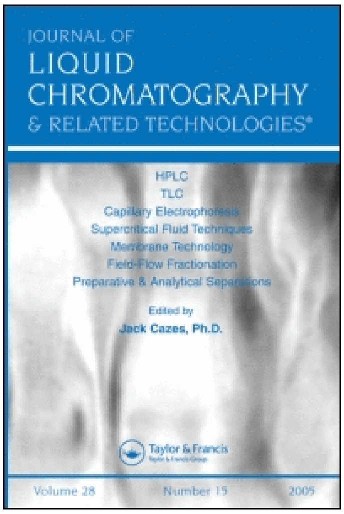

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Unified Theory of Adsorption Chromatography with Heterogenous Surfaces: Gas, Liquid and Supercritical Fluid Mobile Phases

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UNIFIED THEORY OF ADSORPTION CHROMATOGRAPHY WITH HETEROGENOUS SURFACES: GAS, LIQUID AND SUPER-CRITICAL FLUID MOBILE PHASES

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ABSTRACT

In an earlier study, equations describing solute retention in liquid-solid chromatography (LSC) with a homogeneous adsorbent and a binary liquid mobile phase were derived through application of statistical thermodynamics and a mean-field lattice model. That investigation is extended here to obtain and interpret new equations for energetically and/or structurally heterogeneous adsorbents modelled in terms of a discrete distribution of internally homogeneous surface "patches". Then, exploiting the isomorphism between binary-liquid and single-fluid critical behavior, the unified theory of the title, applicable to single-component mobile phases, is derived and discussed in some detail. The primary results, equations 23-29, confirm that the natural mobile-phase state variables are its reduced temperature and reduced density. These equations should find their widest use in supercritical fluid chromatography. As a quantitative example of its utility and efficacy, the theory is applied here to gas-solid chromatography (GSC) with a highly adsorbable mobile phase, where, at higher modifier pressures, the stationary phase becomes more like that encountered in LSC than in GSC. The compression of carrier liquid in contact with the adsorbent surface in LSC is also briefly considered.

INTRODUCTION

This paper represents a further contribution to the development of a unified theory of chromatography. In our earlier studies (1,2), fluid-liquid (absorption) chromatography was treated extensively. Quite recently (3), we developed a unified molecular theory of fluid-solid (adsorption) chromatography for homogeneous surfaces. The present advancement extends this work to heterogeneous adsorbents characterized by a discrete distribution of "patches" of energetically and/or structurally distinguishable adsorption sites (4).

Starting with equations already derived for the solute distribution coefficient with a binary liquid mobile phase and a homogeneous adsorbent and applying straightforward thermodynamics, new equations are derived for the case of heterogeneous adsorbents. Then, exploiting the isomorphism between the upper critical solution temperature (U.C.S.T.) in a binary liquid system and the liquid-vapor critical point in a single-component fluid system (5), a general equation is derived for the distribution coefficient in a chromatographic system where the adsorbent is heterogeneous and the mobile phase is a single-component ideal gas, moderately nonideal gas, supercritical fluid or liquid.

In view of the more advanced state of theory and theoretical treatments of experimental data in gas and liquid chromatography, this unified theory should ultimately find its widest application in the area of supercritical fluid chromatography (SFC), where there is renewed interest in packed-column systems containing unmodified or modified adsorbents (6-11). However, as examples of its utility, the unified theory is applied here to liquid-solid chromatography to examine the compression of carrier liquid in the vicinity of a solid surface (12), and, in more detail, to low-pressure gas-solid chromatography with a highly adsorbable vapor (volatile modifier) in the carrier gas (13,14).

THEORY OF LIQUID-SOLID CHROMATOGRAPHY: BINARY MOBILE PHASE AND HETEROGENEOUS ADSORBENT

The derivations in this section are based on results recently obtained for homogeneous adsorbents (3). In common with our earlier treatments of liquid-solid (adsorption) and liquid-bonded phase chromatography (15-18), statistical thermodynamics and a mean-field lattice model were utilized to derive the relevant equations to describe the equilibrium distribution of solute between a binary liquid mobile phase and a surface phase with a homogeneous adsorbent, and hence, solute retention in such systems. Both entropy and interaction energy effects were rigorously included in treating the competitive equilibrium, at the molecular level, among solvent and solute molecules distributed between generally nonideal mobile and stationary phases, all components being nonelectrolytes. The stationary phase was assumed to be an energetically and structurally homogeneous, planar surface on which is adsorbed (via parallel-layer adsorption) a monolayer of solvent and solute molecules of uniform film thickness.

Denoting (i) the dimensionless coefficient describing the distribution of solute at infinite dilution between the mobile-phase solvent and the monolayer of adsorbed solvent by K, (ii) the adsorption sites of type i (only one type for a homogeneous adsorbent), solute component, strong (good) solvent component, weak (poor) solvent component and solvent mixture by the subscripts i, a, b, c and x (=b+c), respectively, and (iii) the experimental variables of absolute temperature (in kelvin) and solvent volume fraction (with m = mobile phase and i = stationary-phase or surface-phase sites of type i) by T and θ, respectively, the following sets of equations may be written (3),

in terms of the strong solvent (b):

$$\ell n\ K_{b(i)} = [1 - (r_a/r_b)]\ \ell n\ [(z_m-1)/(z_s-1)] + [z_e f_i r_a/k_B T][\varepsilon'_{bi} - \varepsilon'_{ai} + \varepsilon_{ab} - \varepsilon_{bb}] \tag{1}$$

$$\ell n\ K_{x(i)} = \ell n\ K_{b(i)} + (r_a/r_b)\ \ell n\ (\theta_{b(i)}/\theta_{b(m)}) + [z_e r_a/k_B T][(1-f_i)\theta_{b(m)} - (1-2f_i)\theta_{b(i)} - f_i] \cdot [\varepsilon_{ab} - \varepsilon_{ac} + \varepsilon_{bc} - \varepsilon_{bb}] \tag{2}$$

or

$$\ell n\ K_{x(i)} = \ell n\ K_{b(i)} + (r_a/r_b)\ \ell n\ (\theta_{b(i)}/\theta_{b(m)}) + r_a[(1-f_i)\theta_{b(m)} - (1-2f_i)\theta_{b(i)} - f_i][\chi_{ab} + \chi_{bc} - \chi_{ac}] \tag{3}$$

and in terms of the weak solvent (c):

$$\ell n\ K_{c(i)} = [1 - (r_a/r_c)]\ \ell n\ [(z_m-1)/(z_s-1)] + [z_e f_i r_a/k_B T][\varepsilon'_{ci} - \varepsilon'_{ai} + \varepsilon_{ac} - \varepsilon_{cc}] \qquad (4)$$

$$\ell n\ K_{x(i)} = \ell n\ K_{c(i)} + (r_a/r_c)\ \ell n\ [(1-\theta_{b(i)})/(1-\theta_{b(m)})] + [z_e r_a/k_B T][(1-2f_i)\theta_{b(i)} - (1-f_i)\theta_{b(m)}] \cdot [\varepsilon_{ac} - \varepsilon_{ab} + \varepsilon_{bc} - \varepsilon_{cc}] \qquad (5)$$

or

$$\ell n\ K_{x(i)} = \ell n\ K_{c(i)} + (r_a/r_c)\ \ell n\ [(1-\theta_{b(i)})/(1-\theta_{b(m)})] + r_a[(1-2f_i)\theta_{b(i)} - (1-f_i)\theta_{b(m)}][\chi_{ac} + \chi_{bc} - \chi_{ab}] \qquad (6)$$

where χ_{jk}, the interaction parameter involving molecules of types j and k (j,k = a, b, c), is given by

$$\chi_{jk} = [z_e/2k_B T][2\varepsilon_{jk} - \varepsilon_{jj} - \varepsilon_{kk}]. \qquad (7)$$

In the above lattice-model equations for a homogeneous adsorbent, the molecular parameters are defined as follows (3):

r_j = number of segments comprising a molecule of type j (proportional to the van der Waals volume of j)

z_m = three-dimensional (mobile phase), nearest-neighbor lattice coordination number (z_m = 6 for a simple cubic lattice)

z_s = two-dimensional (surface phase), nearest-neighbor lattice coordination number (z_s = 4 for a square planar lattice)

z_e = number of nearest-neighbor external contacts of a molecular segment ($4 < z_e < 6$; $z_e \rightarrow 4$ as $r_j \rightarrow \infty$; $z_e = 6$ for $r_j = 1$)

f_i = fraction of the surface of an adsorbed molecule in contact with adsorption sites of type i (assumed to be the same for the solute and both solvent molecules)

ε_{jk} = attractive interaction energy between nearest-neighbor, single segments on molecules of type j and type k ($j,k = a,b,c$; $\varepsilon_{jk} < 0$)

ε'_{jk} = attractive interaction free energy between a molecular segment of type j and an adsorption site of type i; also, the adhesion free energy per molecular segment ($\varepsilon'_{ji} < 0$).

In eqn. 1 and 4 (neat solvents) the first term on the r.h.s. is associated with the change in configurational entropy for the transfer of a solute molecule from the mobile phase to the stationary phase and the concomitant, reverse transfer of r_a/r_b (pure b) or r_a/r_c (pure c) solvent molecules, while the second term reflects the exchange interaction free energy associated with the displacement process. In eqn. 2 (or 3) and 5 (or 6) the second term on the r.h.s. is associated with the statistics of the displacement process, while the third term reflects the exchange interaction energy involving the solute and solvent molecules (but not the surface), and associated with the competitive equilibrium.

To extend these equations to heterogeneous adsorbents, a "patch" model of the surface is employed (4). In this model it is assumed that the adsorbent consists of a collection of patches, each incorporating a very large number of adsorption sites of a given type (internal homogeneity). That is, the adsorbent is not microscopically heterogeneous; solute and solvent molecules are assumed to adsorb essentially on an array of sites of one type or another within a given patch, and not across the boundary between dissimilar patches. It is further assumed that the internally homogeneous patches are energetically distinguishable (by virture of different ε'_{ji} values) and/or structurally distinguishable (by virture of different f_i values) from each other.

Therefore, if there are n different types of such patches of adsorption sites (i = 1,2,3,....n) and the fraction of the total surface consisting of type-i patches is ϕ_i, where

$$\sum_{i=1}^{n} \phi_i = 1 \qquad , \tag{8}$$

and if the thickness of the surface phase is uniform throughout the entire adsorbent, then the observed (dimensionless) solute distribution coefficient for the heterogeneous adsorbent, K_x, is simply related to the distribution coefficient corresponding to a wholly homogeneous adsorbent containing only type-i sites, $K_{x(i)}$, by

$$K_x = \sum_{i=1}^{n} \phi_i K_{x(i)} \qquad . \tag{9}$$

In terms of a standard specific retention volume for the solute, V_s°, having units of mL solvent/m^2 surface, eqn. 9 becomes

$$V^\circ = \tau_s \sum_{i=1}^{n} \phi_i K_{x(i)} = \sum_{i=1}^{n} \phi_i V^\circ_{s(i)} \qquad (10)$$

where τ_s is the specific volume of the surface phase (or, essentially, the surface film thickness), again in units of mL solvent/m^2 surface.

For the special case of monomeric solute and solvent molecules ($r_a = r_b = r_c = 1$; $z_e = 6$) and a surface with no structural inhomogeneity (for monomers, $f_i = 1/6$ for all i), eqn. 1-9 reduce to similar equations derived and discussed previously (15,16). Also, continuing to designate component b as the "good" solvent, i.e., the preferentially adsorbed solvent component, and component c as the "poor" solvent, and considering the special case where $\theta_{b(i)} \to 1$ ($\theta_{c(i)} \to 0$) for all i and the surface exhibits no structural inhomogeneity (f_i is the same for all i; $f_i = f_s$ = constant), eqn. 3 and 9 yield

$$K_x = K_b \cdot \theta_{b(m)}^{-\nu_{ab}} \cdot \exp[-r_a(1-f_s)(1-\theta_{b(m)})(\chi_{ab}+\chi_{bc}-\chi_{ac})] \qquad (11)$$

where $\nu_{ab} = r_a/r_b$ and $K_b = \sum_{i=1}^{n} \phi_i K_{b(i)}$. If, in addition, cancellation of the molecular interaction energy terms is assumed ($\chi_{ab} + \chi_{bc} - \chi_{ac} = 0$), then eqn. 11 reduces to the familiar Snyder-Soczewinski expression (18-20):

$$\ln K_x = \ln K_b - \nu_{ab} \ln \theta_{b(m)} \quad . \qquad (12)$$

Therefore, the equations derived in the present, more refined treatment of liquid-solid chromatography with binary mobile phases and heterogeneous adsorbents are seen to reduce to earlier and more familiar equations in special (but restrictive) cases.

Finally, full application of the general set of equations, i.e., eqn. 1 and 2 (or 3), or eqn. 4 and 5 (or 6), with eqn. 9, requires the adsorption isotherm describing the equilibrium distribution of the solvent components between the mobile and stationary phases. Scaling the molecular system to the smallest molecule by letting $r_c = 1$ (15,17), one obtains for type-i sites (3):

$$\ell n\ [(1-\theta_{b(m)})^{r_b}/\theta_{b(m)}] + (r_b-1)\ \ell n\ [(z_m-1)/(z_s-1)]$$
$$+ (z_e f_i r_b/k_B T)(\varepsilon'_{bi}-\varepsilon'_{ci}+\varepsilon_{cc}-\varepsilon_{bc}) + 2r_b(1-f_i)\chi_{bc}\theta_{b(m)} =$$
$$\ell n\ [(1-\theta_{b(i)})^{r_b}/\theta_{b(i)}] + 2r_b(1-2f_i)\chi_{bc}\theta_{b(i)} \qquad (13)$$

where, from eqn. 7

$$\chi_{bc} = (z_e/2k_B T)(2\varepsilon_{bc}-\varepsilon_{bb}-\varepsilon_{cc}) \qquad (14)$$

and where $i = 1,2,3,\ldots.n$, and $\theta_{b(i)}$ and $\theta_{c(i)}$ represent solvent volume fractions in the surface phase associated with type-i patches. The overall or composite isotherm ($\theta_{b(s)}$ vs. $\theta_{b(m)}$, or $\theta_{c(s)}$ vs. $\theta_{c(m)}$) can then be constructed from

$$\theta_{b(s)} = \sum_{i=1}^{n} \phi_i \theta_{b(i)} \qquad (15)$$

where $\theta_{c(s)} = 1 - \theta_{b(s)}$, $\theta_{c(m)} = 1 - \theta_{b(m)}$, and $\theta_{b(1)}$, $\theta_{b(2)}$, $\theta_{b(3)}, \ldots.\theta_{b(n)}$ can be determined from eqn. 13.

UNIFIED THEORY OF FLUID-SOLID CHROMATOGRAPHY: NEAT MOBILE PHASE AND HETEROGENEOUS ADSORBENT

In this section we take the final results from the previous section and, as before (2,3), exploit the isomorphism between the critical behavior in a binary liquid mixture and that in a neat (single-component) fluid, and obtain a universal equation for fluid-solid (adsorption) chromatography with heterogeneous adsorbents, where the neat mobile phase may be a gas, liquid or supercritical fluid.

The most convenient set of fundamental equations with which to work is: eqn. 4 (for $\ell n\ K_{c(i)}$), eqn. 6 (for $\ell n\ K_{x(i)}$, in terms of χ_{jk}) in conjunction with eqn. 9, and eqn. 13 (mixed-solvent adsorption isotherm) in conjunction with eqn. 15, where we continue to scale the system by letting $r_c = 1$ in eqn. 4 and 6.

Equations 4, 6 and 13 may be manipulated into reduced form by first noting the critical solution condition applicable to the binary-liquid mobile phase (21):

$$T^* = 2T\chi_{bc}r_b/(1 + \sqrt{r_b})^2 \tag{16}$$

$$\theta_b^* = (1 + \sqrt{r_b})^{-1} \tag{17}$$

where χ_{bc} is given by eqn. 14, T^* refers to the U.C.S.T. (above which the b+c solvent mixture is homogeneous over the entire composition region) and θ_b^* refers to the critical volume fraction of "good" solvent, i.e., the composition corresponding to T^* in the T-$\theta_{b(m)}$ phase diagram (21). Introducing reduced variables (subscript R)

$$T_R = T/T^* = (1 + \sqrt{r_b})^2/2r_b X_{bc} \tag{18}$$

$$\theta_{b(m),R} = \theta_{b(m)}/\theta_b^* = \theta_{b(m)}(1 + \sqrt{r_b}) \tag{19}$$

and making use of eqn. 18 in eqn. 4, 6 and 13 (with $r_c = 1$ in all), one obtains

$$\begin{aligned}\ln K_{c(i)} &= (1-r_a) \ln [(z_m-1)/(z_s-1)] \\ &+ [r_a(1+\sqrt{r_b})^2 f_i/r_b T_R][(\varepsilon'_{ci}-\varepsilon'_{ai}+\varepsilon_{ac}-\varepsilon_{cc})/(2\varepsilon_{bc}-\varepsilon_{bb}-\varepsilon_{cc})]\end{aligned} \tag{20}$$

$$\begin{aligned}\ln K_{x(i)} = \ln K_{c(i)} &+ r_a \ln [(1-\theta_{b(i)})/(1-\theta_{b(m)})] \\ &+ [r_a(1+\sqrt{r_b})^2/r_b T_R][(1-2f_i)\theta_{b(i)} - (1-f_i)\theta_{b(m)}] \cdot \\ &[(X_{ac}+X_{bc}-X_{ab})/2X_{bc}]\end{aligned} \tag{21}$$

$$\begin{aligned}&\ln [(1-\theta_{b(m)})^{r_b}/\theta_{b(m)}] + (r_b-1) \ln [(z_m-1)/(z_s-1)] \\ &+ [(1+\sqrt{r_b})^2 f_i/T_R][(\varepsilon'_{bi}+\varepsilon'_{ci}+\varepsilon_{cc}-\varepsilon_{bc})/(2\varepsilon_{bc}-\varepsilon_{bb}-\varepsilon_{cc})] \\ &+ [(1+\sqrt{r_b})^2(1-f_i)/T_R]\theta_{b(m)} = \\ &\ln [(1-\theta_{b(i)})^{r_b}/\theta_{b(i)}] + [(1+\sqrt{r_b})^2(1-2f_i)/T_R]\theta_{b(i)}\end{aligned} \tag{22}$$

Invoking the analogy between the critical behavior in a binary liquid system and that in a single-component fluid system (5), we utilize the correspondence between the volume fraction of "good" solvent (b) in the former and the volume fraction of space occupied by the molecules in the latter, and similarly with the "poor" solvent (c) and unoccupied space. It follows from eqn. 19 that

$$\theta_{b(m),R} = \rho_{b(m),R} = \rho_{b(m)}/\rho_b^* = \theta_{b(m)}(1+\sqrt{r_b}) \tag{23}$$

where $\theta_{b(m)}$ now becomes the volume fraction of physical space actually occupied by the hard cores of the molecules in the single-component carrier fluid (i.e., the fraction relative to what it would be in a hypothetical close-packed molecular arrangement of these cores, for which $\theta_{b(m)} = 1$), $1 - \theta_{b(m)}$ becomes the volume fraction of "empty" (physically unoccupied) space (and similarly for $\theta_{b(i)}$ and $1 - \theta_{b(i)}$ in the adsorbed monolayer), $\rho_{b(m)}$ is the actual density of the mobile-phase fluid, ρ_b^* is its critical density and $\rho_{b(m),R}$ is its reduced density. Also, $T_R = T/T_b^*$ becomes the usual reduced temperature of a single-component fluid, where T_b^* is its critical temperature.

This correspondence also indicates that $K_{c(i)}$ may be replaced by $K_{o(i)}$, the infinite-dilution solute distribution coefficient for ideal gas-solid chromatography, GSC ($\rho_{b(m)} \to 0$), associated with adsorption sites of type i. Furthermore, it follows that all interactions formerly involving solvent component c, but now representing unoccupied or void space in the model, may be set equal to zero, i.e., $\varepsilon'_{ci} = 0$ and $\varepsilon_{jc} = 0$ ($j = a,b,c$). Accordingly, with the aid of eqn. 7, eqn. 20-22 become

$$\ell n\ K_{o(i)} = (1-r_a)\ \ell n\ [(z_m-1)/(z_s-1)] + [r_a\ (1+\sqrt{r_b})^2 f_i/r_b T_R][\varepsilon'_{ai}/\varepsilon_{bb}] \tag{24}$$

$$\ell n\ K_i = \ell n\ K_{o(i)} + r_a\ \ell n\ [(1-\theta_{b(i)})/(1-\theta_{b(m)})] + [r_a(1+\sqrt{r_b})^2/r_b T_R][(1-2f_i)\theta_{b(i)} - (1-f_i)\theta_{b(m)}][\varepsilon_{ab}/\varepsilon_{bb}] \tag{25}$$

$$\begin{aligned}&\ell n\,[(1-\theta_{b(m)})^{r_b}/\theta_{b(m)}] + (r_b-1)\,\ell n\,[(z_m-1)/(z_s-1)]\\&- [(1+\sqrt{r_b})^2 f_i/T_R][\varepsilon'_{bi}/\varepsilon_{bb}] + [(1+\sqrt{r_b})^2(1-f_i)/T_R]\theta_{b(m)} =\\&\ell n\,[(1-\theta_{b(i)})^{r_b}/\theta_{b(i)}] + [(1+\sqrt{r_b})^2(1-2f_i)/T_R]\theta_{b(i)}\end{aligned} \tag{26}$$

where, from eqn. 9 and 10

$$K = \sum_{i=1}^{n} \phi_i K_i \tag{27}$$

$$V_s^\circ = \tau_s \sum_{i=1}^{n} \phi_i K_i = \tau_s K = \sum_{i=1}^{n} \phi_i V_{s(i)}^\circ . \tag{28}$$

In eqn. 25 and 27, K_i (replacing $K_{x(i)}$) is the solute distribution coefficient for a homogeneous adsorbent containing only type-i sites, when the mobile-phase density is $\rho_{b(m)}$, which, in turn, is related to $\theta_{b(m)}$ through eqn. 23. K (replacing K_x) is the observed distribution coefficient for a heterogeneous adsorbent at a mobile-phase density of $\rho_{b(m)}$, and similarly for $V_{s(i)}^\circ$ and V_s° in eqn. 28. Also, the composite adsorption isotherm for the carrier fluid can be constructed from eqn. 26 and

$$\theta_{b(s)} = \sum_{i=1}^{n} \phi_i \theta_{b(i)} \tag{29}$$

where $\theta_{b(i)}$ is now the volume fraction of physical space occupied by adsorbed carrier molecules in that part of the surface phase (assumed to be a monolayer) containing patches of type i (i = 1,2,3,...n). Note that eqn. 23-29, which comprise the unified molecular theory for heterogeneous adsorbents, are applicable to single-component gaseous, liquid and supercritical-fluid mobile phases.

Equations 26 and 29, which describe the distribution of fluid between the mobile and stationary phases, are required to determine the equilibrium values of the $\theta_{b(i)}$ (hence, the composite or average surface-phase volume fraction, $\theta_{b(s)}$) for a given mobile-phase density, $\rho_{b(m)}$. In eqn. 24 (ideal GSC), the first term on the r.h.s. stems from the change in the molar configurational entropy of the solute when it is transferred from an ideal-gas mobile phase to a bare, adsorbent stationary phase containing patches of type i. The second term reflects the molar interaction free energy of adsorption of the solute on bare surface patches of type i. With knowledge of the frequency distribution of the n different types of surface patches (ϕ_1, ϕ_2, ϕ_3,....ϕ_n), the observed solute distribution coefficient for ideal GSC, K_o, may be determined from eqn. 24 and 27.

In eqn. 25, which links ideal GSC to nonideal GSC, supercritical fluid-solid chromatography (SFSC) and liquid-solid chromatography (LSC), the second term on the r.h.s. is associated with the statistics of the displacement process (the relative availability of void space in the two phases), while the third term reflects the exchange interaction energy associated with the competitive equilibrium between the solute and carrier-fluid molecules. Note that eqn. 25 may also be written in terms of capacity factors (replacing K_i and $K_{o(i)}$ by, respectively, k_i' and $k_{o(i)}'$) or retention volumes.

At this point, several special cases of eqn. 25 and 26 could be considered. However, with the exception of one to be applied in the next section, these are deferred for future study. Consider the case where $\theta_{b(i)} \gg \theta_{b(m)} \approx 0$, for all i, i.e., where there is rapid and appreciable buildup of the carrier fluid on all portions of the adsorbent surface, even at very low mobile-phase densities (or pressures). Accordingly, in this limit, eqn. 25 and 26 become:

$$\begin{aligned} \ell n\, K_i &= \ell n\, K_{o(i)} + r_a\, \ell n\, (1-\theta_{b(i)}) \\ &\quad + [r_a(1+\sqrt{r_b})^2/r_b T_R][\varepsilon_{ab}/\varepsilon_{bb}][(1-2f_i)\theta_{b(i)}] \end{aligned} \tag{30}$$

$$\begin{aligned} \ell n\, \theta_{b(m)} &= \ell n\, \theta_{b(i)} - r_b\, \ell n\, (1-\theta_{b(i)}) \\ &\quad - [(1+\sqrt{r_b})^2(1-2f_i)/T_R]\theta_{b(i)} \\ &\quad + (r_b-1)\, \ell n\, [(z_m-1)/(z_s-1)] \\ &\quad - [(1+\sqrt{r_b})^2 f_i/T_R][\varepsilon'_{bi}/\varepsilon_{bb}]. \end{aligned} \tag{31}$$

APPLICATIONS OF THE UNIFIED THEORY

As the first and most detailed example of its utility, the present extension of the unified theory of adsorption chromatography is applied here to analyze the GSC retention behavior, at 10°C, of n-butane (the solute; component a) on graphitized carbon black (Carbopack C) modified by adsorption of propane (the fluid phase; component b) from the carrier-gas stream (22). Parcher et al. (14, 23) obtained both retention and adsorption-isotherm data for this system, which is a particularly interesting one for the following reasons: (i) With increasing propane pressure, the standard specific retention volume (V_s°) of n-butane first exhibits a minimum, then a maximum and finally a rapid decrease. It has not been possible to account for the minimum on the basis of a homogeneous-adsorbent model (3, 14); (ii) At the higher propane pressures studied, the surface coverage of propane approaches liquid-like densities (14). Therefore, the surface phase becomes more like that in LSC than in GSC.

The molecular segmental numbers for propane and n-butane are $r_b = 8.799$ and $r_a = 11.195$, respectively (3). From the critical density of propane, $\rho_b^* = 0.217$ g/mL, and eqn. 23, we have

$$\theta_{b(m)} = 1.162\ \rho_{b(m)}\ \ (\text{g/mL}). \tag{32}$$

Since the propane pressure, $P_{b(m)}$, corresponding to monolayer coverage of adsorbed propane in ca. 10^3 torr (14), ideal-gas behavior may be safely assumed, with negligible error, to relate $\rho_{b(m)}$ in eqn. 32 to $P_{b(m)}$:

$$\theta_{b(m)} = 2.901 \times 10^{-6}\ P_{b(m)}\ \ (\text{torr}), \tag{33}$$

Equation 33 establishes the relationship between a model variable and an experimental state variable. With $P_{b(m)} \approx 10^3$ torr, $\theta_{b(m)} \approx 0.003$, thus justifying the application of eqn. 30 and 31, which are based on the condition $\theta_{b(m)} \approx 0$.

The critical temperature of propane, T_b^*, is 369.8 K. Thus, the other state variable, the reduced temperature, T_R, has a value of 0.766 at 283.2 K. The only other molecular parameter to which one can securely assign a value at this point is $\varepsilon_{ab}/\varepsilon_{bb} = 1.000$

(butane-propane and propane-propane segmental interaction energies should be the same).

Assuming a discrete, bimodal distribution of adsorption sites ($n = 2$), writing eqn. 30 in terms of V°_s, and substituting into it the numerical values determined or assigned above, one obtains

$$\ln V^\circ_{s(i)} = \ln V^\circ_{s,o(i)} + 11.195 \ln (1-\theta_{b(i)}) + 26.142(1-2f_i)\theta_{b(i)} \qquad (34)$$

where $i = 1, 2$, and $V^\circ_{s(i)}$ and $V^\circ_{s,o(i)}$ correspond to K_i and $K_{o(i)}$, respectively. Also, from eqn. 28

$$V^\circ_s = \tau_s(\phi_1 K_1 + \phi_2 K_2) = \phi_1 V^\circ_{s(1)} + \phi_2 V^\circ_{s(2)} \qquad (35)$$

where ϕ_1 and ϕ_2 are, respectively, the fractions of type-1 and type-2 adsorption sites (with $\phi_1 + \phi_2 = 1$) and τ_s is the (uniform) surface-phase film thickness (here, in units of mL propane/m^2 surface).

Similarly, from eqn. 24, with $z_m = 6$ and $z_s = 4$, we have

$$\ln K_{o(i)} = -5.208 + 26.142 f_i(\varepsilon'_{bi}/\varepsilon_{bb}) \qquad (36)$$

where $i = 1, 2$ and ε'_{ai} has been replaced by ε'_{bi}. (The adhesion free energy of a unit segment of butane with a type-i surface site should be approximately the same as that of propane.) Also, from eqn. 28

$$V^\circ_{s,o} = \tau_s(\phi_1 K_{o(1)} + \phi_2 K_{o(2)}) = \phi_1 V^\circ_{s,o(1)} + \phi_2 V^\circ_{s,o(2)} \; . \qquad (37)$$

Turning to eqn. 31, the applicable adsorption isotherm when $\theta_{b(i)} >> \theta_{b(m)} \approx 0$, substitution of numerical values yields

$$\ell n\ \theta_{b(m)} = \ell n\ \theta_{b(i)} - 8.799\ \ell n\ (1-\theta_{b(i)}) - 20.547(1-2f_i)\theta_{b(i)} + 3.984 - 20.547f_i(\varepsilon'_{bi}/\varepsilon_{bb}) \qquad (38)$$

where i = 1, 2 and, from eqn. 29

$$\theta_{b(s)} = \phi_1\theta_{b(1)} + \phi_2\theta_{b(2)} = C_{b(s)}\cdot\beta \qquad (39)$$

where $\theta_{b(s)}$ is the model surface coverage (volume fraction of space physically occupied by propane molecules in the surface phase), $C_{b(s)}$ is the experimental surface coverage (in μmol adsorbed propane/m^2 surface) and β is a proportionality constant relating the two.

The retention volume and adsorption isotherm results (14, 23) were analyzed using eqn. 33-39. The unknowns are: $\varepsilon'_{b1}/\varepsilon_{bb}$, $\varepsilon'_{b2}/\varepsilon_{bb}$, f_1, f_2, $\phi_1(=1-\theta_2)$, τ_s and β. Preliminary analysis indicated that $\varepsilon'_{b1}/\varepsilon_{bb} \approx \varepsilon'_{b2}/\varepsilon_{bb}$, which was not altogether surprising in view of the fact that the interactions between each of the nonpolar alkane components and the carbonaceous surface should be predominantly through dispersion, and, hence, should depend mainly on the polarizability of the alkane molecules. (This implies that the surface heterogeneity is structural ($f_1 \neq f_2$) rather than energetic.) Accordingly, ε'_{b1} was set equal to ε'_{b2} and denoted as ε'_{bs}. With this assignment, interative analysis of the data gave the following best-fit results:

$\varepsilon'_{bs}/\varepsilon_{bb} = 2.179$

$\phi_1 = 0.0055$

$\phi_2 = 0.9945$

$f_1 = 0.321$

$f_2 = 0.241$

$\beta = 0.1052$

$\tau_s = 0.616 \times 10^{-4}$ (mL propane/m^2 surface)

from which one calculates, using eqn. 36 and 37, values of $V^\circ_{s,o(1)} = 289.98$, $V^\circ_{s,o(2)} = 3.04$ and $V^\circ_{s,o} = 4.62$ (the experimental value), all in mL propane/m^2 surface.

The result for $\varepsilon'_{bs}/\varepsilon_{bb}$ may be compared with that determined for an assumed homogeneous adsorbent, 2.114 (3). The results for ϕ_1, ϕ_2, f_1 and f_2 suggest that the structural inhomogeneity, as measured by ϕ_1, is quite small (ca. 0.5%) and that adsorbed solute and solvent molecules have a greater fraction of their surface in contact with type-1 sites ($f_1 \approx 1/3$) than with type-2 sites ($f_1 \approx 1/4$) on the adsorbent. Nonetheless, even though ϕ_1 is small, at low propane pressures the greater f_1 value has a pronounced effect on V°_s and, in fact, is responsible for the observed minimum in V°_s as a function of $C_{b(s)}$ (vide infra). As to a possible explanation of the ϕ_1, ϕ_2, f_1 and f_2 values, a plausible picture is that the adsorbent consists mainly of patches of a uniform basal-plane surface with which the molecules make the expected contact ($f_1 \approx 1/4$ (3)), but also contains a very small fraction of confined-geometry sites of higher molecule-surface overlap ($f_2 \approx 1/3$), perhaps in the low-surface-area interstices of the column packing (12). Taken at face value, all of this suggests that Carbopack C is apparently not a heterogeneous adsorbent in the usual (energetic) sense, at least toward alkane adsorbates.

Shown in Figure 1 are plots of $\theta_{b(1)}$ and $\theta_{b(2)}$ as a function of $\theta_{b(m)}$, calculated using eqn. 38. With increasing $\theta_{b(m)}$ (or, from eqn. 33, propane pressure, $P_{b(m)}$), the initial buildup of adsorbed propane on surface "patches" of type 1 is much more rapid than on those of type 2. At all pressures, $\theta_{b(1)} > \theta_{b(2)}$ ($\gg \theta_{b(m)}$), because $f_1 > f_2$. However, since $\phi_2 \gg \phi_1$, the overall or composite isotherm, $\theta_{b(s)}$ vs. $\theta_{b(m)}$ (eqn. 39), is essentially determined by type-2 surface sites, even at very low $\theta_{b(m)}$. (For example, at $\theta_{b(m)} = 5.6 \times 10^{-6}$ or $P_{b(m)} \approx 2$ torr, $\phi_1\theta_{b(1)} = 0.0007$, $\phi_2\theta_{b(2)} = 0.0050$ and $\theta_{b(s)} = 0.0057$.)

Shown in Figure 2 is the overall adsorption isotherm in terms of experimental variables ($C_{b(s)}$ vs. $P_{b(m)}$), calculated from eqn. 33, 38 and 39. The excellent agreement between the calculated and measured isotherms is evident. The monolayer capacity of adsorbed propane on the Carbopack C used was estimated to be 5.49 μmol propane/m^2 adsorbent (14). The $\theta_{b(s)}$ value corresponding to this capacity is 5.49 β = 0.578, which, from the surface-phase counterpart of eqn. 32, indicates an adsorbed-propane density of $\rho_{b(s)} = 0.497$ g/mL, compared to an orthobaric liquid density of 0.515 g/mL for bulk propane at 10°C (12). This $\theta_{b(s)}$ value also suggests that if the propane molecules were close-packed in the surface phase (a physical impossibility, given the prohibitive

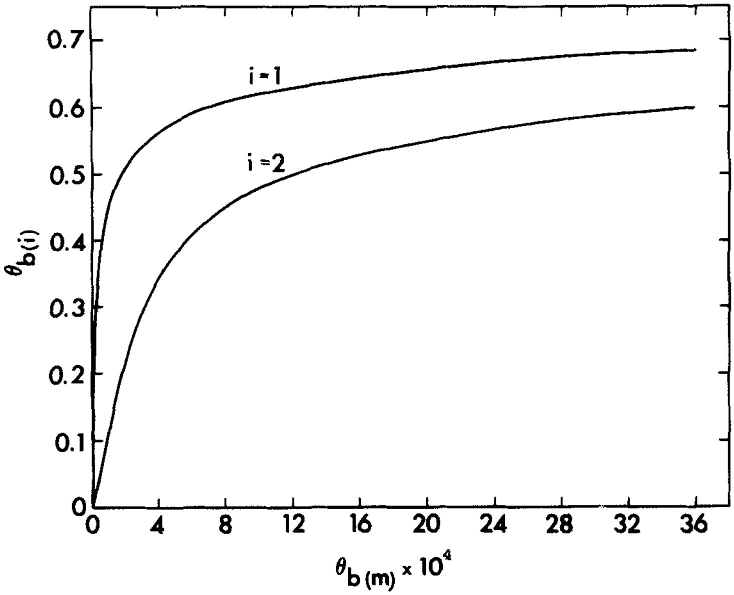

FIGURE 1. Occupied volume fractions in the surface phase associated with type-1 ($\theta_{b(1)}$) and type-2 ($\theta_{b(2)}$) adsorption sites as a function of the occupied volume fraction in the mobile phase ($\theta_{b(m)}$), for propane at 10°C; curves constructed using eqn. 38.

repulsive forces that would have to be overcome), the monolayer capacity would be 9.51 μmol/m^2 (for $\theta_{b(s)} = 1$). Viewed another way, with the estimate of 30.1 Å^2 for the actual specific surface area of a propane molecule adsorbed on Carbopack C (14), this suggests a realistic impenetrable-core area of 17.4 Å^2.

The reasonableness and consistency of the model results are further confirmed by a comparison of the specific volume or film

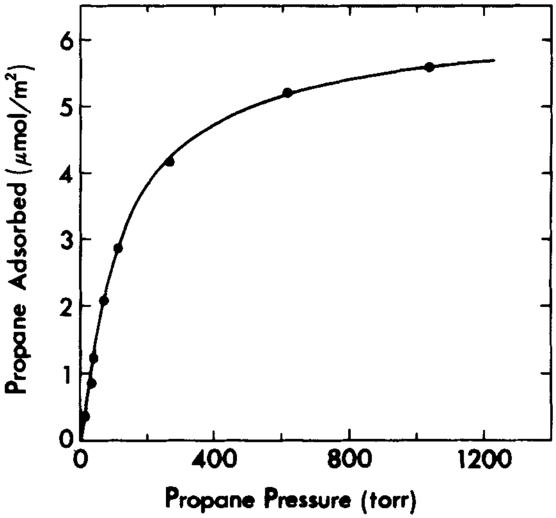

FIGURE 2. $C_{b(s)}$ vs. $P_{b(m)}$: adsorption isotherm of propane on Carbopack C at 10°C (14, 23). Solid line (theory) constructed using eqn. 33, 38 and 39.

thickness of the adsorbed monolayer. From the density of adsorbed propane in the surface phase and a monolayer coverage of 5.49 μmol/m^2 (both estimated quantities), a specific volume of 4.87 x 10^{-4} mL/m^2 (film thickness of 4.9 Å) is calculated, compared to the fitted result of τ_s = 6.16 x 10^{-4} mL/m^2 (film thickness of 6.2 Å). Although the latter is only some 25% higher than the former and, given the assumptions and approximations made, one may consider this to be reasonable agreement, the former is a physically more sensible value (12), and this small discrepancy may indicate that the simple monolayer model is not

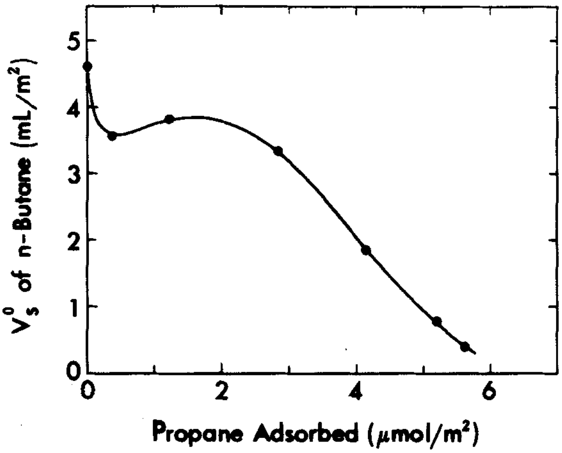

FIGURE 3. V_s^o vs. $C_{b(s)}$: specific retention volume of n-butane as a function of the amount of propane adsorbed on Carbopack C at 10°C (14, 23). Solid line (theory) constructed using eqn. 34-37.

fully adequate and/or the film thickness is not uniform throughout the surface phase.

Turning now to the solute retention volume data, it is seen in Figure 3 that the present theory successfully predicts both a minimum (at $C_{b(s)} \approx 0.42$) and a maximum (at $C_{b(s)} \approx 1.59$) in V_s^o, as well as a decrease in V_s^o with increasing $C_{b(s)}$, beyond the maximum. The agreement shown between the experimental data and the results generated from eqn. 34-37 is virtually quantitative. Moreover, the present model provides a molecular interpretation of the shape of the curve in Figure 3.

At $C_{b(s)} = 0$ ($P_{b(m)} = 0$), the initial retention volume, $V^\circ_{s,o}$, is 4.62 mL/m^2 (23), of which about one-third is contributed from solute adsorption on type-1 sites ($\phi_1 V^\circ_{s,o(1)} = 1.59$) and about two-thirds from type-2 sites ($\phi_2 V^\circ_{s,o(2)} = 3.03$). (Note that, even though $\phi_1 >> \phi_2$, $V^\circ_{s,o(1)} >> V^\circ_{s,o(2)}$ because $f_1 > f_2$ (see eqn. 36 and 37).) With increasing $P_{b(m)}$ (or $C_{b(s)}$), the contribution to V°_s from type-1 sites decreases rapidly, while the contribution from type-2 sites first increases (but not as rapidly as the former decreases), goes through a maximum, and then decreases: $C_{b(s)} = 0.205$ (0.53, 3.16), $C_{b(s)} = 0.398$ (0.30, 3.29), $C_{b(s)} = 1.636$ (0.08, 3.76), $C_{b(s)} = 3.250$ (0.03, 2.90) and $C_{b(s)} = 5.053$ (0.01, 0.85). To understand this behavior, let us examine eqn. 34, with $f_1 = 0.321$ and $f_2 = 0.241$:

$$\ell n\,[V^\circ_{s(1)}/V^\circ_{s,o(1)}] = 11.195\,\ell n\,(1-\theta_{b(1)}) + 9.374\,\theta_{b(1)} \qquad (40)$$

$$\ell n[V^\circ_{s(2)}\,/V^\circ_{s,o(2)}] = 11.195\,\ell n\,(1-\theta_{b(2)}) + 13.556\,\theta_{b(2)} \qquad (41)$$

where eqn. 41 has a maximum at $\theta_{b(2)} = 0.174$ ($C_{b(s)} \approx C_{b(2)} = 1.65$ µmol/m^2), while eqn. 40 exhibits neither a maximum nor a minimum, but only a monotonic decrease with increasing $\theta_{b(1)}$.

The first term on the r.h.s. of eqn. 40 and 41 is associated with the availability of unoccupied adsorption sites and leads to a decrease in V°_s with increasing $P_{b(m)}$, while the second term here reflects the "lateral" interactions between adsorbed propane and butane molecules and leads to an increase in V°_s with increasing $P_{b(m)}$. For type-1 sites, the first term dominates at all

$P_{b(m)}$ (or $C_{b(s)}$), leading to a monotonic decrease in $V^\circ_{s(1)}$ with increasing $P_{b(m)}$, while for type-2 sites, the second term dominates at lower pressures and the first at higher pressures, leading to a maximum in $V^\circ_{s(2)}$. Therefore, as $P_{b(m)}$ begins to increase, the more pronounced initial increase in $\theta_{b(1)}$ relative to $\theta_{b(2)}$ (see Figure 1), first leads to an overall decrease in V°_s at lower pressures (initial decrease in $\phi_1 V^\circ_{s(1)}$ outweighs initial increase in $\phi_2 V^\circ_{s(2)}$). However, as $P_{b(m)}$ increases still further, $\phi_1 V^\circ_{s(1)}$ becomes very small, while $\phi_2 V^\circ_{s(2)}$, which begins to dominate in its contribution to V°_s, continues to increase (first producing a minimum in V°_s), goes through a maximum, and then, as the first term on the r.h.s. of eqn. 41 takes over, decreases markedly.

The source of the maximum in Figure 3 has also been analyzed by Parcher et al. (14), who applied scaled-particle theory (assuming a homogeneous adsorbent) in their treatment of the experimental results. The present model provides an explanation of this maximum in full accord with theirs. Similar maxima (and, presumably, for a similar reason) have been observed by Semonian and Rogers (24) for pyrene with n-pentane as the carrier gas and C_{18} bonded to Porasil B as the column packing. On the other hand, at low pressures, King (11) found only a very rapid drop in k' with increasing carbon dioxide pressure for n-alkane solutes and an alumina column, suggesting that any retention gain due to adsorbed CO_2-solute lateral interactions was far outweighed by the loss from reduced availabiltiy of adsorption sites. These results and ones forthcoming from the author's laboratory (nonideal GSC and SFSC measurements) warrant detailed analysis in the light of the present unified theory.

Finally, let us consider what the theory predicts about the compression of carrier liquid in contact with an adsorbent (as would occur in LSC), using liquid propane and Carbopack C as a convenient example. From the orthobaric density of liquid propane at 10°C (0.515 g/mL (12)), $\theta_{b(m)} = 0.598$ according to eqn. 32. From eqn. 26 and 29 (with $r_b = 8.799$, $z_m = 6$, $z_s = 4$, $f_1 = 0.321$, $f_2 = 0.241$, $\varepsilon'_{b1}/\varepsilon_{bb} = \varepsilon'_{b2}/\varepsilon_{bb} = 2.179$, $T_R = 0.766$, $\phi_1 = 0.0055$, $\phi_2 = 0.9945$ and $n = 2$), one computes a value of $\theta_{b(s)} = 0.783$ or $\rho_{b(s)} = 0.674$ g/mL. Therefore, a compression of about 30% is predicted, compared to about 20% from an experimentally based calculation (12). The implications of this compression with respect to LSC practice (especially in the determination of column holdup volume) are discussed elsewhere (25). The point to be made here is that the theory is capable of handling, in general, this compression effect.

CONCLUSIONS

The unified theory of adsorption chromatography with heterogeneous surfaces is compactly expressed in eqn. 24-29, where $\theta_{b(m)}$ is linked to an experimental state variable (reduced density of the mobile phase) by eqn. 23. As in our unified theory of absorption chromatography (1, 2), these equations clearly reveal that the natural state variables of the mobile phase are its reduced temperature and density.

To demonstrate its utility and efficacy, the theory has been successfully applied here, in quantitative detail, to a single (but not trivial) chromatographic system. As mentioned earlier, additional tests of the theory are clearly in order. Also, as emphasized in the derivation, the present model is based on parallel-layer adsorption of the solute and solvent molecules in the assumed monolayer. However, a monolayer picture may not always be adequate, as Findenegg and Löring (12) have shown in their careful study of propane adsorbed on Graphon (a graphitized carbon black) over a wide temperature range. Therefore, a more complete model, allowing for multilayer adsorption and, perhaps, nonuniformity of the film thickness of the surface phase needs to be explored.

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