

Effect of pore size on the surface excess isotherm of silica packings

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ABSTRACT

Silicas with pore diameters ranging from 100 to 300 Å were used as packing materials in order to evaluate the surface excess isotherms of organic modifiers in binary aqueous systems. The method is based on the measurement of the retention volumes of labelled components of the eluent. The isotherms obtained were compared with each other in order to investigate the effect of pore size on the surface excess isotherm.

INTRODUCTION

The study of chemically modified surfaces for use in liquid chromatography is a matter of great interest. A variety of techniques for probing chemically modified surfaces have been employed, including fluorescence¹, infrared²⁻⁵, and nuclear magnetic⁵⁻¹⁰ spectrometry. Information obtained by these techniques has provided important insights into surface-ligand structures and interactions, bonded layer solvation and segmental and total chain mobility.

It is well known that the organic solvent is enriched in the bonded phase in reversed-phase liquid chromatography. The amount of enriched modifier can be determined as the surface excess amount. The surface excess amount of a given component is defined as the difference between the amount of component actually present in the system and that which would be present in a reference system if the bulk concentrations in the adjoining phases were maintained up to a chosen geometrical dividing surface¹¹. Therefore, the surface excess amount can be used as a measure of the comparison of the chemically modified surface. The surface excess isotherm is accessible to direct experimental determination. General relationships for calculating the surface excess amount from chromatographic retention data were given by Riedo and Kováts¹². Chromatographic methods to determine the surface excess isotherms were based on measurements of the retention volumes of concentration steps (frontal analysis)¹³⁻¹⁵ and labelled components of the eluent¹⁶ and solvent disturbance peaks¹⁷⁻¹⁹.

In order to make it possible to use the surface excess isotherm as a measure of the comparison of chemically modified surfaces with various pore sizes, it is necessary to

investigate the influence of pore size on the surface excess isotherm. In this work, we explored whether the pore sizes of column packings influence their surface excess isotherms or not. The silicas were used as packing materials in order to investigate the net effect of the pore size on the exclusion of the chemically bonded phase. The surface excess isotherms of organic modifiers on these packings were evaluated in binary aqueous systems. The method was based on measurements of the retention volumes of labelled components of the eluent.

EXPERIMENTAL

Apparatus

The liquid chromatograph was constructed from a Model 880-UP pump (Jasco, Tokyo, Japan), a Rheodyne Model 7125 injector and a Shodex RI SE-51 differential refractive index detector (Showa Denko, Tokyo, Japan). A constant-temperature water-bath (Model TM108M; Toyo, Tokyo, Japan) was used to maintain the column temperature, which was measured with an alumel-chromel thermocouple. The chromatograms were recorded on a Chromatopac CR1A (Shimadzu, Kyoto, Japan).

Chemicals and materials

Liquid chromatographic grade solvents and deuterated compounds were obtained from Nacalai Tesque (Kyoto, Japan). Silicas with pore diameters ranging from 100 to 300 Å were used as packing materials. The silicas used were Vydac 101TPB (300 Å) (Separation Group, Hesperia, CA, U.S.A.) and Shiseido's silicagel (120 and 300 Å) and Super Micro Bead silica gel (100, 150 and 300 Å) (Fuji-Davison Chemical, Kasugai, Japan). They were packed by means of the balanced slurry technique into 250 × 4.6 mm I.D. stainless-steel tubes in our laboratory. Data on the column packings are summarized in Table I.

TABLE I
PHYSICAL PROPERTIES OF SILICA MATERIALS

<i>Silica</i>	<i>Particle diameter (μm)</i>	<i>Pore diameter (Å)</i>	<i>Area (m²/g)</i>	<i>Pore volume (ml/g)</i>	<i>pH</i>
<i>Super Micro Bead^a</i>					
100 Å	5.9	108	385	1.04	5.1
150 Å	5.7	167	181	1.08	5.7
300 Å	5.1	321	95	1.07	5.6
<i>Shiseido's silica gel^b</i>					
120 Å	5	124	264	0.80	
300 Å	5	274	168	1.39	
<i>Vydac 101TPB^b</i>					
	5	303	75	0.59	

^a Data provided by manufacturer.

^b Data determined by Y. Shiojima of Shiseido.

Procedures

The retention volumes of labelled components of the eluent were obtained from the flow-rate and retention time, t_R . The nominal flow-rate used throughout the study was 1 ml/min. The actual flow-rate was measured by collecting the column eluent in a 10-ml volumetric flask and recording the collection time. The sample concentration was chosen to be as low as possible while maintaining a suitable signal-to-noise ratio in refractive index detection. Eluents of appropriate compositions were prepared by weighing. The column materials were removed from each column after chromatographic measurements and washed with methanol, dried under reduced pressure and weighed.

Surface excess amounts

Quantitative definitions for the adsorption of binary liquid mixtures at solid-liquid interfaces in terms of surface excess amounts were given by Everett¹¹. Riedo and Kováts¹² derived general relationships for calculating their surface excess amounts from chromatographic retention data.

The necessary expressions for calculating points on the adsorption isotherms are taken from ref. 12. The surface concentration of component 2 is given by

$$\Gamma_2^{(n)} = (V_{R,2^*} - V_{R,1^*})x_2^l x_1^l / S v_m \quad (1)$$

where $\Gamma_2^{(n)}$ is the areal reduced surface excess of component 2 and x_1^l and x_2^l are the mole fraction of components 1 and 2 in the eluent. V_R is the retention volume, S is the surface area of silica and v_m is the mean molar volume of the eluent at

$$v_m = v_1 x_1^l + v_2 x_2^l \quad (2)$$

the composition x_1^l , and v_1 and v_2 are the partial molar volumes of components 1 and 2. The asterisk refers to labelled components of the element, 1* or 2*. The areal reduced surface excess of component 1 is

$$\Gamma_1^{(n)} = - \Gamma_2^{(n)} \quad (3)$$

Layer model

When dealing with an actual system, it is not sufficient to obtain the surface excess isotherm. because it only represents the total change of the system and does not refer to the actual amount of a component present in the mobile phase and adsorbed phase. Therefore, the layer model¹¹ was used to calculate the composition of the adsorbed phase and determine the absolute amount adsorbed.

Assuming that the adsorbed phase consists of t layers of molecules on a plane smooth homogeneous surface, the mole fraction, x_2^s , of component 2 in the surface phase is given by

$$x_2^s = \frac{t x_2^l + a_1^0 \Gamma_2^{(n)}}{t - (a_2^0 - a_1^0) \Gamma_2^{(n)}} \quad (4)$$

TABLE II
VALUES OF t_{\min} SATISFYING THE CRITERIA

Silica	t_{\min}	
	CH_3CN-H_2O	CH_3OH-H_2O
<i>Super Micro Bead:</i>		
100 Å	3	1
150 Å	3	1
300 Å	3	1
<i>Shiseido's silica gel:</i>		
120 Å	3	1
300 Å	3	1
<i>Vydac 101TPB</i>		
	5	2

where a_1^0 and a_2^0 are the molar cross-sectional areas of components 1 and 2, which can be calculated from the molar volumes, v_1 and v_2 , using the equation $a_i^0 = 9200(v_i)^{2/3}$, ($i=1,2$). Using these a_i^0 values and the experimental surface excess data, $\Gamma_2^{(n)}$, the minimum number of layers, t_{\min} , was calculated by satisfying the criteria that the values of x_2^s calculated do not exceed unity, and x_2^s always increased with x_2^l , i.e., $(\partial x_2^s / \partial x_2^l) > 0$. The values of t_{\min} are given in Table II. x_2^s was calculated using eqn.

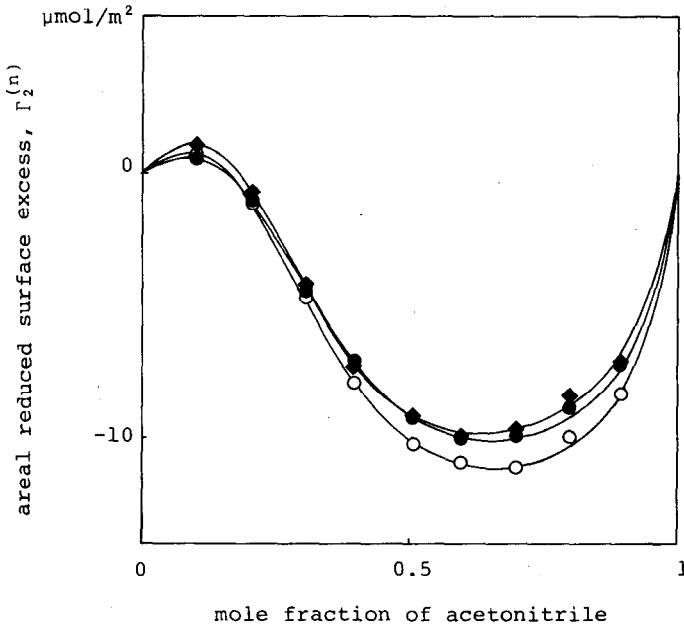


Fig. 1. Surface excess amount of acetonitrile adsorbed at 30°C from an aqueous mixture on Super Micro Bead silica gel plotted against the mole fraction of acetonitrile. Pore size: ● = 100 Å; ○ = 150 Å; ◆ = 300 Å.

4 with values of t_{\min} . In this study, components 1 and 2 correspond to water and organic modifier, respectively.

RESULTS AND DISCUSSION

The method of calculation of adsorption isotherms is based on the existence of solutes which are in every respect identical with components of the eluent with the exception of one property permitting their detection. These solutes were approximated by deuterated compounds, which we used as the solutes in this study although it is certainly not true that they are in every respect identical with non-deuterated compounds.

Acetonitrile–water and methanol–water systems were studied on six column packings at 30°C. In Figs. 1–4, the areal reduced surface excess amounts are plotted against the mole fraction, x_2^l . The negative values of the surface excess amount mean that the adsorbed phase on the silica surface holds a much larger amount of water than the mobile phase. It can be seen from Figs. 1–4 that the value of the surface excess amount is similar among the column packings from the same manufacturer. These results do not reveal a distinct effect of pore size on the surface excess isotherm. It seems reasonable to assume that the difference in pore size has no influence on the surface excess isotherm. It is necessary to take into account the pore distribution and structure. However, the effect of pore distribution might be negligible because the pore size of the silica materials used in this study extends from 100 to 300 Å. With regard to pore structure, it is not apparent whether it influences the surface excess isotherm or not, because there is no information relating to the pore structure. Figs. 5 and 6 show the surface excess isotherms of silicas with pore size 300 Å from different manufacturers. The results suggests that the surface excess isotherm is influenced by the

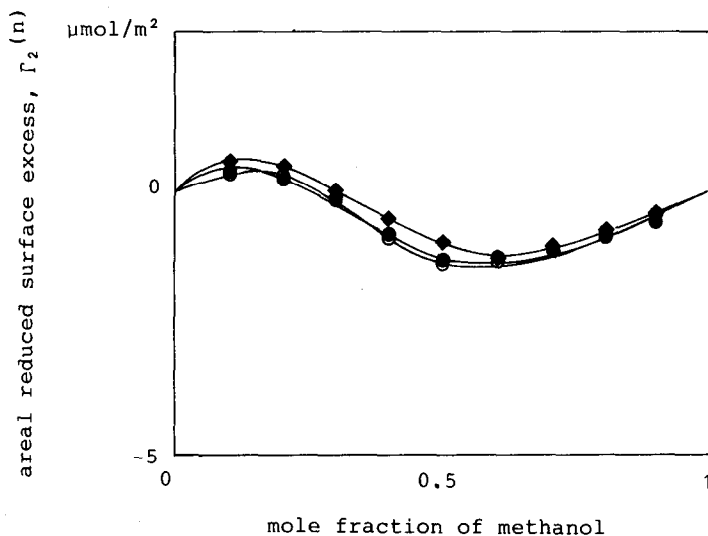


Fig. 2. Surface excess amount of methanol adsorbed at 30°C from an aqueous mixture on Super Micro Bead silica gel plotted against the mole fraction of methanol. Symbols as in Fig. 1.

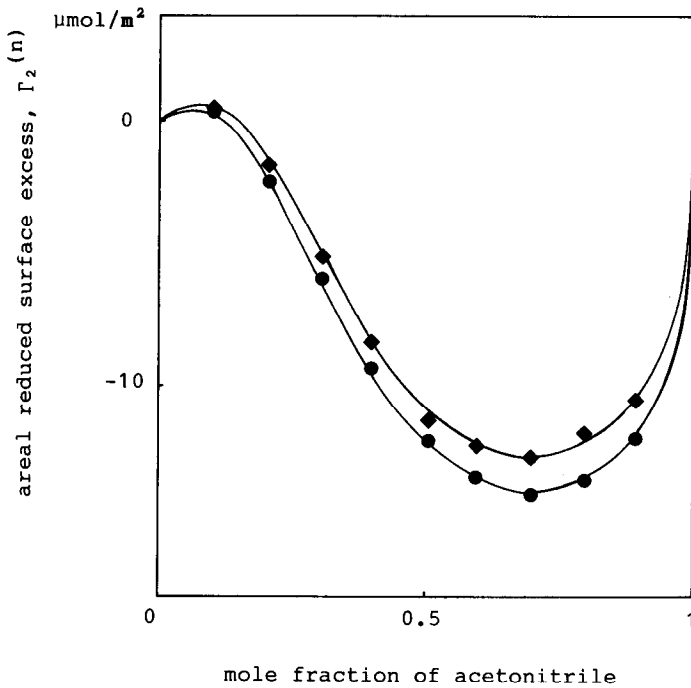


Fig. 3. Surface excess amount of acetonitrile adsorbed at 30°C from an aqueous mixture on Shiseido's silica gel plotted against the mole fraction of acetonitrile. Pore size: ● = 120 Å; ◆ = 300 Å.

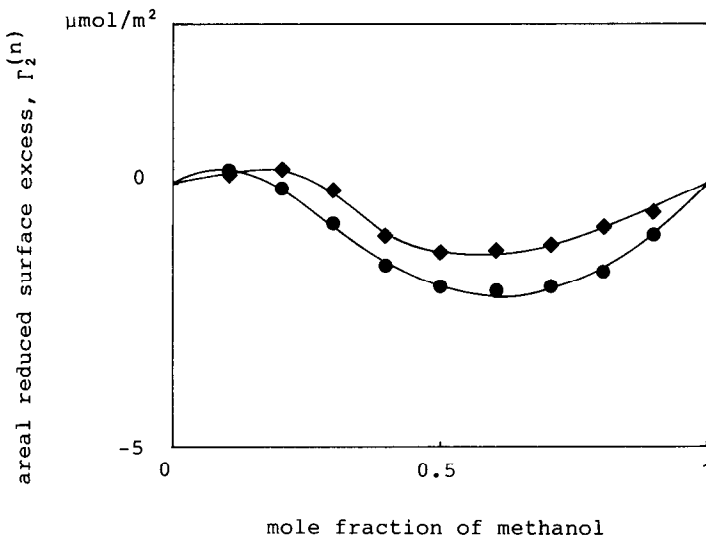


Fig. 4. Surface excess amount of methanol adsorbed at 30°C from an aqueous mixture on Shiseido's silica gel plotted against the mole fraction of methanol. Symbols as in Fig. 3.

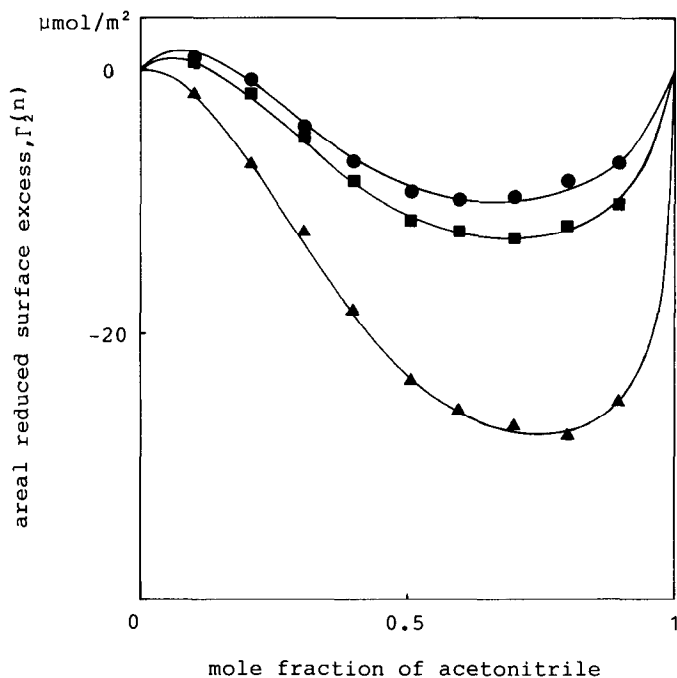


Fig. 5. Surface excess amount of acetonitrile adsorbed at 30°C from an aqueous mixture on silicas with pore size 300 Å plotted against the mole fraction of acetonitrile. ●, Super Micro Bead silica gel; ■, Shiseido's silica gel; ▲, Vydac 101TPB.

substrate rather than pore size. It seems that the difference in the substrate is based on the number of the silanol groups, which plays an important role in the adsorption of water from an aqueous mixture on the silica surface, or the difference in the pore structure. Vydac 101TPB, which shows a large surface excess amount as can be seen in Figs. 5 and 6, is presumed to have a larger number of the silanol groups than the other packing materials, or a unique pore structure. Similarly, the values of t_{\min} given in Table II are greater on Vydac 101TPB than on the other silicas. The compositions of the adsorbed phase on the silica surfaces are given by eqn. 4. The data for the silicas with pore size 300 Å are given in Tables III and IV. The mole fractions of organic modifier in the adsorbed phase on Super Micro Bead silica gel, Shiseido's silica gel and Vydac 101TPB decrease in that order, regardless of the pore diameter, and are smaller than those in the mobile phase except for a few values, as shown in Tables III and IV. Comparison of these data indicates that the silica substrates are significantly different from one another.

Comparison of Fig. 1 with Fig. 2 or Fig. 3 with Fig. 4 indicates that the surface excess amount of water is much greater in aqueous acetonitrile than in aqueous methanol. In previous work²⁰, we found that acetonitrile was more preferentially adsorbed on the chemically modified surface than methanol in aqueous mixtures. These results and the values of t_{\min} given in Table II indicate the difference in the miscible states between the acetonitrile-water and methanol-water systems. In the

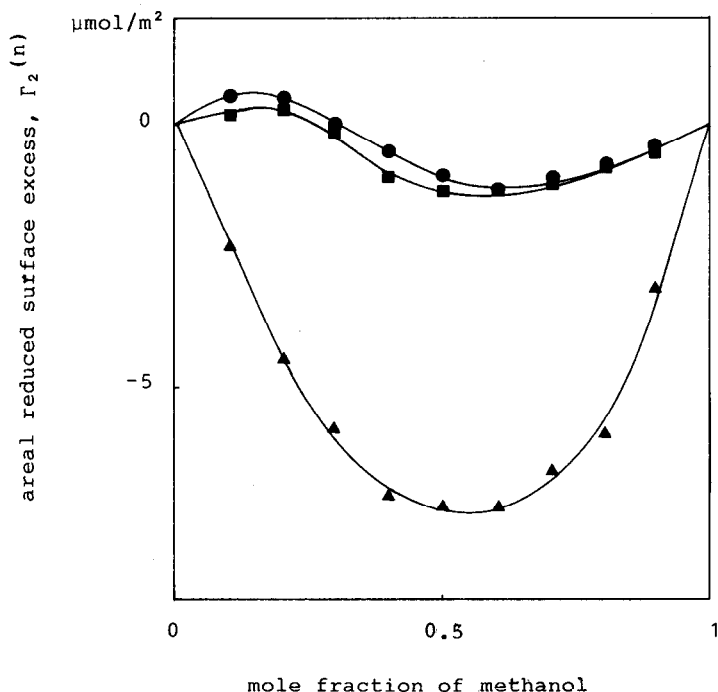


Fig. 6. Surface excess amount of methanol adsorbed at 30°C from an aqueous mixture on silicas with pore size 300 Å plotted against the mole fraction of methanol. Symbol as in Fig. 5.

acetonitrile–water system, the weak association between acetonitrile and water seems to promote the adsorption of water on the silica surface or acetonitrile on the chemically modified surface because silica has a strong affinity for water through hydrogen bonding with silanol groups, and the chemically modified surface prefers an

TABLE III

COMPOSITION OF THE ADSORBED PHASE ON THE SILICAS WITH PORE SIZE 300 Å FOR THE ACETONITRILE (2)–WATER (1) SYSTEM

x_2^l	x_2^s		
		<i>Super Micro Bead</i>	<i>Shiseido's silica gel</i>
			<i>Vydac 101 TPB</i>
0.893	0.643	0.544	0.432
0.798	0.524	0.435	0.327
0.697	0.407	0.334	0.263
0.595	0.317	0.265	0.201
0.506	0.260	0.213	0.160
0.397	0.210	0.185	0.133
0.305	0.198	0.176	0.128
0.205	0.186	0.162	0.105
0.099	0.124	0.110	0.074

TABLE IV

COMPOSITION OF THE ADSORBED PHASE ON THE SILICAS WITH PORE SIZE 300 Å FOR THE METHANOL (2)-WATER (1) SYSTEM

x_2^l	x_2^s		
		<i>Super Micro Bead</i>	<i>Shiseido's silica gel</i>
			<i>Vydac 101TPB</i>
0.898	0.856	0.842	0.746
0.805	0.734	0.724	0.545
0.706	0.611	0.599	0.433
0.603	0.493	0.493	0.320
0.500	0.420	0.393	0.233
0.398	0.357	0.319	0.151
0.297	0.298	0.286	0.103
0.202	0.237	0.222	0.056
0.103	0.139	0.115	0.028

organic solvent to water owing to the non-polarity of bonded hydrocarbon chains. In aqueous methanol, the low surface excess amount might be due to keeping a strongly associated state of methanol and water as a result of strong hydrogen bonding.

In conclusion, the data obtained from this study suggest that the surface excess isotherm on the silica surface was influenced by the substrate itself rather than pore size. This means that the surface excess isotherm can be used as a measure of the comparison of chemically modified surfaces. Further, the surface excess isotherm reflects the difference of the miscible states between acetonitrile-water and methanol-water systems. Therefore, the comparison of isotherms may be useful in studying the state of binary mobile phases.

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