-HPLC) is a convenient method for the evaluation of partition coefficients for solutes adsorbing onto a hydrocarbonaceous surface [4]. Furthermore, the method is useful for evaluating secondary equilibria that occur in solutions [5]. The predominant surface utilized in reversed-phase liquid chromatography is an octadecyl-silane bonded phase. The surface is fairly inert and with proper "end capping" and selection of solvents, the surface may be "deactivated" toward a solute of interest. Polystyrene-divinylbenzene copolymeric sorbents have been utilized in reversed-phase liquid chromatography and, in fact, these are promising reversed-phase adsorbents [6].

Since a chromatographic approach mimics the equilibria occurring in a batch method, it was decided that reversed-phase high performance liquid chromatography might be the most efficient approach to studying the preferential interaction of solutes on polystyrene surfaces. The approach can be extended to any polymer which can be sieved to a small range of sizes and then packed into a chromatographic column. The approach promises to open up a whole new range of studies on the preferential interaction of solutes or solvents on polymeric surfaces. To our knowledge, hitherto, HPLC has only been used sparingly for the evaluation of polymer-solute interactions [7].

EXPERIMENTAL

The chromatographic system used in this study was a Tracor, Model 985 solvent delivery system (Tracor Instruments, Austin, Texas) with a model 7125 automatic syringe loading sample injector (Rheodyne, Berkeley, California) with a 20- μ L sampling loop, a model 970A variable wavelength detector (Tracor), a model 951 HPLC pump (Tracor), and a model 3390A reporting integrator (Hewlett-Packard, Avondale, Pennsylvania). The octadecylsilica bonded column was an ultrasphere ion-pair 5 μ m (Altex, Berkeley, California), while the styrene-divinylbenzene copolymeric column was a PRP-1 (Hamilton Company, Reno, Nevada).

Methanol (MCB Manufacturing, Cincinnati, Ohio) was distilled, then aspirated through 0.50 μ m Millipore filters. Filters were purchased from Rainin, Woburn, Massachusetts. Water was distilled and then

aspirated through 0.50 μM cellulose acetate filters. The mobile phases were degassed using helium prior to use. The mobile phase flow rate was maintained at 1.00 mL/min.

Acids and salts used in this study include 2-naphthalenesulfonic acid sodium salt (NAS) and picric acid (PA) purchased from Eastman, and toluenesulfonic acid (TS) purchased from Fisher, Fair Lawn, New Jersey.

All solutes were prepared as concentrated solutions and then diluted to the desired mobile phase composition. All samples were dissolved in the mobile phase. The retention volume (V_R) of the solutes was measured at a flow rate of 1 mL/min. The V_R was calculated by measuring the time associated with the first moment of the eluted peak, t_r , and multiplying by the flow rate. The capacity factor, $k' = (V_R - V_M)/V_M$ was then measured by adjusting V_R for V_M , where V_M is the volume of eluent required to elute an unretained solute (1×10^{-4} M NaNO_3). The area/height (A/H) ratios were obtained on a model 3390A reporting integrator and are a measure of peak width, and indirectly peak asymmetry.

RESULTS AND DISCUSSION

In chromatographic systems, peak shape is governed by diffusion, transport, and mass transfer-associated phenomena. The contribution of each of these has been mathematically formulated in terms of plate height in liquid chromatography [8, 9]. Furthermore, it has been established that for hydroorganic solvent mixtures in reversed-phase chromatography, as the volume percent of the organic solvent increases, retention as measured by the capacity factor k' diminishes [4]. When k' eventually reaches a minimum value, the solute elutes near the solvent front. The hydrophobic effect is no longer the paramount contributor to the solute retention process [10, 11].

Recently we have measured the retention of ionized solutes on an octadecylsilane (ODS) bonded phase and on a polystyrene-divinylbenzene (PS-DVB) copolymeric surface [12]. Methanol-water was used as the eluting solvent mixture. It was found that as the concentration of water in the eluent diminishes, the capacity factor decreases until eventually its value reaches a minimum. This behavior has been observed both on ODS-bonded phase and on PS-DVB and conforms with the generally expected results in RP-HPLC. However, if methanol-water mixtures contain less than approximately 10% H_2O , PS-DVB packed columns begin to exhibit a preferential interaction with polarizable solutes such as picric acid, naphthalenesulfonic acid, and toluenesulfonic acid. These solutes show a strong affinity for PS-DVB column as demonstrated by an increase in k' (see Fig. 1) and also peak asymmetry as demonstrated by picric acid (see Fig. 2); whereas the same solutes only show a slight

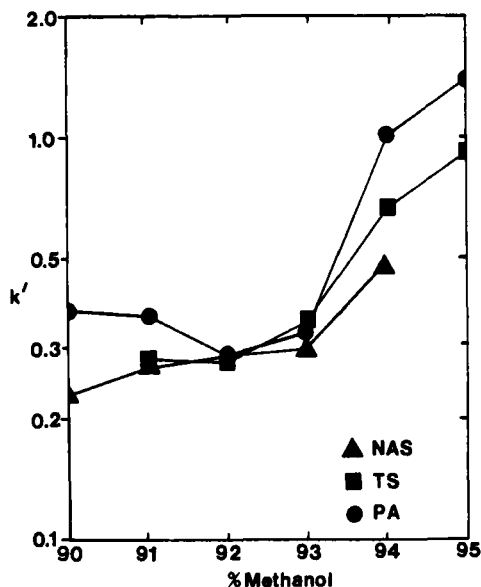


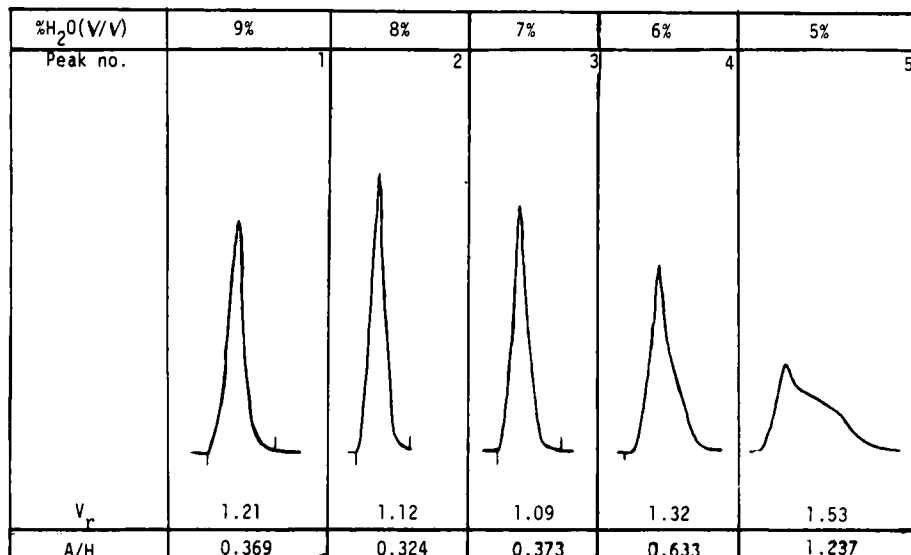
FIG. 1. Variation in the capacity factor with mobile phase composition.

increase in k' but not peak asymmetry when ODS-bonded phase is used as the sorbent (see Fig. 3). The increase in k' for ODS-bonded phase may be due to an increase in the phase ratio.

The results indicate that under water-lean eluent conditions (less than 10% H_2O), polarizable solutes can interact preferentially with PS-DVB but not with ODS-bonded phase. Picric acid, naphthalenesulfonic acid, and toluenesulfonic acid preferentially solvate the copolymer, but not the octadecylsilane bonded phase. The polarizable solutes probably form charge transfer complexes with the phenyl groups of PS-DVB, but can only interact weakly via van der Waal type interactions with the ODS-bonded phase.

The mobile-phase composition at which specific interactions begin to occur bears a striking resemblance to the turbidity point previously observed in studies on polystyrene dissolved in mixed solvents containing methanol [13].

Several lattice model theories for polymer adsorption are available in order to evaluate the experimental results. Most of these theories successfully address the molecular mechanism of retention and selectivity in both normal-phase [14] and reversed-phase chromatography [15]. In Roe's theory [16] no particular conformation is assumed for



Area = 6.5×10^7 ($\pm .4 \times 10^7$) counts

Solute = picric acid (1×10^{-3} M)

Mobile phase = (Methanol: H₂O) unbuffered

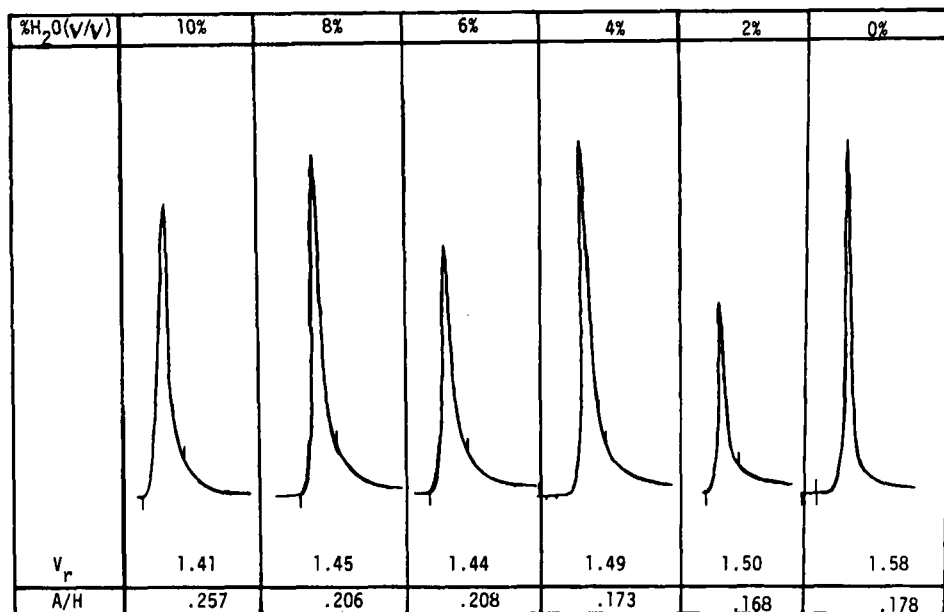
Stationary phase = Polystyrene-divinylbenzene (Hamilton)

Attenuation = 9

FIG. 2. Variation in the elution profile of picric acid with polystyrene-divinylbenzene copolymer as sorbent.

adsorbed molecules, Silberberg's theory [17] assumes the loop-train conformation, and Scheutjens-Fleer's theory [18] is based on the loop-train-tail conformation. It should be noted that in all these theories, experimental parameters such as surface sites occupied by the solute molecules (θ), fraction of solute molecules adsorbed (p), and surface excess (Γ) can be calculated as a function of the volume fraction (θ), the degree of polymerization (η), the Flory-Huggins's interaction parameter (χ), and the solute-surface interaction parameter (χ_s).

It is hoped that the results of our research might shed light on thermodynamic interaction parameters governing solvent interactions with polymeric materials. However, details of the calculations of the experimental parameters based on polymer-solution theories will be the subject of a future communication.



Area = $4.0 \times 10^7 (\pm .8 \times 10^7)$ counts

Solute = picric acid ($1 \times 10^{-3}M$)

Mobile phase = (Methanol: H₂O) unbuffered

Stationary phase = Octadecylsilane Bonded Phase (Altex)

Attenuation = 9

FIG. 3. Variation in the elution profile of picric acid with ODS-bonded phase as sorbent.

CONCLUDING REMARKS

Adsorption of the polarizable solutes onto polystyrene-divinylbenzene copolymeric and octadecylsilane bonded phases in methanol-water mixed solvent systems at 25°C was studied using reversed-phase high performance liquid chromatography. The asymmetry of the peak at high methanol concentrations in the case of polystyrene-divinyl benzene copolymer was attributed to a thermodynamic preferential interaction of the solute at the surface. This effect is predominantly due to the presence of active sites that are freely available to the polarizable solute molecules such as picric acid. On the other hand, peak asymmetry was not observed with the octadecylsilane bonded phase even at a composition of 100% methanol; the latter surface had no specific interactions with the solute molecules in solution.

More experiments are needed with several other surfaces utilizing both chromatographic and nonchromatographic procedures in order to evaluate the magnitude of the thermodynamic interaction parameters.

ACKNOWLEDGMENTS

We would like to thank Terri King and Donna Bennett for performing the HPLC experiments. In addition W. E. Rudzinski would like to thank The Robert A. Welch Foundation (Grant AI-809) for partial support of this work. Tejraj Aminabhavi would like to thank the administrators of Karnatak University, India, for the opportunity of a leave of absence.

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Accepted by editor October 5, 1982

Received for publication November 5, 1982