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Macromolecular porosimetry

Lev Z. Vilenchik, Jawed Asrar, Roger C. Ayotte, Leo Ternorutsky and Christopher J. Hardiman*

Monsanto Chemical Co., Mail Zone Q1A, 800 N. Lindbergh Boulevard, St. Louis, MO 63167 (USA)

ABSTRACT

A new method for the determination of pore size distribution in porous materials has been developed. The method is based on measuring the probability of solubilized macromolecules to penetrate the pore space of a solid substrate. In the absence of any interaction between the macromolecules and the matrix of the porous material, the value of the probability is determined only by ratio of sizes of the macromolecules and the pores. A special software package was developed for slit, cylindrical, and mixed pores.

INTRODUCTION

Porous structure is one of the most important characteristics of numerous materials. Several analytical methods are available to investigate pore size characteristics including mercury porosimetry [1], adsorption of the vapour of inert solvents [2], and small-angle X-ray scattering [3].

The first two methods can be used only for porous materials in the desolvated state. Small-angle X-ray scattering is used to study the structure of polymer materials in the swollen state. This method is complex regarding both the performance of the experiment and the interpretation of results and is therefore seldom used in investigations of porous materials. The porosimetric patterns obtained by these methods usually differ.

The method of macromolecular porosimetry can serve as a universal method for determination of pore structure. It is particularly efficacious for the porosimetry of sorbents used in the chromatography of polymers, since the pore size distribution determined by the aid of this method corresponds to the chromatographic distribution of the macromolecules.

The first attempts to determine pore sizes of porous materials by means of the macromolecular porosimetry were made in the early 1970s [4–6]. A number of different approaches to verify this method have been proposed [7–21]. The most advanced from them has been developed in ref. 20, where the authors could reduce the problem of solving of the integral equation to a simple algebraic equation. However, their approach is valid only for hard spherical macromolecules. In this paper we report further development of the porosimetry method using a special approach for the modeling of flexible chain macromolecules. We have also developed a special software package and two different experimental methods for the determination of pore size distribution in porous materials.

THEORY

Solubilized macromolecules are used as specific probes in the method of macromolecular porosimetry. Unlike solutions of low-molecular-mass substances, a polymer solution is a kind of "double" statistical ensemble. On the one hand,

* Corresponding author.

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it is an ensemble consisting of macromolecules as structural elements. On the other hand, each macromolecule can be considered as a statistical ensemble of elementary segments. Each of these ensembles obeys the laws of thermodynamics and statistical physics with all the ensuing consequences. For example, the concepts of thermodynamic potentials, free energy, entropy, etc. can be used to characterize both the state of the whole polymer solution and that of the individual macromolecules [22]. The interdependence between the changes in the state of the macromolecules and the solution as a whole leads to relationships that have not been observed in the behavior of the solutions of low-molecular-mass substances in the porous medium.

In the absence of any adsorption interaction between macromolecules and the matrix of the porous medium, reliable expressions for the distribution coefficient (K_d) value for macromolecules with different shapes are known [23]. The K_d expressions for spherical macromolecules (proteins, ficols) have recently been validated experimentally [24]. It is possible to write these expressions using only one equation with different meanings for the pore shape parameter [23]:

$$K_d = (1 - R/r)^q \quad (1)$$

where $q = 1$, 2 or 3 for spherical, cylindrical and split pores respectively.

For the slit case we should take into account the existence of wedge-shaped pores; the model used to account for the varying angle of pore walls must be an average of all angles present in the specific porous material being investigated (see Fig. 1). For example, if for the wedge-shaped pores the variation of the angle ranges from 60 to 90° then we replaced eqn. 1 with

$$K_d = 1 - (R/r)(6/\pi)\int_{\pi/3}^{\pi/2} (1/\sin x)\,dx$$

$$= 1 - R/(r_{av}/1.05) \quad (2)$$

where r_{av} corresponds to the average pore radius for the usual slit model, and r is the average effective pore radius taking into account the slope between pore walls

$$r = r_{av}/1.05 \quad (3)$$

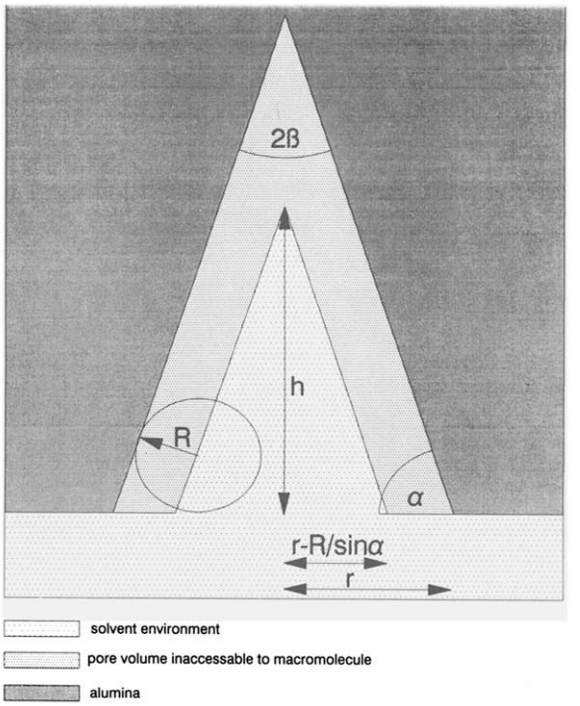

Fig. 1. Model of wedge-shaped macropore in Unisphere alumina.

Flexible-chain macromolecules do not have a definite form and size. Their conformations are changing continuously, and we can observe only some average states. For such kind of macromolecules the coefficient of distribution between free solution and a porous medium is determined by changing the number of macromolecular conformation when a macromolecule may enter into a pore of the medium [25]. However, it was possible to obtain the expression for K_d of these macromolecules only without taking into account an interaction of macromolecular segments with the solvent. Perhaps, it is a reason why theoretical and experimental data are in poor agreement [25].

Meanwhile, it was shown [26] that distribution of flexible-chain macromolecules between free solution and porous medium is determined by ratio of their hydrodynamic radius $\langle R_h \rangle$ and pore radius r. The $\langle R_h \rangle$ value is an average characteristic of the macromolecule. It is equal to the radius of an equivalent hydrodynamic sphere which behaves itself like the macromole-

cule during the interphase transition. In principle, we can assign to each macromolecular conformation an equivalent sphere [8]. Then, for all conformations we will have an ensemble of such equivalent spheres with radii R_h. Averaging according to this ensemble gives us $\langle R_h \rangle$ value for the macromolecule. We can suggest, that the distribution R_h values in this ensemble obeys Gauss' law

$$G(R_h) = 4\pi(2\pi\langle R_h^2\rangle)^{-3/2} R_h^2 \exp(-3R_h^2/2\langle R_h^2\rangle) \quad (4)$$

where $\langle R_h^2 \rangle$ is the mean square sphere radius of the ensemble of the equivalent spheres.

Now, we can use eqn. 1 to calculate K_d value for each sphere from the ensemble $G(R_h)$ in eqn. 4. Averaging according to all spheres of the ensemble has to give the observing value for the coefficient of distribution. Taking into account that any porous material has a distribution of pore sizes $P(r)$, we must average the K_d expression according to the pore size distribution. As a result, we obtain

$$K_d(\langle R_h \rangle) = \int_0^\infty P(r) \int (1 - R_h/r)^q G(R_h)\, dR_h\, dr \quad (5)$$

Eqn. 5 shows that we can calculate the K_d value for a macromolecule with an average size of hydrodynamic radius $\langle R_h \rangle$ if the pore size distribution $P(r)$ and the shape of the pores are known.

It is possible also to solve a reverse problem: to calculate the pore size distribution $P(r)$ from eqn. 5 using known value for distribution coefficient $K_d(\langle R_h \rangle)$. We can use for this goal different kinds of macromolecules: proteins, ficols, or flexible-chain coils with known R_h values. However, in each particular case we should apply the function $G(R_h)$ in a different expression. For flexible-chain macromolecules this is the function G from eqn. 4; for proteins this is a delta function, for ficols this is a special distribution. This is the basis for the new porosimetric method: macromolecular porosimetry, in which solubilized macromolecules are used as specific probes to determine pore size distribution in any porous medium.

EXPERIMENTAL

To measure the distribution coefficient K_d of macromolecules between a free solution and a porous medium being investigated we can use two different types of experiment: batch (static) mode and chromatographic (dynamic) mode.

Static experiment

A known amount of the porous medium being investigated is placed into test tube and is flooded by a macromolecular solution with known concentration. The solution penetrates into the pore space of the medium and distributes between two phases of the system (free volume and pores) owing to a tendency towards thermodynamic equilibrium. As a result, the concentration of macromolecules in free volume became to be less than in primary solution. This decreasing of the concentration is a function of the ratio pore and macromolecules sizes, pore size distribution, and shapes of the pores.

If we use C_0 as the concentration of our primary solution, then C_1 and C_2 are the concentrations in the free volume and porous space of the medium after setting of the thermodynamic equilibrium. We will call C_1 the concentration of a secondary solution. Now we can write

$$V_0C_0 = V_1C_1 + V_2C_2 \quad (6)$$

where V_0 is a primary volume of the solution, V_1 is a volume of the free solution, and V_2 is pore volume.

It is true that

$$V_0 = V_1 + V_2 \quad (7)$$

Now, using the standard definition for the K_d value, we can rewrite eqn. 6 as

$$K_d = C_2/C_1 = X(V_0/V_2) - V_1/V_2 \quad (8)$$

where

$$X = C_0/C_1 \quad (9)$$

To determine ratios V_0/V_2 and V_1/V_2 we can use the following phenomenon: the distribution coefficient for the largest macromolecules is equal to zero if pores of the medium being investigated are not available for the macromolecules because of their sizes.

$$K_d = 0 = X_0(V_0/V_2) - V_1/V_2 \quad (10)$$

where X_0 is the ratio (eqn. 9) for the macromolecules with $K_d = 0$. We have from eqn. 10

$$V_1/V_0 = X_0 \quad (11)$$

Combining eqns. 7 and 11 we can obtain

$$V_2/V_0 = 1 - X_0 \quad (12)$$

Now we can rewrite eqn. 8

$$K_d = (X - X_0)/(1 - X_0) \quad (13)$$

To determine the values X_0 and X we should measure the concentrations C_1 of the biggest macromolecules (with $K_d = 0$) and different other macromolecules into the free volume of our test tube. Knowledge of the primary concentrations C_0 led us to calculate the X_0 and X values according to eqn. 9. The easiest way to measure C_0/C_1 values is the injection of the primary and secondary solutions into a chromatographic column and carrying out a size-exclusion chromatographic (SEC) experiment. Since the area under the SEC chromatogram is proportional to the concentration, the ratio of these areas for primary and secondary solutions gives X and X_0 values.

Dynamic experiment

In this experimental mode a chromatographic column is packed with porous material to be investigated. Then solutions of different macromolecules have to run through this column in the SEC mode. Known standard procedure allow us to determine very easily the distribution coefficients for these macromolecules:

$$K_d = (t - t_0)/(t_1 - t_0) \quad (14)$$

where t is the retention time for macromolecules with given size, t_0 is the retention time for largest macromolecules with $K_d = 0$, and t_1 is retention time for low molecular weight substances with $K_d = 1$.

RESULTS

Silica gel G, Nucleosil 100, and the blend of 60% silica gel G and 40% Nucleosil 100 were investigated by means of the static experiment.

TABLE I

EXPERIMENTAL K_d VALUES FOR SILICA GEL G, NUCLEOSIL 100, AND BLEND FOR DIFFERENT MOLECULAR MASS POLYSTYRENES

M	K_d		
	Silica gel G	Nucleosil 100	Blend
580	0.677	0.767	0.715
2 450	0.497	0.647	0.560
9 200	0.150	0.332	0.115
22 000	0.074	0.169	0.225
66 000	0.009	0.030	0.018
170 000	0.003	0.009	0.004
333 000	0.001	0.002	0.001
3 040 000	0.000	0.000	0.000

Polystyrene standards were used as macromolecular probes. Tetrahydrofuran was chosen as the solvent. Table I shows the distribution coefficients for polystyrene standards with different molecular masses.

The software which was developed in this work, allowed us to calculate on the basis of eqn. 5 a pore size distribution $P(r)$ for each of these porous materials. The distributions for silica gel G and Nucleosil 100 were sought as triangles (*i.e.* the coordinates of their tops). We attempted to achieve the best coincides between experimental values of the distribution coefficients of macromolecules with different molecular weights and K_d value calculated via eqn. 5 using the cylindrical pore model (the value of q equals 1).

Finally, for silica gel G we have obtained P(r) function with the following parameters: the left top on the base line of the triangle has coordinate $r = 15$ Å; right top: $r = 35$ Å; and top at maximum: 30 Å. The corresponding coordinates for Nucleosil 100 are 35, 55 and 50 Å, respectively. For the pore size distribution of these a blend of these porous materials we have obtained a superposition of these two triangles (Fig. 2).

A dynamic mode for pore size determinating was used for new sorbent for SEC: Unisphere alumina (Al_2O_3) (Biotage, Charlottesville, VA, USA) [27–29]. This is a new modification of the old known alumina particles. Unisphere alumina particles look like crystals extending radially

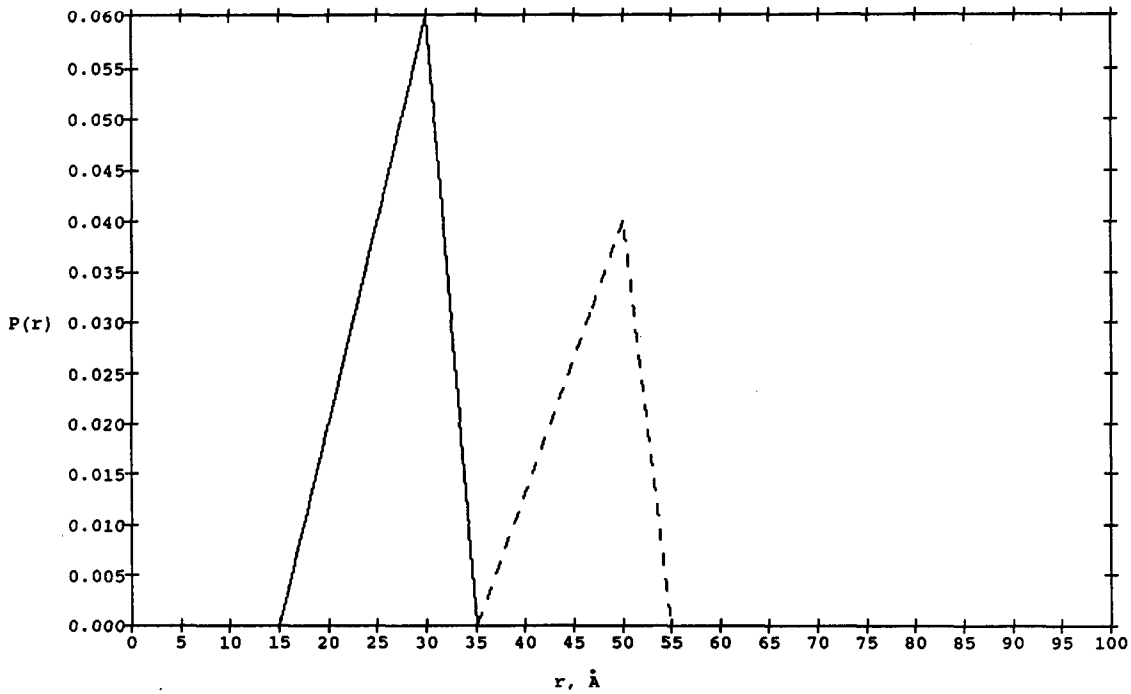

Fig. 2. Pore size distribution for silica gel G (——) and Nucleosil 100 (- - -).

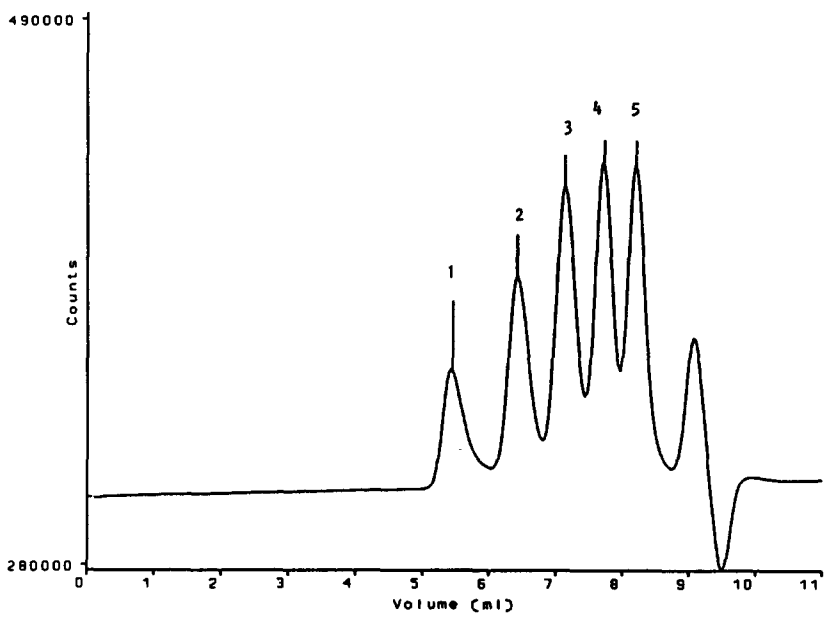

Fig. 3. Typical SEC chromatogram for polystyrene mixture on column packed with Unisphere alumina. Polystyrene standard mixture M_r $8.5 \cdot 10^6$ (peak 1), $1.03 \cdot 10^6$ (2), $1.56 \cdot 10^5$ (3), $2.85 \cdot 10^4$ (4) and $3.25 \cdot 10^3$ (5).

outward from a central core *i.e.* giving wedge-shaped macropores. Each individual plate also contains micropores whose shape is largely cylindrical. Thus the Unisphere alumina particles have a bimodal pore size distribution (PSD). It is known that sorbents with this type of PSD may give good separation of macromolecules ranging from oligomers to high polymers [30].

To check the sensitivity of the macromolecular porosimetry method to small changes of PSD, three different modifications of the Unisphere alumina have been investigated. Two are coated with different amounts of polysiloxane and one is not coated. The chromatographic columns have been packed with these different alumina particles. Each column has been installed in a liquid chromatograph employing tetrahydrofuran as mobile phase. Different mixtures, containing different polystyrene standards, were evaluated using these columns. Thus a total of seventeen polystyrene standards from a molecular mass of 580 to $8.5 \cdot 10^6$ plus toluene, were used. Fig. 3 shows a typical chromatogram from one of these experiments with a polystyrene mixture containing five standards. Molecular mass (M) calibration curves were determined for the alumina columns, and appear in Fig. 4. The retention volume V_0 of the polystyrene standard with M = 8 500 000 was taken to be the exclusion volume of the column, and the retention volume V_t of toluene was also taken to be the total volume of the column. The K_d for the standards was determined according to the eqn. 14, where retention times t_0 and t_1 correspond to the values V_0 and V_t. Table II shows the experimental and theoretical values (according to eqns. 14 and 5, respectively) for the coefficient of distribution K_d for all the polystyrene standards used in the experiment for each of the three chromatographic columns (coated and uncoated). A plot of K_d *versus* log polystyrene molecular mass for all three columns appears in Fig. 5. There is significant differentiation in the low-molecular-mass range only. For polymer molecular mass greater than 10^6 the coefficients of distribution are all similar. The addition of polysiloxane coating

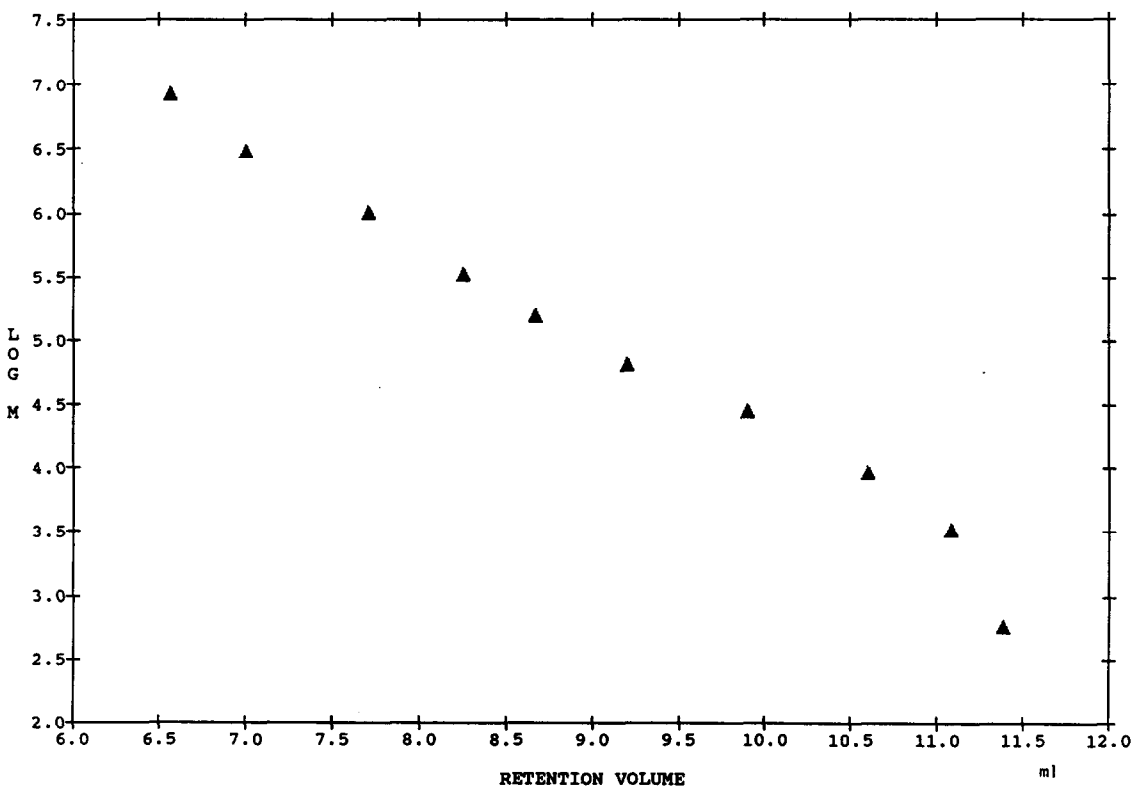

Fig. 4. Calibration of column packed with Unisphere alumina.

TABLE II

EXPERIMENTAL AND CALCULATED K_d VALUES FOR THREE DIFFERENT MODIFICATIONS OF UNISPHERE ALUMINA FOR POLYSTYRENES OF DIFFERENT MOLECULAR MASS

exp = Experimental; calc = calculated; Al = alumina; +15% and +20% = +15% siloxane and +20% siloxane, respectively.

Log M	$\langle R_h \rangle$	K_d(exp), Al	K_d(calc), Al	K_d(exp), Al + 15%	K_d(calc), Al + 15%	K_d(exp), Al + 20%	K_d(calc), Al + 20%
2.76	6.2	0.95	0.95	0.89	0.89	0.87	0.85
3.23	10.3	0.92	0.91	0.80	0.83	0.76	0.77
3.39	12.3	0.91	0.89	0.78	0.80	0.73	0.73
3.51	14.1	0.90	0.88	0.76	0.78	0.70	0.71
3.96	23.1	0.80	0.81	0.70	0.69	0.60	0.60
4.06	26.3	0.77	0.78	0.68	0.67	0.57	0.58
4.34	37.9	0.69	0.70	0.62	0.61	0.52	0.52
4.46	44	0.66	0.67	0.60	0.59	0.50	0.50
4.56	49	0.62	0.64	0.59	0.58	0.48	0.49
4.82	71	0.53	0.55	0.53	0.53	0.44	0.44
5.19	116	0.45	0.44	0.45	0.46	0.38	0.38
5.23	122	0.44	0.43	0.44	0.45	0.37	0.37
5.52	178	0.37	0.36	0.37	0.38	0.32	0.31
5.57	189	0.36	0.35	0.36	0.37	0.30	0.30
6.01	341	0.23	0.23	0.23	0.23	0.20	0.19
6.47	621	0.1	0.11	0.10	0.10	0.09	0.08
6.93	1137	0.02	0.03	0.02	0.03	0.02	0.02

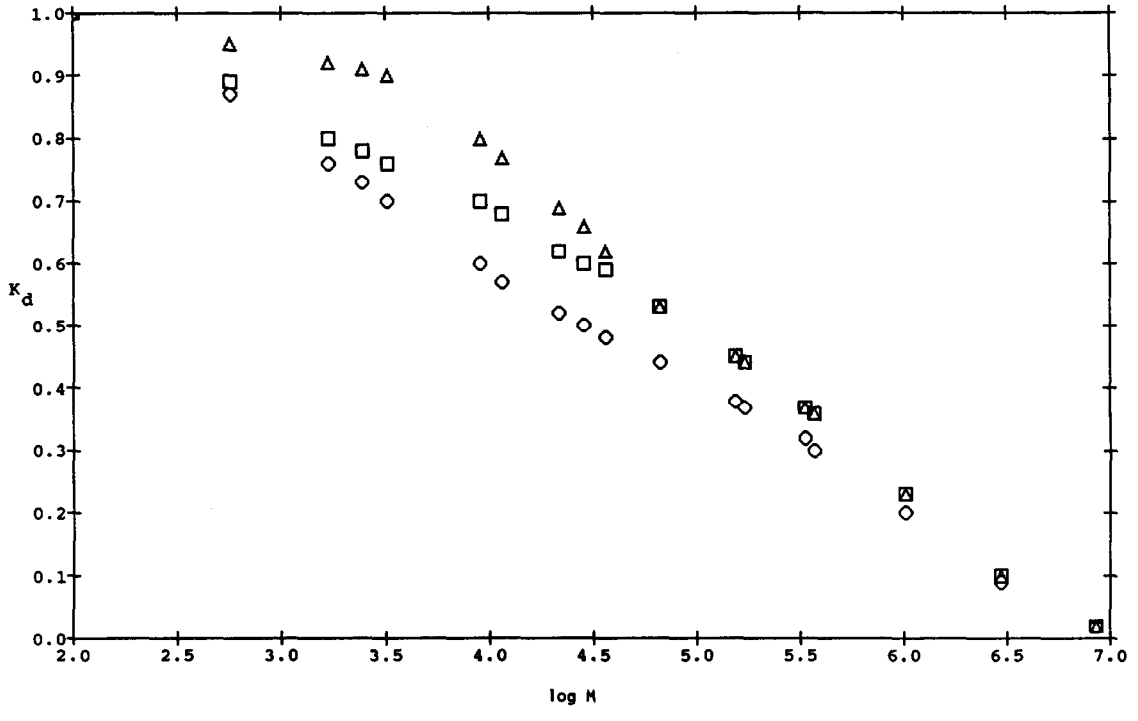

Fig. 5. Distribution coefficient of polystyrene *versus* log M for three different modifications of Unisphere alumina. △ = Unisphere; □ = Unisphere + 15% siloxane; ◇ = Unisphere + 20% siloxane.

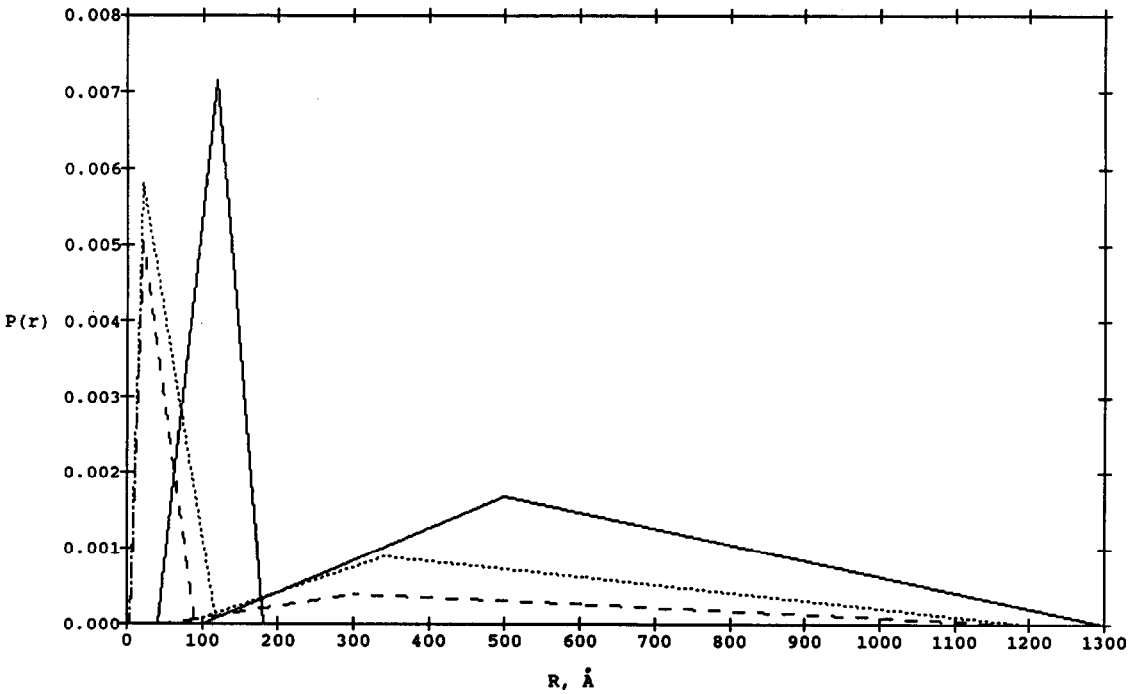

Fig. 6. Pore size distribution for three different modifications of Unisphere alumina. —— = Unisphere; - - - = Unisphere + 15% siloxane; – – – = Unisphere + 20% siloxane.

does not significantly affect distribution coefficient for macromolecules of $M \geq 10^6$.

The theoretical values for the coefficients of distribution were obtained by means of the same computer program which was used to calculate PSD for the blend of silica gel G and Nucleosil 100. All the data are shown in Table II. The functions of the distribution of the pore sizes were chosen to give the best coincidence of the theoretical and experimental K_d for all seventeen polystyrene standards. It was found that these functions are bimodal distributions. For the mode of distribution with small pore size we used cylindrical model and for the large pore size mode we used a wedge-shaped model with angle averaging as described in eqn. 2. The key parameters that define these functions are the upper and lower limits of each mode of distribution, their maxima, and the relative fraction of the two modes. We have obtained the distribution functions for the three materials as shown in Fig. 6. As this figure shows, each mode of the distribution represents approximately equal fractions of the total pore volume. After coating with polysiloxane, due to the resulting change in the net pore size distribution, the K_d coefficients for low-molecular-mass polystyrenes significantly decrease while for high molecular mass only a minor decrease is observed. Presumably the loss of pore volume in the small pore size mode is due to pore filling by the coating.

Comparison of these results with data obtained via BET shows a good coincidence for small pore size (Fig. 7). Unfortunately the BET method is unable to determine the distribution of pore sizes over the total range of large PSD.

CONCLUSIONS

It is possible to use macromolecules as probes, in either a static or dynamic mode, to determine pore size distribution of porous solids. The distribution of these macromolecular probes between the pore space and the interparticle space is a function of molecular size relative to the pore size, shape, and distribution thereof. The approaches developed in this and earlier work [4–21] are the basis of a new porosimetric method.

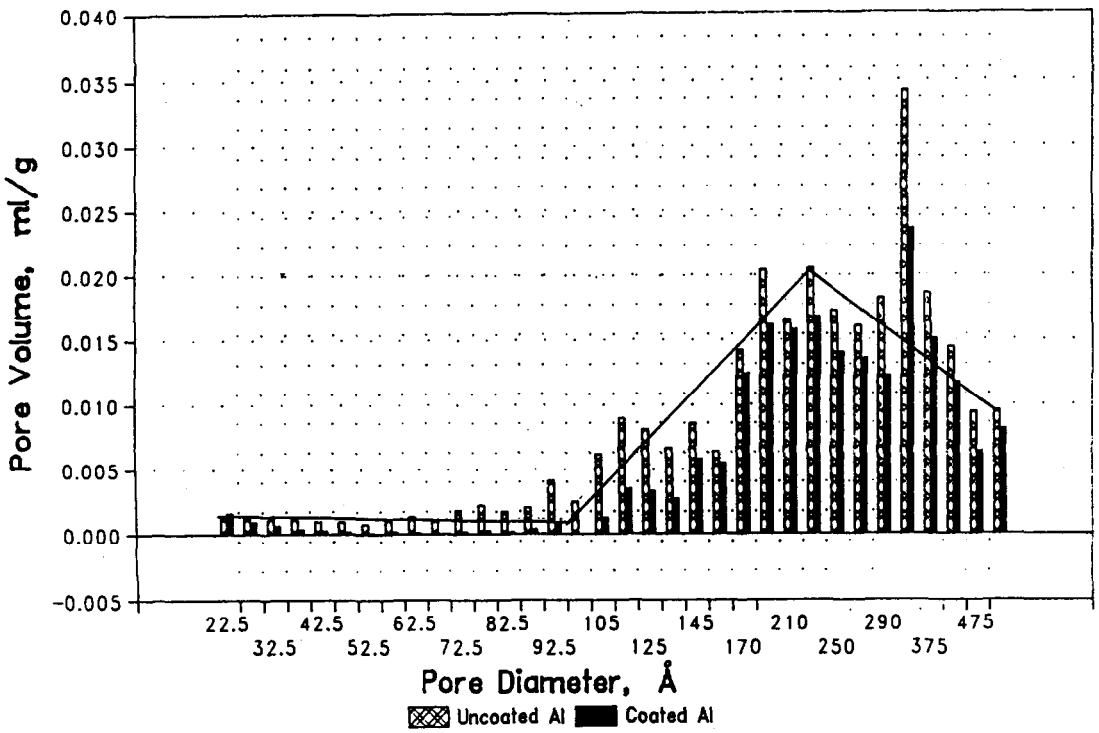

Fig. 7. Pore volume distribution for Unisphere alumina from desorption isotherm data.

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