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Effect of Concentration on Partitioning of Polystyrene within Finely Porous Glass

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We recently published a study (Colton et al., 1975) of diffusion and partitioning of solutions of nearly monodisperse polystyrene ($M = 600$ to 670 000) in leached borosilicate glass cubes having a narrow pore size distribution and pore radii of from 2.5 to 47.6 nm. In that work, bulk solute concentrations were equal to or less than 0.1% (w/v). Here we report an extension of that study in which the effect of solute concentration on the equilibrium partition coefficient is investigated, thereby making possible the extrapolation of the partition coefficient to infinite dilution for comparison with theory. The effect of solute concentration, which we have found to be surprisingly large, is in qualitative agreement with theory and may be of importance itself in connection with understanding various liquid phase reactions catalyzed by porous solids in which the size of the reacting molecules is comparable to that of the pores.

EXPERIMENTAL METHODS

The porous glass cubes employed were from our previous study. Physical properties of the cubes, denoted henceforth as types A, B, and C, were, respectively, as follows: volumetric mean pore radii (r_{P1}) from mercury porosimetry data, 18.5, 23.4, and 47.6 nm; specific pore volumes (V_P), 1.07, 0.62, and 0.68 cm^3/g; specific surface areas (S_P) from BET data (Quantachrome Co., Glenvale, N.Y.), 66.2, 31.5, and 14.9 m^2/g; equivalent cylindrical pore radiii ($r_{P2} = 2V_P/S_P$), 32.3, 39.4, and 91.3 nm. The ratio r_{P2}/r_{P1} was 1.75, 1.68, and 1.92 for cube types A, B, and C, respectively. Before use, the glass cubes were reacted under vacuum at 120°C with hexamethyl disilazane (HMDS) to prevent adsorption of polystyrene. After each run, the cubes were regenerated by rinsing with methylene chloride for 2 days in a soxhlet extractor, then dried in a vacuum oven and stored in sealed containers. Molecular weights and root mean square radii of gyration (calculated as described in our previous study) of the monodisperse polystyrene (Pressure Chemical Co., Pittsburgh, Pa.) were 37 000 (6.75 nm), 110 000 (12.7 nm), 200 000 (18.0 nm), 498 000 (30.6 nm), and 670 000 (36.3 nm). The solvent was reagent grade chloroform, a good solvent for polystyrene. Concentrated solutions of polystyrene in chloroform were prepared in advance and allowed to stand for a few days in darkness to permit complete solution in the solvent. The maximum concentration that could be studied was limited to about 20 to 25 mg/cm^3 because of the difficulty in working with the highly viscous liquids which formed in more concentrated solutions.

To measure the partition coefficient, polystyrene solution of

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known concentration was added to clean porous cubes (0.5 cm^3 pore volume), previously saturated with chloroform, in a weighing vial and into an identical, empty reference vial. The latter was used to account for the possible effects of solvent loss by evaporation or polymer loss by adsorption on the vial. Both vials were sealed with stopcock grease (Nonaq, Fischer Scientific Co.) and placed in a temperature controlled (20 ± 0.3°C) shaker bath. After 72 hr, shown to be adequate to reach equilibrium (Turckheim, 1976), known volumes of bulk solution were removed, diluted, and their concentration measured by absorbance spectrophotometry at 262 nm using a Perkin-Elmer Model 111, UV-VIS spectrophotometer. The absorbance was a linear function of concentration in the range (0.0 to 1.0 mg/cm^3) that was used after dilution; it could be determined with a standard deviation of about 0.5%. The expected error for the partition coefficient, from propagation of error analysis, was about 0.04. Further details are given by Turckheim (1976).

In our previous study, no polystyrene adsorption was found in measurements with dilute solution exposed to HMDS treated Vycor powder. Vycor is a nonporous material made by leaching borosilicate glass followed by heat treatment to fuse and eliminate the pores; it should have about the same surface properties as the porous cubes used here. To test for possible adsorption at higher concentration, polystyrene ($M = 670\,000$) in five different concentrations ranging from 5 to 23 mg/cm^3 was contacted with HMDS treated Vycor in an amount providing a total surface area (11.3 m^2) approximately the same as in the partition experiments with the type B cubes for which $r_{p1} = 23.4$ nm. After 2 days, the sample with Vycor powder was centrifuged, filtered, and the bulk concentration measured and compared to that from a reference vial containing no Vycor powder. Two similar experiments were carried out in which polystyrene ($M = 200\,000$) was contacted with an identical amount of untreated and HMDS treated porous glass cubes (type B) which had been crushed in a ball mill.

RESULTS AND DISCUSSION

In the adsorption experiments, the ratio of the bulk concentration in the vials containing powdered glass to that in the reference vial averaged 1.05 ± 0.07, 0.98 ± 0.03, and 0.97 ± 0.02 for the experiments with powdered Vycor and with treated and untreated powdered porous glass cubes, respectively. No trend with polystyrene concentration was observed. By contrast, in partitioning experiments with type B porous glass cubes and 670 000 molecular weight polystyrene, the same concentration ratio dropped from 0.91 ($K_p = 0.20$) to 0.75 ($K_p = 0.66$) as concentration increased from about 5 to 23 mg/cm^3. In agreement with those of our previous study, these results demonstrate that polymer adsorption did not play a significant role in the partition coefficient measurements.

Values of the equilibrium partition coefficient K_p for all pore sizes and solute concentrations studied are plotted in Figure 1 as a function of equilibrium bulk concentration C_b. Each set of data corresponds to one type of porous cubes and one solute molecular weight and is characterized by values of $\lambda_1 = <s^2>^{1/2}/r_{p1}$ and $\lambda_2 = <s^2>^{1/2}/r_{p2}$. The filled symbols, from our previous study at low concentration, are shown for comparison and agree well with the results of this study.

For each set of data, K_p is an increasing function of C_b. For $\lambda_1 \lesssim 1.5$, K_p has a finite value at infinite dilution and increases roughly linearly with concentration. The straight portions of the curves in Figure 1 were obtained by linear regression analysis using the points of this study spanned by the straight lines. For $\lambda_1 \gtrsim 1.5$, linear regression with any reasonable selection of data points yields a slightly negative intercept, thereby suggesting that K_p is essentially zero at infinite dilution. At higher concentrations, the increase of K_p with concentration is markedly diminished, but it is not clear whether the data would become asymptotic to some value of K_p less than unity.

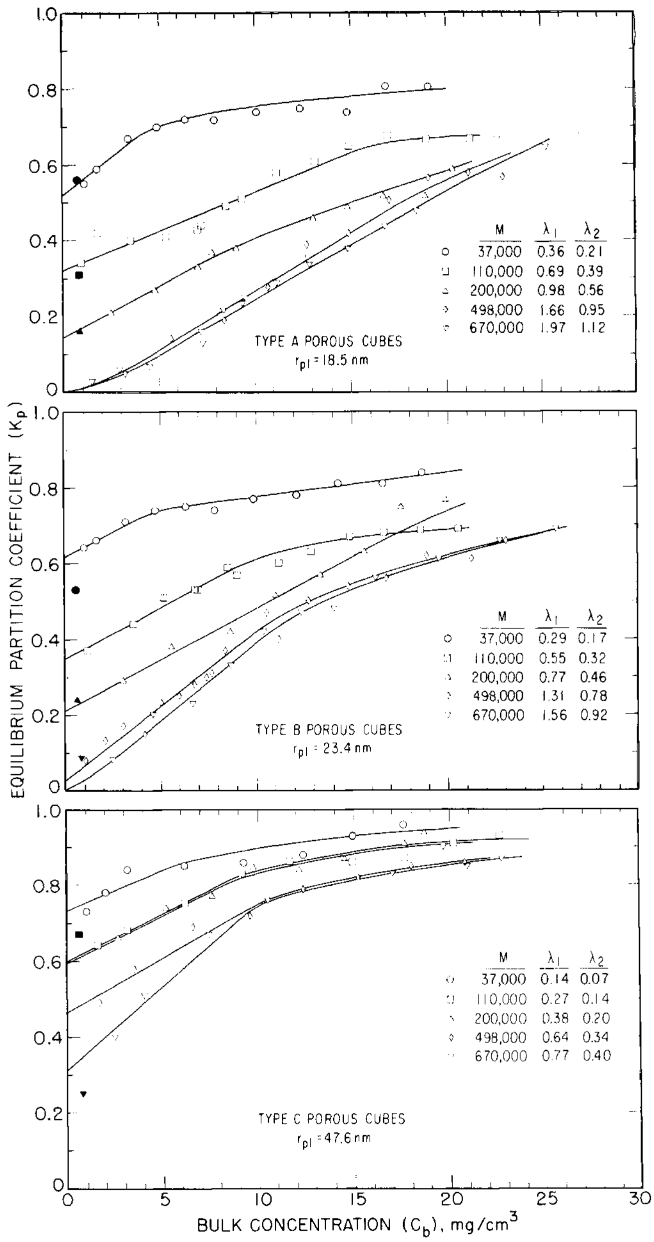

Fig. 1. Effect of polystyrene bulk concentration C_b on equilibrium partition coefficient K_p. Each graph contains data from one type of porous cubes.

The overall increase in K_p, particularly for large values of λ, is substantial. With minor exceptions, K_p decreases with increasing λ at fixed C_b. The variation of K_p with λ is much more pronounced at low concentrations than at high.

Values of the partition coefficient at infinite dilution, linearly extrapolated from the data as shown in Figure 1, are plotted vs. λ_1 and λ_2 in Figure 2 and compared with the dilute solution data of Yau and Malone (1971) and the theoretical prediction from Casassa (1967). Following the suggestions of Yau and Malone (1971) and Casassa (1976), the manner of comparing data and theory differs in two important respects from that used in our previous study. First, the pore radii from mercury intrusion porosimetry are those of averaged equivalent circular cross sections of pores. If pore size a is taken to be half the thickness of a slit shaped cavity, or the radius of a cylinder or sphere, the effective radii (designated here by r_p) should be identified as $2a$, a, and $2a/3$ for the idealized uniform slit, cylinder, and sphere. The effect of this change

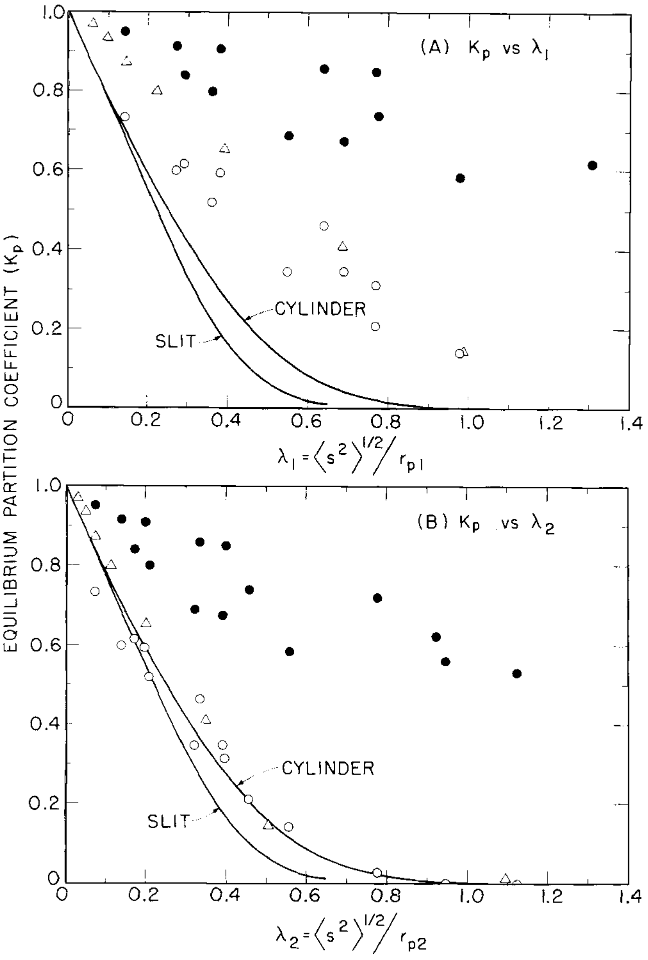

Fig. 2. Dependence of K_p on λ_1 and λ_2. Theoretical curves (solid) are plotted as recommended by Casassa (1976). ○ this study, infinite dilution; ● this study, $C_b = 20$ mg/cm^3; △ data of Yau and Malone (1971).

is to collapse the theoretical prediction of K_p for all shapes together onto that for the cylinder so that the value of $[\partial K_p/\partial\lambda]_{\lambda\to 0}$ is the same for all three pore shapes. Second, as a result of the ink bottle effect in porosimetry, large voids with constricted openings are counted as having the cross section of the entrance, and the measured pore size is too small. Therefore, the data in Figure 2 are plotted vs. both λ_1 (as in our previous study) and λ_2. In the latter quantity, pore volume (from mercury porosimetry) and surface area (from BET nitrogen adsorption measurement) have been used to provide an alternative and possibly more realistic pore radius estimate r_{p2}. When plotted vs. λ_1, all the data are higher than theoretical prediction. When plotted vs. λ_2, the data from this study and from Yau and Malone (1971) agree well with each other and with the theoretical prediction for a cylindrical pore.

Also plotted in Figure 2 are values of partition coefficients at a concentration of 20 mg/cm^3 taken from the curves in Figure 1. These data are uniformly much higher than those at infinite dilution and are much less sensitive to the value of λ. Rigorous quantitative theoretical prediction is not available for comparison with the data at high concentration. However, consideration of two phenomena known to occur suggests that the effects observed with increasing concentration are qualitatively reasonable (at least from a qualitative standpoint).

First, the radius of gyration decreases with increasing concentration (Flory, 1953). As a result of intramolecular interactions, the actual radius of gyration is related to that for a purely random flight configuration by $\langle s^2\rangle^{1/2} = \alpha\langle s_0^2\rangle^{1/2}$. For polystyrene at infinite dilution in benzene (which gives the same Mark-Hauwink exponent as in chloroform, 0.76) at 20°C, α is 1.23 and 1.54 for $M = 44\,500$ and 694 000, respectively (Tanford, 1961), whereas $\alpha = 1$ in a bulk polymer. Daoud et al. (1975) have found that the square of the radius of gyration of polystyrene in carbon disulfide, another good solvent, varies with bulk concentration according to $\langle s^2\rangle \sim C_b^m$, where $m = -0.25$. Other less negative values of m for polystyrene in different solvents have also been reported (Aharoni, 1977). Thus, the effective size of the polymer decreases with increasing concentration, the relative effect being greater in the lower concentration range than in the higher. However, the magnitude of this effect is not large enough to account quantitatively for the results in Figures 1 and 2.

The second phenomenon is the interpenetration of polymer chains, which also increases with concentration. Daoud and de Gennes (1977) have theoretically examined the effect of concentration on the partitioning of macromolecular chains confined in a slit or cylinder of comparable dimensions. Their scaling relationships indicate that at concentrations sufficiently high so that interpenetration is extensive, the concentration in the pore is only slightly smaller than that in the bulk, a result which is intuitively appealing. We take the maximum possible critical polymer concentration attainable without interpenetration to be that corresponding to close-packed spheres of radius $\langle s_0^2\rangle^{1/2}$, which we estimate to be about 16 mg/cm^3 for polystyrene ($M = 670\,000$) in chloroform. It is likely that interpenetration actually begins at substantially lower concentration. Therefore, it seems reasonable that overlap of polymer domains is the predominant factor that causes markedly increased values of K_p with the highest molecular weight solutes studied. The cause of the behavior of the lower molecular weight solutes is less clear, but relatively little interpenetration would be required to account for the more modest effects observed. In any event, these results suggest that partitioning experiments may provide a more sensitive measure of polymer interpenetration than is attainable with other measurements of solution properties.

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NOTATION

C_b = solute concentration in bulk solution, mg/cm^3
C_p = solute concentration in pores, mg/cm^3
K_p = C_p/C_b, equilibrium partition coefficient
M = solute molecular weight
r_{p1} = volumetric-mean pore radius from mercury porosimetry data, nm
r_{p2} = $2V_p/S_p$, equivalent cylindrical pore radius from pore volume and surface area measurements, nm
$\langle s^2\rangle^{1/2}$ = root mean square radius of gyration, nm
$\langle s_0^2\rangle^{1/2}$ = root mean square radius of gyration for unperturbed polymer chain following random flight statistics, nm
S_p = specific pore surface area from BET gas adsorption measurement, cm^2/g
V_p = specific pore volume from mercury porosimetry data, cm^3/g
α = Flory-Fox expansion factor
λ = $\langle s^2\rangle^{1/2}/r_p$, ratio of solute radius to pore radius. λ_1 is based upon r_{p1}, and λ_2 is based upon r_{p2}

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Interpolating Equations Between Two Limiting Cases For The Heat Transfer Coefficient

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Simple analytical solutions are available for the heat transfer coefficient for laminar forced or free convection along a vertical plate when Prandtl number is sufficiently large. When, however, both forced and free convection are superimposed, no simple solution can be obtained. Equations expressing the Nusselt number Nu_x in terms of the Nusselt number $Nu_{x,F}$ for forced convection and the Nusselt number $Nu_{x,N}$ for natural convection have been suggested for laminar, assisting, forced, and free convection. They have the form

$$Nu_x = Nu_{x,F}^n + Nu_{x,N}^n \tag{1}$$

The exponent n was chosen between 2 and 4. Churchill (1977) has reviewed recently this kind of expressions and shows that $n = 3$ gives the best representation of the data. Some new arguments are adduced in what follows supporting Churchill's choice. An approach is used (Ruckenstein, 1962) which can interpolate between two extreme cases when each extreme can be treated in terms of a boundary-layer approximation. This kind of interpolation was used before (Ruckenstein, 1962) to obtain the heat transfer coefficient during inpulsive heating of a liquid in steady laminar flow along a plate, as well as to obtain an equation for the mass transfer coefficient between a spherical drop and the continuous phase covering as limiting cases the Hadamard and Stokes flows (Ruckenstein, 1964).

For large Prandtl numbers, only the region very near the wall contributes appreciably to the rate of heat transfer. Since in this region the inertial (nonlinear) terms are small compared to the other terms, the velocity components u and v will be written as the sum of two components

$$u = u_1 + u_2 \quad \text{and} \quad v = v_1 + v_2 \tag{2}$$

where u_1 and v_1 are the velocity components for pure forced convection and u_2 and v_2 are those for free convection. Consequently, for large Prandtl numbers, the temperature field satisfies the equation

$$(u_1 + u_2)\frac{\partial T}{\partial x} + (v_1 + v_2)\frac{\partial T}{\partial y} = a\frac{\partial^2 T}{\partial y^2} \tag{3a}$$

while the velocities u_2 and v_2, due to the free convection, satisfy the equations

$$u_2\frac{\partial u_2}{\partial x} + v_2\frac{\partial u_2}{\partial y} = \nu\frac{\partial^2 u_2}{\partial y^2} + \beta g(T - T_\infty) \tag{3b}$$

and

$$\frac{\partial u_2}{\partial x} + \frac{\partial v_2}{\partial y} = 0 \tag{3c}$$

Since the velocities u_1 and v_1 are known, the decomposition (2) has partially decoupled free and forced convection. Equations (3) are still difficult to solve, and therefore a complete decoupling is carried out by computing u_2 and v_2 with the temperature profile for pure free convection [hence solving Equations (3*b*) and (3*c*) together with $u_2(\partial T/\partial x) + v_2(\partial T/\partial y) = a(\partial^2 T/\partial y^2)$ instead of with Equation (3*a*)]. It is difficult to specify exactly how good is this approximation. An upper bound of the error can be obtained as follows. First one may notice that the equations represent well the two limiting cases $Re_x \to 0$ and $Ra_x \to 0$. The difficult region is that in which both effects are equally important. This happens when u_1 and u_2 are of the same order. Using a velocity half as large as

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