Journal of Chromatography, 360 (1986) 13–24
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 549

DIRECT MEASUREMENT OF LIQUID CHROMATOGRAPHIC SORPTION–DESORPTION KINETICS AND THE KINETIC CONTRIBUTION TO BAND BROADENING

DAVID B. MARSHALL*, JAMES W. BURNS and DAVID E. CONNOLLY
Department of Chemistry, University of Idaho, Moscow, ID 83843 (U.S.A.)
(First received November 25th, 1985; revised manuscript received February 6th, 1986)

SUMMARY

The kinetics of sorption–desorption in an octadecylsilica, ion pairing chromatographic system have been directly measured for the first time, via the pressure-jump relaxation kinetics method. The sorption rate constant was found to be $1.4 \cdot 10^9$ l/mol s. The rates of sorption–desorption were found to correlate with differences in the chromatographic efficiency of the stationary phase studied, with more efficient phases showing more rapid sorption–desorption equilibration times. This indicates that, at least for the systems studied here, that the dynamics of the primary sorption–desorption process play a significant role in determining the performance of the octadecylsilicas as liquid chromatographic stationary phases.

INTRODUCTION

The kinetics of sorption–desorption can be the major contributor to the chromatographic bandwidth of solutes, particularly in heterogeneous materials[1,2]. Direct measurement of these kinetics, under conditions where there is an absence of other complicating factors such as those that arise in typical chromatographic experiments, should help to guide the production of materials where this kinetic contribution to chromatographic performance is minimized. Although many excellent studies of the kinetics of silica surface modification have been performed, to our knowledge no direct measurements have been made to date of the kinetics of sorption–desorption of molecules on such modified surfaces. Chemically-modified silicas are of course widely used in chromatography and many other fields, and understanding the interactions of the modified silica surface with wetting liquids and solute molecules is necessary for further advances in these fields. Direct measurement of the dynamics of sorption–desorption of probe molecules, on modified silica surfaces in liquid suspension, should provide some interesting insights into the mechanisms of these interactions, and how these mechanisms change with variations in the original surface modification chemistry.

Relaxation kinetic methods were developed by Eigen and DeMaeyer[3]. These methods have been comprehensively described in a text by Bernasconi[4]. All of the

0021-9673/86/$03.50

relaxation kinetics methods involve the measurement of rapid reactions by starting with a system at equilibrium, then rapidly changing (jumping) some physical property. If the equilibrium constant for the system is a function of this property, then the position of the equilibrium is shifted. The "relaxation" of the system to the new equilibrium position is then followed with an appropriate detection system. The most rapid relaxation one can follow is limited by the rate at which the physical property can be changed. A properly conducted relaxation kinetic experiment results in a first-order relaxation signal, due to the "linearization of the rate equations"[4].

The relaxation kinetic method used in this study is the pressure jump (P-jump) method. The P-jump apparatus used in this study is based on a design by Knoche and Wiese[5]. In this apparatus, a brass cell is slowly pressurized to several thousand p.s.i. The cell is sealed at one opening with a thin brass membrane. At a particular pressure (determined by the membrane thickness), the membrane abruptly ruptures, rapidly decreasing the pressure back to ambient. The shock wave from this event dissipates in 50–80 μs thus any process slower than that can be monitored. The successful observation of a relaxation signal also depends of course on being able to detect the change and in observing an equilibrium that is significantly perturbed by the change in pressure. The magnitude of the equilibrium shift depends on the following thermodynamic relation[4]:

$$\left(\frac{\partial \ln K}{\partial P}\right)_T = \frac{-\Delta V}{RT}$$

where P = pressure; T = temperature; K = equilibrium constant; V = molar volume; R = molar gas constant. For "small" perturbations, *i.e.*, small relative changes in K, this becomes:

$$\frac{\Delta K}{K} = \frac{-\Delta V}{RT} \cdot \Delta P$$

Thus, perturbation of an equilibrium depends upon both the size of the pressure change and the magnitude of the change in molar volume. Usually only those equilibria that involve changes in total charge are successfully perturbed, due to the large ΔV term resulting from electrostriction of solvent molecules by the charged species.

EXPERIMENTAL

Materials

Dimethyloctadecylchlorosilane, trimethylchlorosilane (TMCS), and hexamethyldisilazane (HMDS) were used as received (Petrarch Systems, Bristol, PA, U.S.A.). 8-Anilino-1-naphthalene sulfonate (sodium salt) (ICN-K&K, Plainview, NY, U.S.A.) was recrystallized twice from water and dried in a vacuum dessicator. Trimethylhexadecylammonium bromide (Aldrich, Milwaukee, WI, U.S.A.) was used as received. Triglyme (Aldrich) was dried by vacuum distillation from lithium aluminium hydride. Tetrahydrofuran (THF) was stored over sodium before use. Lithium aluminium hydride (Aldrich) was purified by Soxhlet ectraction in an inert atmosphere with dry diethyl ether. Reagent grade toluene was purified and dried by frac-

tional distillation followed by distillation from calcium hydride and stored over sodium metal. Pyridine (Aldrich) was fractionally distilled and stored over barium oxide. The silica used was LiChrosorb Si-100 from EM Reagents, with a surface area of 300 m^2/g, mean pore diameter of 10 nm, and a mean particle diameter of 10 μm. The silica was kept in a oven at 130°C for at least one week prior to use. All other solvents used were HPLC-grade and were degassed before use. Trimethylsilylphosphine (TMSP) was prepared according to the procedure of Finholt *et al.*[6], as described in greater detail elsewhere[7].

Synthesis of bonded phases

One of the octadecyl phases studied was formed by pre-treating the Si-60 silica with a small amount of trimethylmethoxysilane before exhaustive octadecylation and final end-capping with TMCS. This procedure and its advantages for the production of higher-efficiency reversed phases is described in greater detail elsewhere[8,9]. Another aliquot of the Si-60 silica was first octadecylated by refluxing dimethyloctadecylchloro silane with the dry silica in toluene with added pyridine for 24 h, then end-capped with TMCS by stirring in toluene at 50°C for several hours. An aliquot of the Si-100 was octadecylated then treated with a 2:1 (v/v) mixture of HMDS and TMCS in refluxing pyridine for several hours, according to the procedure of McCall[10]. The above three phases were washed with dichloromethane, acetone, methanol, methanol–water (50:50), and methanol, then Soxhlet extracted overnight with methanol. A final aliquot (1.3 g) of octadecylated Si-100 silica was treated with TMSP by a high vacuum line procedure reported elsewhere[7]. All phases were packed into 25 cm × 3.2 mm I.D. stainless-steel columns, using the downward slurry method with isopropanol–Tween 80 (90:10, v/v) as the slurry mixture and methanol followed by methanol–water (50:50) as the driving solvents.

Chromatographic measurements

Chromatographic data were obtained with a high-performance liquid chromatography (HPLC) system consisting of Beckman 112 pumps, Altex injector (5 μl loop size), a Kratos 520 UV–VIS variable-wavelength detector, and a strip-chart recorder. All data were obtained with solvents and phases thermostated in a water bath at 25.0 ± 0.02°C. Peaks were recorded and analyzed as exponentially-modified Gaussians according to the procedures recommended by Foley and Dorsey[11]. Plate numbers are thus based on the definition of N as t_R^2/m_2, where t_R is retention time and m_2 the second statistical moment, equal to $\sigma^2 + \tau^2$, where σ and τ are the peak width and peak tailing parameters of an exponentially-modified Gaussian curve, respectively. Thus, unlike the formulas used more typically to calculate N (based on an assumption of a purely Gaussian peak shape), the plate numbers reported here are a measure of *both* peak broadening and tailing effects. The numbers are thus lower than those that are typically reported for these types of material, but are a more realistic representation of column performance. All plate numbers represent the average of at least three injections for each of the test solutes.

Kinetics measurements

The pressure jump experiment was conducted, as indicated above, in a pressure cell constructed according to a design similar to that given in the literature[5]. The

pressure cell consists of two chambers, for the sample and for a pressurizing fluid. The internal volume of the sample chamber is 6.7 ml, and has three quartz windows for spectrophotometric detection. The sample chamber is chemically isolated from the pressurizing fluid by a flexible membrane. The pressurizing fluid is typically methanol. Methyl red dye is added to the methanol to permit visual inspection of the sample chamber after an experiment, to ensure that no leakage of pressurizing fluid across the flexible membrane has occurred. The pressurizing chamber is closed at the other end by a thin brass strip. The pressure is gradually increased by closing the system and turning a hand crank connected to a line leading to the pressurizing chamber. The pressure jump occurs when the brass strip abruptly ruptures. A shock wave is generated (observable in the fluorescence output as a small "wiggle") that dissipates in 50 μs. The abrupt pressure change causes the generation of a voltage spike from a piezoelectric crystal which is used to trigger an oscilloscope. The oscilloscope monitors the (pre-amplified) output from an RCA 1P28A photomultiplier. The resulting trace is photographed and subsequently hand-digitized for time decay analysis.

The results reported here are from sorption–desorption of an ion pair. The ion pair equilibrium is easily perturbed by the pressure change, and this equilibrium is coupled to the sorption–desorption equilibrium. The anion partner in the ion pair system is 1-anilino-8-naphthalene sulfonate (ANS^-). This molecule undergoes a large increase in its fluorescent quantum yield when sorbed to low polarity chemically-modified surfaces from polar solvents. Its emission maximum under these conditions is near 480 nm, with excitation of 366 nm. HPLC-grade methanol was used as the solvent. Kinetic and chromatographic measurements were made at a temperature of 25.00 ± 0.02°C. Under these conditions, ANS^- alone is not appreciably adsorbed on the octadecylated silica surfaces (no chromatographic retention). When present as the ion pair with trimethylhexadecylamonium ion, however, the ion pair *is* sorbed ($k' = 1.05$ for all phases tested here) and a significant increase in ANS emission intensity is observed[12]. The relaxations were therefore observed by monitoring the total ANS^- emission intensity, using a fast photomultiplier and 500-W mercury lamp excitation. A monochromator was used on the excitation side, set at 366 nm. Filters were used on the emission side to block scattered light at the excitation wavelength. Although the sample slurries were reasonable stable over a period of several minutes, slow settling of the slurry was observed over the course of several pressure jump experiments as a gradual decrease in the amplitude of the relaxation signal. However, no significant changes in decay time were observed with this change in amplitude, as expected for this slow, macroscopic change (the indicator concentrations should rapidly adjust to any change in effective silica surface "concentration").

RESULTS

For this entire study, relatively small amounts of ANS^- (10^{-6}–10^{-8} M in total ANS^-) were used, with relatively large amounts of $TMHDA^+$ (0.0100 M in $TMHDA^+$). These are therefore conditions of pseudo-constant [$TMHDA^+$]. All of the silica slurry/ion pair probe systems studied gave a relaxation signal with the same qualitative appearance. Following dissipation of the shock wave (which could be observed as a small "wiggle" in the photomultiplier output), a rapid increase (1–5

TABLE I

RECIPROCAL RELAXATION TIMES (τ) FOR ODS

$[S]$	$[A^-C^+]_m$	$[A^-C^+]_s$	τ^{-1} (s^{-1})
$1.33 \cdot 10^{-3}$	$5.74 \cdot 10^{-9}$	$4.26 \cdot 10^{-9}$	435
$1.33 \cdot 10^{-3}$	$5.74 \cdot 10^{-8}$	$4.26 \cdot 10^{-8}$	606
$1.33 \cdot 10^{-3}$	$5.74 \cdot 10^{-7}$	$4.26 \cdot 10^{-7}$	1272
$0.65 \cdot 10^{-3}$	$5.74 \cdot 10^{-7}$	$4.26 \cdot 10^{-7}$	250

ms) in the fluorescence intensity was observed. The response is fit well by a single exponential, as expected for a typical relaxation response. The rise-time of this response is dependent on the total analytical concentration of the ion pair, the type of chemical modification method used to synthesize the silica, and the amount of silica present. The direction of this response (a rise, indicating an increase in fluorescence) is consistent with the expected direction of the shift in the coupled equilibrium system for the primary sorption–desorption step. The signal is absent when any one of the system components is removed. The equilibrium value of the fluorescence intensity is different at different pressures. This fast rise is followed by a significantly slower fall (25–100 ms) in the intensity. The response is not fit well by any of several functions tested. The time response of this fall is independent of ion pair concentration, type of chemical modification method, or amount of silica present. This slow response is discussed in a later section.

Results from measuring the exponential rise-time of the fast response for one of the silicas (ODS) as a function of ion pair concentraton and amount of silica added are shown in Table I. The concentration of the silica was estimated from the weight of silica added, the percentage carbon from elemental analysis, and the molecular weight of a dimethyloctadecyl group. The number of moles of octadecyl ligand were calculated from these data. An admittedly crude assumption of a 1:1 octadecyl chain–(ANS^- $TMHDA^+$) stoichiometry was also made. Although it is unlikely that this is the true picture of this ion pair-modified surface interaction, the value reported in Table I should represent good order-of-magnitude values, and permit an investigation of the qualitative effects of varying concentration on the decay time. Concentrations of the ion pair species were determined from Langmuir isotherm data, obtained via the frontal elution method as recently described by Horváth and co-workers[13]. The m and s subscripts refer to free solution and sorbed ion pair, respectively.

The kinetic results reported in Table I are consistent with a mechanism involving a pre-equilibrium of ANS^- and $THMDA^+$, followed by sorption of the ion pair A^- = anion; C^+ = cation on the silica surface (S):

$$A^- + C^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^-C^+ \qquad (1)$$

$$A^-C^+ + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^-CS^+$$

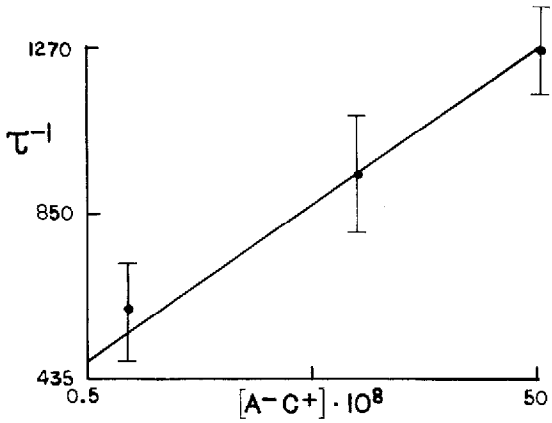

Fig. 1. Plot of reciprocal relaxation time *vs.* concentration term for the ODS stationary phase.

This mechanism has the following dependence of the reciprocal relaxation time (τ) on the concentration terms of the species involved[4]:

$$\tau^{-1} = k_2 \{[A^-C^+] + [S] \cdot R\} + k_{-2} \tag{2}$$

with R as a constant term equal to

$$\frac{k_1[C^+]}{k_1[C^+] + k_{-1}}$$

The implications of this choice of mechanism for ion pair chromatography will be described in greater detail elsewhere[14]. Independent measurement of the factor R is required for a complete and accurate determination of all the rate constants of the mechanism. This can be achieved by independent measurement of the dynamics of the initial ion pair formation equilibrium. Unfortunately, this step is too fast for the P-jump method. However, a good value for k_2 can be obtained from the slope of a linear τ^{-1} *vs.* $[A^-C^+]$ plot, under conditions of constant [S]. This value of k_2 will be in error depending upon the error in the value of [S]. A plot of the data in Table I is shown in Fig. 1. From the plot, a value for k_2 of $1.4 \cdot 10^9$ l/mols. is obtained (correlation coefficient = 0.994). This is a reasonable order-of-magnitude figure for the (presumably diffusion controlled) sorption step.

If it is assumed that the forward sorption step is indeed diffusion controlled, and that this diffusional process may be represented as a three-dimensional diffusion (both assumptions are either crude, untested, or both: further work to test these assumptions is needed), then the value of the sorption rate constant may be used to calculate a value for the local viscosity in the sorption region. This value is calculated by first determining a diffusion coefficient (D_{AC}) for the (neutral) ion pair[15]:

$$k_D = 4\pi (D_{AC} + D_S) r_c \frac{N}{1000}$$

where r_c is the contact radius, k_D the diffusion-controlled rate constant, and N is Avogadro's number. The diffusion coefficient for the macroscopic modified silica particle is assumed to be zero. From the value of D_{AC} thus obtained, the Stokes–Einstein relation may be used to calculate a viscosity (η):

$$D = RT/6\pi\eta \, Nr$$

This relationship assumes a spherical solute, with r taken as equal to r_c. However, deviations from this relationship due to departures from a spherical geometry are known to be relatively slight[15]. More serious is the assumption that the sorption process between an ion pair and a surface with both a double layer and a complex, pseudo-two-dimensional geometry may be safely represented by a simple three-dimensional diffusion model that assumes motion of a macroscopic body against a continuous solvent background (a uniform potential with no molecular-level directed interactions between solvent and solute). A more refined diffusional model is needed, and awaits (among other things) a more realistic representation of the dimensionality of the system. This will probably involve the use of a fractal geometric representation[16]. With all these caveats in mind, and taking the reaction radius as roughly equal to the ion pair radius, the value of the sorption rate constant determined here gives a value of 1.2 cP for the viscosity. This compares with a viscosity of bulk methanol at the experimental temperature (25°C) of 0.547 cP[17].

Results of kinetic studies for all silicas

The value of k_2 found above should be roughly the same for all silicas. Differences in the value of τ^{-1} for different silicas will thus depend on differences in the desorption rate constant k_{-2}, under conditions of identical [S], [A^-C^+], and [A^-CS^+]. The dependence of τ^{-1} for all four silicas under these conditions is shown in Table II. These silicas have nearly identical Langmuir isotherm behavior for the ion pair system, as shown in the plots of the Langmuir isotherm for the silicas in Fig. 2. Concentration conditions were adjusted so that, for all silicas, [A^-C^+] = $5.5 \cdot 10^{-8}$ M, [A^-CS^+] = $4.5 \cdot 10^{-8}$ M, and [S] = $1 \cdot 10^{-3}$ M.

As indicated in Table II, the relaxation time for the O/TMSP silica was too fast to measure on the pressure-jump time scale. (A response was observed, that followed the change in pressure, relaxing on the same time scale or faster than the dissipation of the shock wave). In comparing these relaxation time values, the phases with faster relaxations undergo more rapid equilibration of the primary sorption–desorption process. In chromatographic terms, this should result in higher efficiency

TABLE II

RECIPROCAL RELAXATION TIMES (τ) FOR SILICAS

Silica	τ^{-1} (s^{-1})
O/HT (Si-100, 10 μm)	585 ± 80
O/DTMSP (Si-100, 10 μm)	>2000
ODS (Si-60, 10 μm)	600 ± 20
TM/ODS (Si-60, 10 μm)	740 ± 60

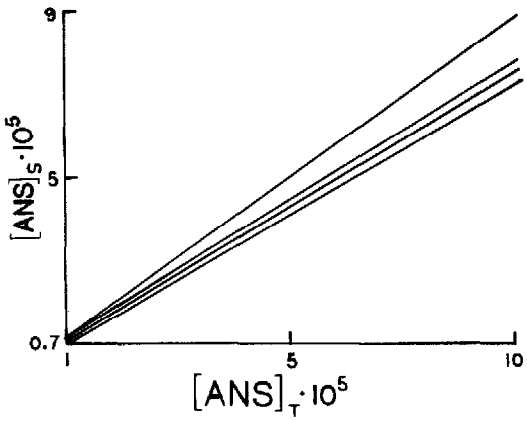

Fig. 2. Langmuir isotherms for the ANS^-TMHDA^+ ion pair on the octadecylated silicas. Nineteen data pairs per curve, evenly spaced along the concentration axis. Scatter in the points is less than the width of the line. Lines correspond, from upper to lower, to the O/HT, ODS, ODS/TMSP, and TM/ODS Silicas, respectively.

of the faster-equilibrating silicas as liquid chromatographic stationary phases. That this is in fact the case is shown below.

Chromatographic results

The differences in chromatographic retention and bandwidth (efficiency) for the ion pair system are negligible for the different phases. However, retention times and plate numbers for various test solutes measured under standard reversed-phase operating conditions reveal significant differences between the phases. (Reasons why the kinetics under ion pairing conditions show significant differences are discussed below). The following chromatographic data were obtained using methanol–water (70:30) as the mobile phase, at an operating temperature of 25.00 ± 0.05°C. The values reported here were determined at a flow-rate of 1.00 ml/min. Differences in plate numbers determined at several other flow-rates are consistent with the efficiency differences reported here. Capacity factors (with t_0 determined by sodium nitrate) are given in Table III. Plate numbers, calculated from an exponentially modified Gaussian peak model (as outlined in the Experimental section) are reported in Table

TABLE III

CAPACITY FACTORS (k') FOR VARIOUS TEST SOLUTES

Solute	k'			
	O/HT	*O/TMSP*	*ODS*	*TM/ODS*
Aniline	0.96	0.97	0.87	0.76
Phenol	0.81	0.85	0.91	0.91
3-Phenhyl-1-propanol	1.46	1.44	1.78	1.80
Benzene	2.00	2.10	3.24	3.45
Naphthalene	4.78	5.04	9.03	10.04
Anthracene	14.47	15.47	30.52	35.57

TABLE IV

ADJUSTED PLATE NUMBERS (N) FOR VARIOUS TEST SOLUTES

Limits of precision (95%) of all N values are ± 50–100 units.

Solute	*N*			
	O/HT	*O/TMSP*	*ODS*	*TM/ODS*
Aniline	1330	3220	2070	4400
Phenol	★	★	1345	★
3-Phenyl-1-propanol	3780	5930	1860	4970
Benzene	3670	14 800	4250	6130
Naphthalene	2570	4450	3750	4780
Anthracene	2290	3880	1610	3690

★ The second moment values for these solutes were too close to that of sodium nitrate (within the limits of precision) to give reliable results upon subtraction: spuriously high or negative answers were obtained. See text for an explanation of the method used to calculate the adjusted N values.

IV. These values were further adjusted for differences in packing efficiency by subtracting the second moment of the elution band of sodium nitrate (taken as an unretained solute) from the second moment of the solute band before calculation of the N value[18]. This method of course assumes that the diffusion in the mobile phase is equal for all solutes and equal to that of sodium nitrate. While not strictly true, this method does provide a convenient first-order correction for packing efficiency differences.

As can be seen from the data in this and the previous section, those phases with higher chromatographic efficiencies (for most of the test solutes) are indeed those materials that show more rapid equilibration of the primary sorption–desorption process. This indicates that, at least for these materials, the primary sorption–desorption process is most likely a significant contributor to the overall chromatographic band broadening observed when the materials are used as liquid chromatographic stationary phases.

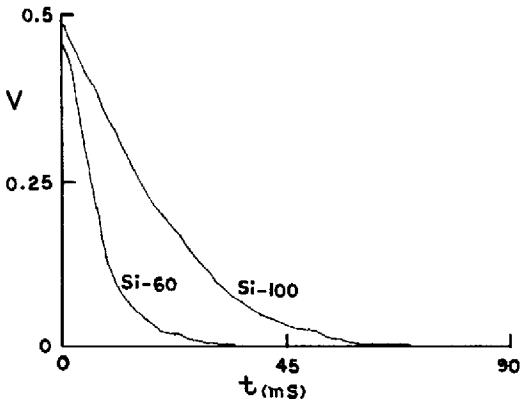

Fig. 3. Slow relaxation response for Si-100 and Si-60 silicas.

Slow relaxation response

The second, slower fall in fluorescence intensity mentioned above is independent of the concentration of ion pair in solution, the amount of silica, and the chemical modification scheme used to make the silica. The response curve does not fit a single or a double exponential. However, inspection of all the data shows that the time required for complete relaxation is roughly constant for both O/HT and O/TMSP, and that this time is about 2.5 times longer than the time required for ODS and TM/ODS. The times for these last two silicas are also roughly the same. Recall that O/HT and O/TMSP were made from the Si-100 silica (average pore diameter of 10 nm), whereas ODS and TM/ODS were made from the Si-60 silica (average pore diameter of 6 nm). Representative slow responses for these two types of silicas are shown in Fig. 3. The slower fall in fluorescence intensity is likely due to the kinetics of pore intercalation, with a decay in fluorescence intensity observed as the probe molecules penetrate deeply into the particle and become harder to observe spectrophotometrically. A search for the appropriate mathematical model for this process, based on diffusion equations, is in progress. It will be most interesting to compare the response time for this process for other pore structures, and for spherical silica particles. Relaxation kinetics may thus prove to be a way of directly measuring pore diffusional effects in these materials.

DISCUSSION

The studies described here represent the first direct measurements of sorption–desorption rates in a liquid chromatographic system. These initial results are intriguing but of course raise more questions than they answer. As a result, the discussion below is often speculative in nature, and is offered in that spirit. Only further studies (in progress) can clarify many of the points discussed.

It may be asked why it is necessary to measure chromatographic sorption–desorption kinetics via the direct relaxation kinetic method described in this study. The kinetics should also be derivable from simple measurements of k' and/or isotherm studies, which yield the thermodynamic equilibrium constant for the sorption–desorption process. Together with the assumption of a diffusion-controlled sorption event, the rate constant for desorption may be easily determined by taking the simple ratio of the sorption rate constant to the equilibrium constant (*cf.* ref. 2). However, there are some difficulties with this purely chromatographic measurement approach.

First, as the value for the sorption rate constant determined in this study shows, the estimation of a diffusion-controlled process in these complicated systems is fraught with dangers. Errors in this estimation will of course give errors in the calculated desorption rate, as well as giving an unrealistically high value for the rate at which the sorption–desorption equilibrium is established. It has not yet been unequivocally established whether the sorption rate is in fact diffusion controlled and the same for all phases (under identical mobile phase and temperature conditions).

In addition, the rate constants determined from chromatographic measurements represent a "lumped" process, with factors other than the primary sorption–desorption event included. Even if chromatographic measurements were to give reliable values for these lumped sorption and desorption rates, the relaxation technique

described here provides a much cleaner means of determining the rates of the primary sorption–desorption process, with this process cleanly separated, in the dynamic sense, from other processes such as pore intercalation kinetics.

Finally, the chromatographic (or sorption isotherm) measurement occurs on a timescale where lateral diffusion from sorption site to sorption site is likely to occur. In contrast, the relaxation kinetics method essentially measures a single (averaged over all participating molecules) sorption event. This should have the effect of amplifying slight differences from phase to phase of these kinetics, differences that will be "blurred" in the relatively static chromatographic measurement. In fact, this is clearly shown in this study, where significant differences in equilibration kinetics were observed between phases in an ion pair system, despite the fact that the chromatographic measurement of retention and bandwidths in the ion pair situation showed no differences between phases. These kinetic differences did correspond, however, to differences in stationary phase efficiency measured under standard reversed phase conditions.

A further question arises of why, if the pore diffusion effect is so much slower than the sorption–desorption kinetics, the diffusional kinetics do not dominate the chromatographic behavior of these materials? Apparently, the total number of times a particular molecule undergoes a primary sorption–desorption event is greater than the number of times it experiences a lag due to a pore diffusional event. Thus, the cumulative effect of the sorption–desorption process is larger.

The relaxation data reported here are consistent with a reaction mechanism that includes the stationary phase material as an explicit reaction partner, leading to a collision theory second-order rate constant for the sorption process. Since the overall sorption rate is k_2 $[A^-C^+]$ [S], the rate of sorption equilibration will necessarily increase with increasing [S].

It is likely that a combination of chromatographic and relaxation kinetics measurements will prove to be a powerful tool for unraveling the contributions from the many factors responsible for liquid chromatographic performance.

CONCLUSION

It seems remarkable that any differences in the rates of sorption–desorption with type of octadecylsilica were observed at all. The test probe system used, a relatively weakly retained (k' near 1 for all columns) ion pair system with a large excess of a cation that is itself strongly sorbed by the surface, would be expected to mask slight differences in stationary phase composition. Despite this, differences *were* observed that are consistent with differences in the chromatographic characteristics of the phases examined here. The differences would be expected to be much greater in a regular reversed-phase system, one without the presence of high concentrations of a modifier. Efforts are underway to find a workable indicator system that will allow measurement of solute sorption–desorption kinetics under these conditions. These initial results do indicate, however, that direct measurement of solute sorption–desorption kinetics in chromatographic systems provides some useful insights into the mechanism of the sorption process, and a sensitive means of measuring slight differences in those stationary phase–solute interactions that are responsible for determining the chemical contributions to the efficiency of the stationary phase.

ACKNOWLEDGEMENTS

We would like to gratefully acknowledge the assistance of Professor Zoltan Schelly, for providing diagrams and advice concerning construction of the P-jump cell. The cell was constructed by Mr. Bill Alspach and associates at Washington State University Technical Services. Grateful acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to NSF (Grant No. CHE 83-06881) for financial support of this research.

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