

New model of surface diffusion in reversed-phase liquid chromatography

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Abstract

A new model of surface diffusion in reversed-phase liquid chromatography (RPLC) was derived by assuming a correlation between surface and molecular diffusion. Analysis of surface diffusion data under different conditions of sample compounds, mobile and stationary phases, and temperature in RPLC systems validates this assumption and shows that surface diffusion should be regarded as a molecular diffusion restricted by the adsorptive interactions between the adsorbate molecule and the stationary phase surface. A surface-restricted molecular diffusion model was proposed as a first approximation for the mechanism of surface diffusion. The model is formulated according to the absolute rate theory. The activation energy of surface diffusion (E_s) was quantitatively interpreted assuming that E_s consists of the contributions of two processes, a hole-making and a jumping one. The former contribution is nearly equal to the activation energy of molecular diffusion and is correlated with the evaporative energy of the mobile phase solvent. The latter contribution is a fraction of the isosteric heat of adsorption. An appropriate explanation based on this new model of surface diffusion is provided for two contradictory results related to the relationship between retention equilibrium and surface diffusion in RPLC and to the surface diffusion coefficient for weakly retained sample compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Surface diffusion; Diffusion; Thermodynamic parameters; Mobile phase composition; Liquid chromatography, reversed-phase

1. Introduction

Surface diffusion plays an important role in the mass transfer inside the intraparticle space of porous adsorbents [1,2]. The fundamental characteristics of surface diffusion have mostly been studied from the viewpoints of the dependence of the surface diffusion coefficient (D_s) on the amount of adsorbate molecules adsorbed and on the temperature. According to the Arrhenius equation, the temperature de-

pendence of D_s is usually studied on the assumption that surface diffusion is an activated process, with:

$$D_s = D_{s0} \exp\left(\frac{-E_s}{RT}\right) \quad (1)$$

where D_{s0} and E_s are the frequency factor and the activation energy of surface diffusion, respectively, R is the universal gas constant, and T the absolute temperature. It is frequently assumed that E_s is a fraction of the isosteric heat of adsorption (Q_{st}), that is, $E_s = \alpha'(-Q_{st})$ [1,2]. The following correlation is then derived from Eq. (1):

$$D_s = D_{s0} \exp\left[\frac{-\alpha'(-Q_{st})}{RT}\right] \quad (2)$$

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where α' has been reported to be smaller than unity for surface diffusion [2]. Eq. (2) has commonly been used as the most basic equation for analyzing the temperature and the concentration dependence of D_s in gas–solid and liquid–solid adsorption systems. Many models were derived on the basis of Eq. (2) in order to explain the dependence of D_s on the amount adsorbed [1,2].

However, two contradictory situations arise in the analysis of surface diffusion data using Eq. (2). The first one is in the correlation between the two thermodynamic parameters E_s and Q_{st} . Surface diffusion is an activated mass transfer process in the adsorbed state. When an adsorbate molecule migrates from one adsorption position to another by surface diffusion, the molecule must gain E_s to overcome the energy barrier between the two close adsorption sites. The value of E_s should be smaller than $-Q_{st}$ because the adsorbate molecule does not need to be completely desorbed to move between two close sites. The ratio $E_s/(-Q_{st})$ should be smaller than unity. As expected, in many cases of surface diffusion in gas–solid adsorption, $E_s/(-Q_{st})$ was found to be smaller than unity [1–6]. In contrast, values of E_s larger than $-Q_{st}$ have frequently been reported for liquid–solid adsorption systems [2,5,7–9]. The presence of surface diffusion should be denied under such conditions because it is then energetically more advantageous for the adsorbate molecule to be desorbed first from the surface and to diffuse in the solution rather than to migrate along the surface. On the other hand, there are also a few reports of values of E_s smaller than $-Q_{st}$ in liquid–solid adsorption systems [2,10–12]. Eq. (2) provides no adequate interpretation for these contradictory and different correlations between E_s and Q_{st} in liquid–solid adsorption systems.

The second contradiction is the value of D_s for weakly retained compounds. Of course, no surface diffusion takes place if the molecules of the sample are not adsorbed on the stationary phase surface. Eq. (2) obviously indicates that D_s tends toward D_{s0} when the adsorptive interactions between the adsorbate molecule and the stationary phase surface decrease, i.e. when Q_{st} tends toward zero. Values of D_{s0} between ca. 10^{-4} and 10^{-1} cm² s⁻¹ have been reported in different liquid–solid systems [2,5,10,12]. On the other hand, it is well known that

molecular diffusivity (D_m) is usually of the order of ca. 10^{-6} to 10^{-5} cm² s⁻¹ in liquid phase systems, as estimated by the Wilke–Chang equation [13–16]:

$$D_m = 7.4 \cdot 10^{-8} \cdot \frac{(a_{sv} M_{sv})^{1/2} T}{\eta_{sv} V_{b,a}^{0.6}} \quad (3)$$

where a is the association coefficient, M the molecular weight, η the viscosity, and V_b the molar volume at the normal boiling point. The subscripts a and sv denote the solute and the solvent, respectively. These data suggest that D_s would be a few orders of magnitude larger than the corresponding D_m when $-Q_{st}$ is small. This conclusion is unreasonable because molecular diffusion cannot be affected by any adsorptive interactions while surface diffusion obviously is. These observations suggest that Eq. (2) should not be used for a detailed analysis of surface diffusion of weakly retained compounds when $-Q_{st}$ is small. However, there is no information regarding the acceptable range of Q_{st} , let alone the conditions of validity of Eq. (2).

Mass transfer inside porous adsorbents is frequently accounted for by assuming that intraparticle diffusion is explained by parallel contributions of pore and surface diffusion [2,17], with:

$$D_e = D_p + \rho_p K D_s \quad (4)$$

where D_e is the intraparticle diffusivity, D_p the pore diffusivity (lower than D_m because of the steric hindrance of tortuous pores), ρ_p the density of the porous adsorbent, and K the adsorption equilibrium constant. When K tends toward zero, the contribution of the second term in the right hand side of Eq. (4) becomes negligibly small, irrespective of the value of D_s . Because the contribution of surface diffusion is small at low values of K , few detailed studies have so far been made on the dependence of D_s on the intensity of the adsorptive interactions between adsorbate molecules and adsorbent surfaces, in contrast to the extensive studies on the temperature and concentration dependence of D_s , as described earlier [1,2]. The lack of a correlation more satisfactory than Eq. (2) results from the insufficient number of studies concerning the correlation between surface diffusion and adsorption energy of the adsorbate molecules. Surface diffusion should be studied in more detail because this process has a large contribu-

tion to the intraparticle mass transfer [1,2,5,18–20]. In conclusion, a new model must be derived for better understanding of the characteristic features and of the mechanism of surface diffusion.

The analysis of surface diffusion data measured under different RPLC conditions indicates that the value of D_s depends primarily on that of D_m and that D_s tends toward the corresponding value of D_m with decreasing retention. This demonstrates a strong correlation between surface diffusion and molecular diffusion and also shows that surface diffusion of adsorbate molecules is restricted by their retention behavior on the stationary phase surface. On the basis of these results, a surface-restricted molecular diffusion model was derived as a first approximation for the mechanism of surface diffusion. In this model, surface diffusion is regarded as molecular diffusion restricted in the potential field of adsorption, within which surface diffusion should take place. The new model provides an adequate interpretation for the contradictory thermodynamic correlations between E_s and Q_{st} in liquid–solid systems and for the values of D_s of weakly retained compounds.

2. Experimental

2.1. Chemicals and reagents

Six columns packed with different RPLC packing materials (i.e. C₁-, C₄-, and C₁₈-silica gels) were used. They were prepared from the same base silica gel, of which the average particle diameter was 45 μm. This coarse-particle silica material was chosen

in order to facilitate the derivation of accurate values of D_s as explained later. Table 1 lists the information about the alkyl ligands bonded to the base silica gel. Four C₁₈-bonded materials were used, with bonding densities in the range between 0.59 and 3.2 μmol m⁻². These values were estimated on the assumption that the typical density of silanol groups is about 8 μmol m⁻² on the surface of silica gels [21].

Methanol–water mixtures of different compositions ($\varphi = 60$ –80%, v/v) were used as the mobile phase. This range of φ is rather typical for the concentration of organic modifiers in RPLC [16,22,23]. For instance, it seems that most manufacturers carry out an initial evaluation of the efficiency of packed columns using mobile phase solvents in this range of φ . Sample compounds were alkylbenzene derivatives and *p*-alkylphenol derivatives. Sample solutions were prepared by dissolving the compounds with the mobile phase solvents. Uracil and sodium nitrate were used as inert tracers.

2.2. Apparatus

A high-performance liquid chromatograph system, LC-6A (Shimadzu, Kyoto, Japan), was used for the pulse response experiments. A valve injector, model-7125 (Rheodyne, Cotati, CA, USA), was used for injecting small amounts of the sample solutions into the column. A thermostatted water-bath was used for circulating temperature-controlled water around the column to keep the column temperature at the intended level. The concentration of the sample compounds at the column exit was monitored with

Table 1
Physical properties of RPLC columns

	Main alkyl ligand					
	C ₁	C ₄	C ₁₈	C ₁₈	C ₁₈	C ₁₈
Carbon content (%)						
before end-capping	4.1	6.7	3.6	6.4	12.8	17.1
after end-capping	^a –	^a –	6.6	8.6	13.7	17.1
Main ligand density, (μmol m ⁻²) ^b	13.4	3.7	0.59	1.1	2.3	3.2

^a No end-capping treatment was made.

^b Calculated from the carbon content before end-capping, the surface area of the base silica gel (290 m² g⁻¹), and the density of silanol groups on the surface of the base silica gel (assumed to be 8 μmol m⁻²).

the ultraviolet detector of the HPLC system (SPD-6A).

2.3. Procedure

Elution peak profiles were measured using the pulse response method (i.e. elution chromatography) under linear isotherm conditions while changing the mobile phase flow velocity ($1\text{--}2\text{ cm}^3\text{ min}^{-1}$) and the column temperature ($288\text{--}308\text{ K}$). The information on the retention equilibrium and the mass transfer kinetics in the columns was derived from the first moment (μ_1) and the second central moment (μ_2') of the elution peaks, respectively. Some thermodynamic parameters concerning the retention behavior and surface diffusion were estimated from the temperature dependence of the related equilibrium and kinetic parameters. More detailed information about the moment analysis is available in the literature [2,5,16,17,24–27]. The data analysis procedure is briefly explained below.

First, K was derived from μ_1 . Then, the information about the mass transfer kinetics was derived from μ_2' [2,5,16,17,24–28]. D_s was estimated by subtracting from μ_2' the contributions to band broadening of the other mass transfer processes, that is, axial dispersion, external mass transfer, and pore diffusion. The band broadening contribution of the real adsorption–desorption kinetics at actual adsorption sites was assumed to be negligibly small [29]. This assumption is widely accepted in studies of mass transfer kinetics in liquid–solid adsorption systems [2,5,16,17]. The external mass transfer coefficient was derived from the Wilson–Geankoplis equation [2,14,17] and the corresponding contribution to μ_2' was subtracted. Then, the contributions of axial dispersion and intraparticle diffusion were separated by taking advantage of the difference in the mobile phase flow-rate dependence of their contributions to μ_2' . At this time, two kinetic parameters, i.e. the axial dispersion coefficient and D_e , are estimated. The value of D_s was derived from D_e by subtracting the contribution of pore diffusion (D_p) to intraparticle diffusion on the basis of Eq. (4). According to the parallel pore model [2,17], D_p was calculated from D_m , the internal porosity of the stationary phase particles, and the tortuosity factor of

the pores. The information about the intraparticle porosity and tortuosity factors was derived from the pulse response experiments made using the inert tracers. The influence of the extra-column volumes on μ_1 and μ_2' was measured by performing the same measurements without column. This information was used to correct the experimental data.

As described above, the contributions of a few other mass transfer processes in the column and that of the extra-column volumes to μ_2' must be subtracted to derive D_s from μ_2' of the elution peaks. The use of a coarse-particle material in this study allows a more accurate estimate of the values of D_s . The influence of the other sources of error on the estimation of D_s was minimized because μ_2' was originally relatively large.

The influence of the peak asymmetry (tailing or fronting) on the estimation of the moments μ_1 and μ_2' of the elution peaks was considered. There are several possible causes of the peak distortion, e.g. heterogeneous mass transfer kinetics [16] and column radial heterogeneity [30–32]. In this study, only the radial heterogeneity of the column was regarded as a possible origin of the peak skew. The possibility of the heterogeneous mass transfer kinetics was ignored because the surface of C_{18} -silica gels behaves as energetically homogeneous toward the compounds used here. For these compounds, (1) the phase equilibrium on C_{18} -silica gels is usually accounted for by the simple Langmuir isotherm [5,16,18,29,33–35], (2) Q_{st} is nearly constant, irrespective of the amount of sample molecules adsorbed [5,33], and (3) E_s is also independent of the amount adsorbed [5,33]. The assumption of an apparent uniformity of the C_{18} -silica gel surface was also supported by a theoretical analysis of the adsorption behavior of 2-phenylethanol and 3-phenylpropanol on a C_{18} phase, from a methanol–water mixture [36].

Finally, the influence of the width of the sample pulses on the moments μ_1 and μ_2' of the elution peaks was corrected by assuming that the injection pulses had a rectangular profile. However, this effect was found negligible because of the extremely small size of the sample pulses injected. These corrections described above are responsible for the error made in the estimation of D_s . It seems that this error is of the order of several percent [5].

3. Results and discussion

3.1. Thermodynamic and kinetic properties in RPLC

Table 2 gives the three thermodynamic and/or kinetic parameters measured, i.e. Q_{st} , E_s , and D_{s0} , for the 14 samples studied, in 70% (v/v) methanol, on the C_{18} -silica gel with an alkyl ligand density of $3.2 \mu\text{mol m}^{-2}$. The values of Q_{st} and D_{s0} are of the same order of magnitude as others previously reported [2,5,10,12,37–43]. As described earlier, the results in Table 2 illustrate the contradictory situation relating to the mechanism of surface diffusion, with values of E_s nearly twice as large as those of Q_{st} . The presence of surface diffusion cannot be expected under such conditions because surface diffusion is a mass transfer process in the adsorbed state. The value of E_s should be smaller than $-Q_{st}$.

The second problem is the value of D_s of weakly retained compounds. According to Eq. (2), D_s tends toward D_{s0} when Q_{st} tends toward zero. The experimental values of D_{s0} listed in Table 2 are all between ca. $1 \cdot 10^{-3}$ and $1 \cdot 10^{-1} \text{ cm}^2 \text{ s}^{-1}$. This result implies that surface diffusion of weakly retained compounds is two to four orders of magnitude faster than molecular diffusion. As is well known, the value of D_m is of the order of $1 \cdot 10^{-6}$ to $1 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ in liquid phase systems [2,13–17]. Surface

diffusion must be more restricted compared with molecular diffusion because it is a mass transfer process taking place in narrow and tortuous microscopic channels. Additionally, surface diffusion takes place in the potential field of adsorption. Values of D_s larger than D_m are unreasonable. D_s should be smaller than D_m . These contradictory results strongly suggest that a new model and formulation, different from Eq. (2), must be derived for a detailed study of the characteristics and mechanism of surface diffusion.

3.2. Correlation between surface diffusion and molecular diffusion

The values measured for D_s at $\phi=60$ and 80% (v/v) (symbols) are compared with those at $\phi=70\%$ (v/v) in Fig. 1. The two dashed lines show the correlations between values of D_m at different ϕ values. The solid lines are the extrapolations of these dashed lines. The plots of D_s are located around the solid lines, suggesting that the same correlation applies to D_s and D_m . An increase in ϕ is accompanied with a proportional increase in D_s . A similar tendency is also observed between D_m and ϕ . These

Table 2
Thermodynamic properties in RPLC

Sample compound	$-Q_{st}$ (kJ mol ⁻¹)	E_s (kJ mol ⁻¹)	D_{s0} (cm ² s ⁻¹)
Benzene	6.7	19.4	$7.0 \cdot 10^{-3}$
Toluene	8.7	20.5	$8.7 \cdot 10^{-3}$
Ethylbenzene	9.7	22.0	$1.4 \cdot 10^{-2}$
Propylbenzene	11.4	22.6	$1.4 \cdot 10^{-2}$
Butylbenzene	13.0	25.7	$4.0 \cdot 10^{-2}$
Pentylbenzene	15.2	26.3	$4.3 \cdot 10^{-2}$
Hexylbenzene	17.5	28.3	$8.0 \cdot 10^{-2}$
<i>p</i> -Xylene	10.3	23.4	$2.5 \cdot 10^{-2}$
Phenol	8.3	16.9	$2.2 \cdot 10^{-3}$
<i>p</i> -Cresol	8.5	16.8	$1.7 \cdot 10^{-3}$
<i>p</i> -Ethylphenol	10.0	18.9	$3.2 \cdot 10^{-3}$
<i>p</i> -Propylphenol	11.4	20.8	$5.2 \cdot 10^{-3}$
<i>p</i> -Butylphenol	13.2	21.9	$6.6 \cdot 10^{-3}$
<i>p</i> -Hexylphenol	16.7	23.4	$7.7 \cdot 10^{-3}$

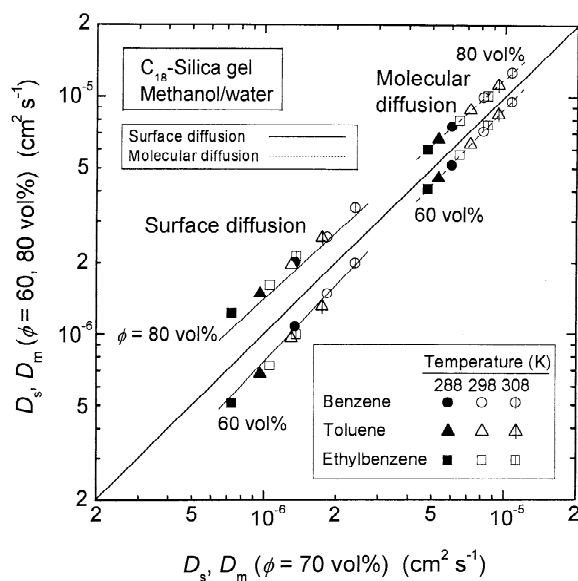


Fig. 1. Comparison of the dependence of surface diffusion coefficient on the mobile phase composition with that of molecular diffusivity.

observations are explained in part by considering that the viscosity of methanol–water mixtures decreases almost linearly with increasing φ in the range $\varphi = 60$ to 80% (v/v) [16]. The results in Fig. 1 demonstrate that the mobile phase composition influences molecular migration by either surface or molecular diffusion. It was also reported that the value of D_s depends on characteristics of the mobile phase, e.g. the nature of the organic modifier [5,20,44–47], and of the stationary phase, e.g. the length of the alkyl ligands and the density of the C_{18} chains [5,19]. These observations suggest that surface diffusion probably takes place in the actual adsorbed monolayer, which consists of the mobile phase solvents and the stationary phase surface. The results in Fig. 1 also indicate that φ has almost the same influence on surface and molecular diffusion, suggesting that there is a strong correlation between the two diffusive processes [5,45,46,48–52].

Figs. 2 and 3 illustrate the influence of retention on surface diffusion. In Fig. 2, the ratio of D_s to D_m is plotted against K at 298 K. The ratio D_s/D_m fluctuates around a curved line and increases with decreasing K . The extrapolated intercept is probably close to unity. This suggests that D_s of weakly retained compounds is of the same order of magnitude as D_m . In Fig. 3, the values of D_s/D_m are

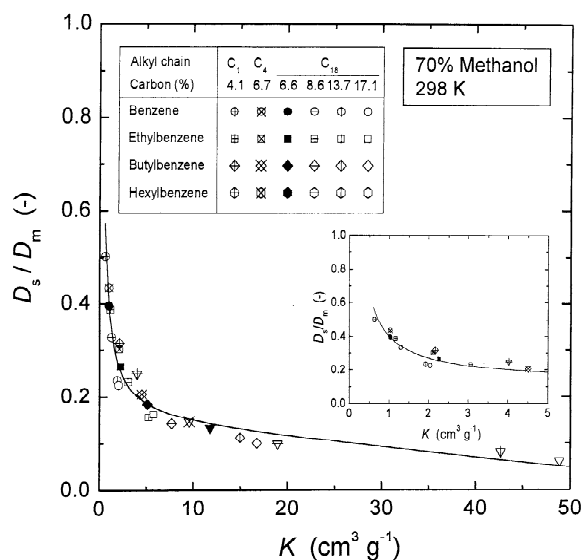


Fig. 2. Correlation between the ratio of surface diffusion coefficient to molecular diffusivity and adsorption equilibrium constant.

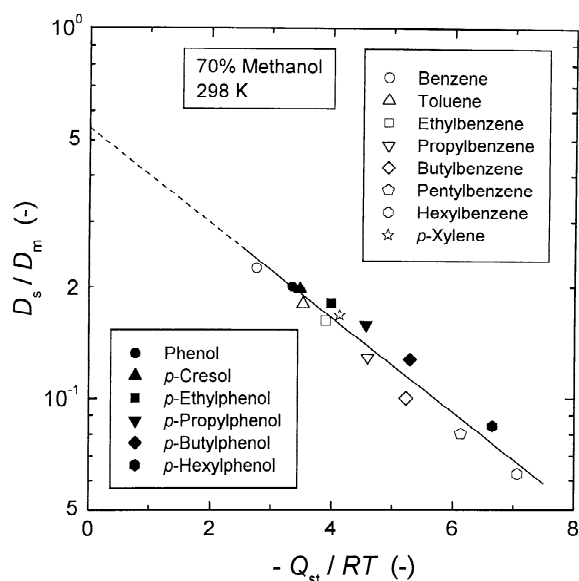


Fig. 3. Correlation between the ratio of surface diffusion coefficient to molecular diffusivity and isosteric heat of adsorption of different sample compounds.

plotted versus $-Q_{st}/RT$ and give a straight line. The negative value of the slope of this line indicates that the migration of adsorbate molecules by surface diffusion is restricted by the adsorption interactions [5,20,48–52]. Again, the value of the extrapolated intercept suggests that D_s at $Q_{st} \approx 0 \text{ kJ mol}^{-1}$ is close to D_m , a result consistent with the one in Fig. 2.

The extrapolated intercept in Fig. 3 is approximately 0.54, indicating that D_s may not be exactly equal to D_m at $Q_{st} = 0 \text{ kJ mol}^{-1}$. This discrepancy probably arises from several factors. As described earlier, the sample molecules migrating by surface diffusion are in the vicinity of the stationary phase surface, where the physico–chemical properties of the mobile phase are somewhat different from those of the bulk phase. The organic modifiers in the aqueous mobile phase are preferentially attracted to the hydrophobic surface of the non-polar stationary phase [53]. The concentration of the organic modifier is higher near the stationary phase surface than in the bulk mobile phase. The presence of alkyl ligands also influences the structure of the mobile phase solvents. It is known that short alkyl ligands are structure breakers while longer alkyl chains are

structure makers. Solvent molecules near longer alkyl ligands could be organized by hydrophobic repulsion. Molecular diffusion of molecules depends on the solvent structure. Additionally, the obstruction of molecular migration by surface diffusion increases with increasing length and/or density of the bonded alkyl ligands. These reasons explain why D_s at $Q_{st} = 0 \text{ kJ mol}^{-1}$ is not exactly equal to D_m . These effects are under investigation.

The results in Figs. 1–3 suggest that the mechanism of surface diffusion is originally similar to that of molecular diffusion. However, the migration of adsorbate molecules is restricted by the adsorptive interactions. These results allow us to assume that surface diffusion is a form of molecular diffusion, restricted by adsorption interactions. On the basis of this assumption, D_s is formulated as follows:

$$D_s = D_m \exp \left[\frac{-\beta(-Q_{st})}{RT} \right] \quad (5)$$

where β should be positive and smaller than unity, as expected from the slope of the straight line in Fig. 3. It is not required for molecules adsorbed on the surface to be desorbed into the bulk mobile phase because surface diffusion is a mass transfer process in the potential field of adsorption, that is, it takes place in the adsorbed state.

In Eq. (5), the ratio D_s/D_m varies with temperature, φ , and the nature of the sample compounds because both D_s and D_m depend on these three parameters. On the other hand, Q_{st} depends also on φ and on the nature of the sample compounds. However, because Q_{st} is derived from the temperature dependence of K , according to the Van't Hoff equation, it does not depend on the temperature. Also, the temperature excursion in this study is only 20 K or about 6% of T , a rather small interval; this justifies neglecting the influence of the difference between the heat capacities of the sample in the adsorbed and the dissolved states. Thus, the ratio $\beta(-Q_{st})/(RT)$ is almost independent of the temperature, suggesting that the temperature dependence of D_s can be explained by taking that of D_m into account, although both D_s and D_m are temperature dependent. Fig. 4 shows plots of D_s against D_m for the three benzene derivatives at different values of φ and of the column temperature. Linear correlations

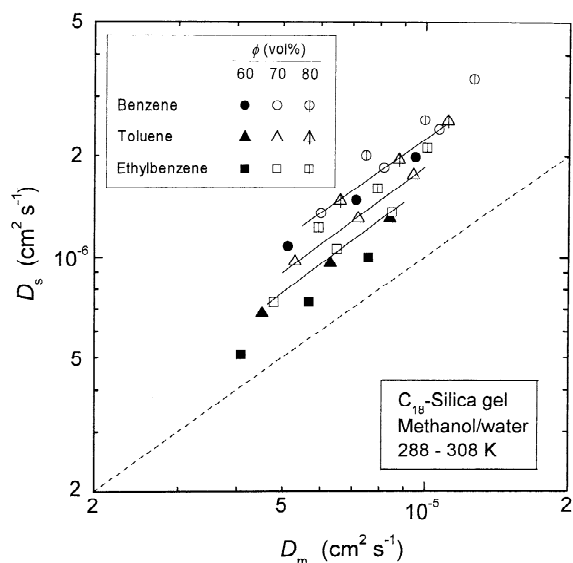


Fig. 4. Correlation between surface diffusion coefficient and molecular diffusivity.

are observed for the different temperatures, sample compounds, and values of φ . As examples, three linear correlations are indicated in Fig. 4 for the data at $\varphi = 70\%$ (v/v). The three straight solid lines are parallel to each other and to the dashed line having a slope of unity. These results suggest that the dependence of D_s on the temperature is the same as that of D_m .

The ratio D_s/D_m of the different sample compounds is represented as a linear function of $Q_{st}/(RT)$ in Fig. 3. The results in this figure indicate that the difference in the D_s values of the various sample compounds is correctly interpreted by correlating D_s with both D_m and Q_{st} . Fig. 5 also shows the correlation between D_s/D_m and $Q_{st}/(RT)$ for three sample compounds, benzene, toluene and ethylbenzene, at different temperatures and φ values. The whole set of data (symbols) are scattered around the straight solid line, although those for benzene at $\varphi = 60\%$ (v/v) are slightly offset from this line. The solid line was derived by a linear regression of all the experimental data. The results in Fig. 5 indicate that the dependence of D_s on φ is correctly interpreted by considering the correlation of the ratio D_s/D_m with $Q_{st}/(RT)$, as described in Eq. (5).

The dashed line in Fig. 5 reproduces the linear

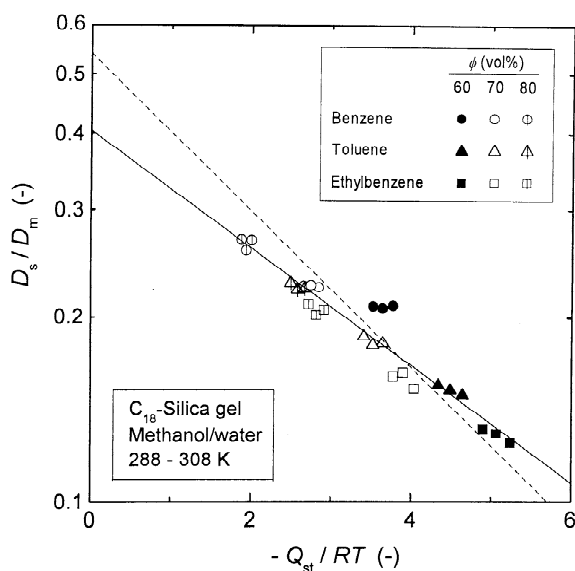


Fig. 5. Correlation between the ratio of surface diffusion coefficient to molecular diffusivity and isosteric heat of adsorption at different temperatures and mobile phase compositions.

correlation in Fig. 3. It is very close to the solid line. The discrepancy between these lines originates mostly from the difference in the two sets of experimental data used in the two regressions to Eq. (5). It is concluded that Eq. (5) accounts well for the dependence of D_s on the temperature, φ , and the sample compounds. Eq. (5) provides a comprehensive interpretation of D_s under the various experimental conditions of RPLC. This subject is under further investigation.

3.3. Mechanism of surface diffusion and molecular diffusion

Molecular diffusion is usually assumed to be an activated process. D_m is represented by the following Arrhenius type equation:

$$D_m = D_{m0} \exp\left(\frac{-E_m}{RT}\right) \quad (6)$$

where D_{m0} and E_m are the frequency factor and the activation energy of molecular diffusion, respectively. The temperature dependence of D_m is accounted for by Eq. (6).

According to the absolute rate theory [54], the

mechanism of molecular diffusion is assumed to consist of two processes. One is a hole-making process in the bulk solvent. The other is a jumping process of a solute molecule into the hole. At this time, the solvation interaction between the solute molecule and the surrounding solvent molecules must be broken. E_m should be the sum of the two contributions due to these hole-making (E_h) and jumping processes (E_j). However, E_j is relatively small compared with E_h , by a factor of about ten [54]. Calculations based on the temperature dependence of D_m in Eq. (3) showed that E_m in 70% (v/v) methanol is about 21 kJ mol⁻¹. The contributions of E_h and E_j are estimated as about 19 and 2 kJ mol⁻¹, respectively. E_m is almost equal to E_h .

The vaporization energy (ΔE_v) of a solvent corresponds to the energy needed for making a hole having the size of the solvent molecule, by removing one such molecule from the bulk phase. However, according to the absolute rate theory [54], it would be sufficient for molecular diffusion to generate a hole having a volume about 1/2 to 1/3 of that of the solute molecule. It seems that E_m is correlated with ΔE_v although the sizes of the solute and the solvent molecules are different:

$$E_m \approx E_h = \alpha \Delta E_v \quad (7)$$

ΔE_v for 70% (v/v) methanol is estimated as about 43 kJ mol⁻¹ from the temperature dependence of the viscosity. The value of α is calculated as about 0.5, which properly corresponds to the correlation between the activation energy of viscosity and ΔE_v . Analysis of the temperature dependence of the viscosity suggests that E_h is equal to about 0.4· ΔE_v ($\alpha \approx 0.4$) [54]. Viscosity corresponds to the migration of a solvent molecule in a bulk phase made of the same molecules. On the other hand, in the case of molecular diffusion, a solute molecule migrates among solvent molecules that are different. The size of the solute molecule is larger than that of the solvent molecule in most cases. It seems reasonable that α be larger for molecular diffusion than for viscosity.

A similar mechanism could be considered for surface diffusion. However, there is one major difference in this case because surface diffusion takes place in the potential field of adsorption. The adsorption energy (E_{ads}) between an adsorbate mole-

cule and the stationary phase surface must also be broken when the molecule migrates by surface diffusion. The value of E_s would be almost equal to the sum of the two contributions due to the hole-making process (E_h or $\alpha \Delta E_v$) and the breaking of the adsorption interactions (E_{ads} or $\beta(-Q_{st})$) [5,34,55]. Thus:

$$E_s = E_h + E_{ads} = \alpha \Delta E_v + \beta(-Q_{st}) \quad (8)$$

A linear correlation is expected between E_s and Q_{st} .

Fig. 6 shows linear plots of E_s against Q_{st} . The value of β is estimated as about 0.5 from the slope of the straight lines in Fig. 6. In other words, the contribution to the activation energy for surface diffusion of the partial desorption of the sorbate molecule is only half its desorption energy. So, it is still energetically favorable for the sorbed molecule to diffuse along the surface than to desorb totally and diffuse in the bulk. Furthermore, the intercepts of the straight lines in Fig. 6 are close to the value of E_h previously estimated, i.e. 19 kJ mol⁻¹. These observations are consistent with the new model for surface diffusion formulated in Eq. (5), that is, a surface-restricted molecular diffusion model, as a first approximation of the mechanism of surface diffusion.

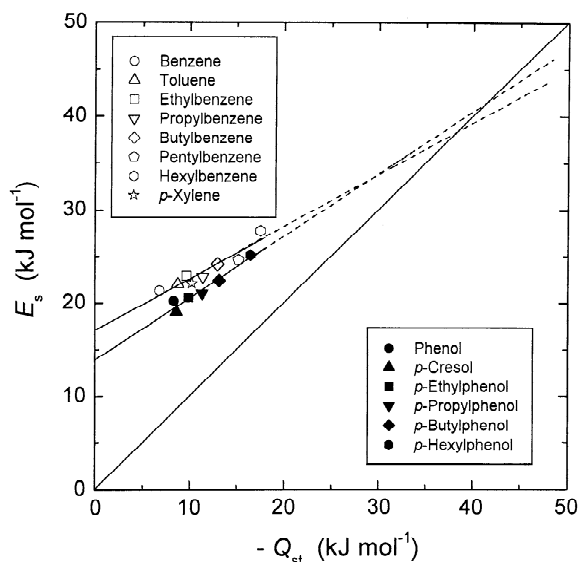


Fig. 6. Correlation between the activation energy of surface diffusion and isosteric heat of adsorption.

3.4. Interpretation of the contradictory results relating to surface diffusion

If the new model is valid, it should explain the two contradictory results described earlier. The first contradiction is the apparently unreasonable result that E_s is larger than $-Q_{st}$. In Fig. 6, the diagonal line, having a slope of unity, is steeper than the extrapolated dashed lines and intersects them at $-Q_{st} \approx 40$ kJ mol⁻¹, suggesting that E_s would be smaller than $-Q_{st}$ when $-Q_{st}$ is larger than about 40 kJ mol⁻¹. However, the value of $-Q_{st}$ in RPLC is usually smaller than this threshold [5,19,20,33,37–43,45–52]. This is why the experimental ratio $E_s/(-Q_{st})$ is larger than unity as listed in Table 2. This explanation is also supported by several experimental data obtained in other liquid–solid adsorption systems using an activated carbon and hydrophobic polymers as adsorbents and giving E_s smaller than $-Q_{st}$ but with $-Q_{st}$ larger than about 40 kJ mol⁻¹ [2,10–12]. In conclusion, there are actually three contributions to the activation energy of surface diffusion, the contribution of the partial desorption of the adsorbate molecule from the stationary phase surface and those of the hole-making and jumping processes common to all diffusion processes. It turns out that the contributions of the partial desorption and that of the hole-making process are important and should be taken into account when discussing the mechanism of surface diffusion from a thermodynamic point of view. When this is done, it becomes obvious that surface diffusion is energetically favorable. Mass transfer in the potential field of adsorption (surface diffusion) should be regarded as the original molecular migration (molecular diffusion in liquid–solid system) but restricted by the field of adsorption energy. The thermodynamic characteristics of surface diffusion in gas–solid systems can also be interpreted following this hypothesis [49]. The surface-restricted molecular diffusion model should provide a consistent interpretation for the mechanism and characteristics of surface diffusion in both liquid–solid and gas–solid systems.

The second contradiction in the experimental results concerning surface diffusion is the correlation between D_s and D_m for weakly adsorbed compounds. The following equation is derived from Eqs. (1) and (8):

$$D_s = D_{s0} \exp \left[\frac{-E_h - \beta(-Q_{st})}{RT} \right] \quad (9)$$

The numerical values of $D_{s0} \exp(-E_h/RT)$ calculated from our experimental data are between $1 \cdot 10^{-6}$ and $1 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at room temperature, when values of D_{s0} and E_h are taken as about $10^{-2} \text{ cm}^2 \text{ s}^{-1}$ and 19 kJ mol^{-1} , respectively. This result is now fairly consistent with the range of D_m . Again, the apparent contradiction arose from neglecting the energy contribution of the hole-making process that is quite significant compared with that of adsorption.

4. Conclusions

The analysis of surface diffusion data in RPLC measured under different experimental conditions demonstrates that there is an intimate correlation between surface and molecular diffusion and that surface diffusion should be regarded as molecular diffusion restricted by the potential of adsorption energy in which it takes place. These conclusions differ from the conventional concept that surface diffusion and molecular diffusion are two completely different modes of mass transfer and that there is no correlation between their mechanisms. By contrast with molecular diffusion of the sample molecule in the bulk mobile phase, the mass transfer of molecules diffusing in the potential field of adsorption near the stationary phase surface is restricted because of the adsorption energy of the adsorbate molecule. On the basis of our systematic experimental results, the surface-restricted molecular diffusion model was derived as a first approximation for the mechanism of surface diffusion. The apparent contradictions between experimental observations concerning the thermodynamic properties in RPLC and the D_s values of weakly retained compounds can adequately be explained by applying the new model for surface diffusion. This model allows a comprehensive interpretation for the mass transfer mechanism and of the intrinsic characteristics of surface diffusion in liquid–solid adsorption systems.

5. Nomenclature

a Association coefficient

D_e	Intraparticle diffusivity ($\text{cm}^2 \text{ s}^{-1}$)
D_m	Molecular diffusivity ($\text{cm}^2 \text{ s}^{-1}$)
D_{m0}	Frequency factor of molecular diffusion ($\text{cm}^2 \text{ s}^{-1}$)
D_p	Pore diffusivity ($\text{cm}^2 \text{ s}^{-1}$)
D_s	Surface diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)
D_{s0}	Frequency factor of surface diffusion ($\text{cm}^2 \text{ s}^{-1}$)
E_{ads}	Adsorptive interaction between adsorbate molecules and the stationary phase surface (kJ mol^{-1})
E_h	Activation energy of hole-making process (kJ mol^{-1})
E_j	Activation energy of jumping process (kJ mol^{-1})
E_m	Activation energy of molecular diffusion (kJ mol^{-1})
E_s	Activation energy of surface diffusion (kJ mol^{-1})
ΔE_v	Evaporative energy of a solvent (kJ mol^{-1})
K	Adsorption equilibrium constant ($\text{cm}^3 \text{ g}^{-1}$)
M	Molecular weight (–)
Q_{st}	Isosteric heat of adsorption (kJ mol^{-1})
R	Universal gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$)
T	Absolute temperature (K)
V_b	Molar volume at the normal boiling point ($\text{cm}^3 \text{ mol}^{-1}$)

Greek symbols

α	Ratio of E_h to ΔE_v
α'	Ratio of E_s to $-Q_{st}$
β	Ratio of E_{ads} to $-Q_{st}$
φ	Composition of the organic modifier in the mobile phase solvent (% , v/v)
η	Viscosity (Pa s)
μ_1	First moment (s)
μ_2	Second central moment (s^2)
ρ_p	Particle density (g cm^{-3})

Subscripts

a	Solute
sv	Solvent

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