

UNIFIED THEORY OF ADSORPTION CHROMATOGRAPHY: GAS, LIQUID AND SUPERCRITICAL FLUID MOBILE PHASES

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SUMMARY

Utilizing statistical thermodynamics and a mean-field lattice model, and exploiting isomorphic elements of binary-liquid and single-fluid critical behavior, the unified theory of the title is derived and discussed in some detail. The final results confirm that the natural mobile-phase state variables are its reduced temperature and reduced density. As an example of its utility and efficacy, the theory is applied to gas–solid chromatography with a highly adsorbable mobile phase. Potential refinements of the model are noted.

INTRODUCTION

Recently, we developed a unified molecular theory of absorption or fluid–liquid chromatography^{1,2}. The present advance extends this work to adsorption or fluid–solid chromatography.

Researchers in many areas of the physical sciences have been attempting to develop unified theories in the form of master equations to describe, succinctly and quantitatively, related physical phenomena. For instance, the isomorphism among various types of critical phenomena has been recognized and treated³, suggesting some quantitative universal laws. Also, the search continues in physics for a unified theory to describe the effects of different, fundamental force fields. However, with the exception of our recent theory and a classic study by Giddings on the dynamics of chromatography⁴, such unified approaches have been lacking in the area of chromatography, despite their conceptual and practical advantages.

Starting with equations derived for the solute distribution coefficient in the case of a binary liquid mobile phase and a solid adsorbent stationary phase, and then, exploiting the isomorphism between the upper critical solution temperature (UCST) in a binary liquid system and the liquid–gas critical point in a single-component fluid system³, a general equation is derived for the solute distribution coefficient in a chromatographic system where the stationary phase is an adsorbent and the mobile phase is a single-component ideal gas, moderately non-ideal gas, supercritical fluid or even a 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 adsorbents⁵⁻¹⁰. However, as an example of its utility, the unified theory is applied here to low-pressure gas-solid chromatography with a highly adsorbable vapor (volatile modifier) in the carrier gas^{11,12}.

THEORY OF LIQUID-SOLID CHROMATOGRAPHY WITH A BINARY MOBILE PHASE

In common with our earlier treatments of liquid-solid (adsorption) and liquid-bonded phase chromatography¹³⁻¹⁶, statistical thermodynamics and a mean-field lattice model are utilized to derive the relevant equations to describe the equilibrium distribution of solute between a binary liquid mobile phase and an adsorbent stationary phase, and, hence, solute retention in such systems. Also, the present, more refined treatment examines (as before) the competitive equilibrium at the molecular level among solvent and solute molecules distributed between generally non-ideal mobile and stationary phases, all components being non-electrolytes. Both entropy and interaction energy effects are rigorously included.

The stationary phase (subscript *s*) is assumed to be an energetically homogeneous, planar surface on which is adsorbed a monolayer of solvent and solute molecules. Although a variety of molecular structures may be considered within the general framework of the model^{1,13-15,17}, for present purposes the molecules are assumed to be completely flexible chains, each having r_i singly-connected (terminal) or doubly-connected (internal) cubic segments, each of volume l^3 . (Therefore, the hard-core volume of a molecule of type i is $r_i l^3$.) Parallel-layer adsorption and, hence, a uniform thickness of all of the molecules in the adsorbed monolayer are also assumed. The adsorbent surface is modelled as a two-dimensional, square-planar lattice having a nearest-neighbor coordination number of $z_s = 4$ and containing M_s equivalent surface sites, each of area l^2 . Occupying these sites in a restricted random walk^{1,18} are $N_{a(s)}$ solute molecules, each occupying r_s sites, and $N_{b(s)}$ and $N_{c(s)}$ solvent molecules, each occupying r_b and r_c sites, respectively, where $M_s = r_a N_{a(s)} + r_b N_{b(s)} + r_c N_{c(s)}$. Accordingly, the volume of the stationary phase is equal to the surface area of the adsorbent ($M_s l^2$) times the monolayer thickness (l), *i.e.*, $M_s l^3$.

The mobile phase (subscript *m*) is modelled as a three-dimensional, simple-cubic lattice having a nearest-neighbor coordination number of $z_m = 6$ and containing M_m cubic cells or sites, each of volume l^3 . Similarly, $M_m = r_a N_{a(m)} + r_b N_{b(m)} + r_c N_{c(m)}$ and the volume of the mobile phase is $M_m l^3$.

The dimensionless configurational entropy of the stationary-phase ($x = s$) or mobile-phase ($x = m$) mixture, S_x/k_B , is given by^{1,18}

$$\begin{aligned}
 -S_x/k_B = & \sum_{i=a}^c (N_{i(x)} \ln N_{i(x)} - N_{i(x)}) - \\
 & \sum_{i=a}^c N_{i(x)} (r_i - 1) \ln \{ (z_x - 1) / M_x \} - \\
 & M_x \ln M_x + M_x
 \end{aligned} \tag{1}$$

where $M_x = \sum_{i=a}^c r_i N_{i(x)}$ and k_B is the Boltzmann constant. If the attractive interaction energy between nearest-neighbor segments on molecules i and j is denoted by ε_{ij} , and between a molecular segment on i and a surface site by ε_{is} , the dimensionless total interaction energy in phase x , $E_x/k_B T$, is^{1,18}

$$\begin{aligned} E_x/k_B T = & (z_e f_x / k_B T) \sum_{i=a}^c r_i N_{i(s)} \varepsilon_{is} + \\ & (z_e f_x / k_B T M_m) \sum_{i,j=a}^c r_i N_{i(m)} r_j N_{j(s)} \varepsilon_{ij} + \\ & [z_e (1 - 2f_x) / 2k_B T M_x] \sum_{i,j=a}^c r_i N_{i(x)} r_j N_{j(x)} \varepsilon_{ij} \end{aligned} \quad (2)$$

where T is the temperature (K), ε_{ij} and ε_{is} are negative (attractive), and z_e denotes the number of nearest-neighbor, external contacts of a molecular segment. (For sufficiently large r_i , where the number of terminal segments is small compared to the number of internal segments, $z_e \approx 4$ in this model.) Also, f_x is the fraction of the molecular surface which is in contact with the adsorbent surface. For the mobile phase ($x = m$), $f_m = 0$ and only the third term on the right hand side (r.h.s.) of eqn. 2 survives. For the stationary phase ($x = s$), $f_s > 0$. (Again, for sufficiently large r_i , $f_s \approx 1/4$ in this model.) The first term on the r.h.s. of eqn. 2 represents the total (dimensionless) molecular energy of adhesion to the adsorbent surface. Also, it is assumed that the same fraction, f_s , of the molecular surface opposite that in contact with the adsorbent interacts with the mobile-phase molecules in contact with the adsorbed monolayer (second term on the r.h.s. of eqn. 2). Therefore, the "lateral" molecular interactions in the stationary phase are reflected in the third term on the r.h.s. of eqn. 2. Finally, if we denote the cell partition function per segment of molecule i in phase x by $q_{i(x)}$ and include the contribution¹

$$A'_x/k_B T = - \sum_{i=a}^c r_i N_{i(x)} q_{i(x)} \quad (3)$$

the entire dimensionless Helmholtz free energy of the mixture, $A_x/k_B T$, consistent with the Bragg-Williams approximation¹⁸, is simply given by the sum of eqs. 1, 2 and 3:

$$A_x/k_B T = (A'_x/k_B T) + (E_x/k_B T) - (S_x/k_B) \quad (4)$$

The dimensionless chemical potential of the h th component in phase x , $\mu_{h(x)}/k_B T$, is determined from

$$\mu_{h(x)}/k_B T = \left[\frac{\partial (A_x/k_B T)}{\partial N_{h(x)}} \right]_{T, N_{-h(x)}, N_{i(y)}} \quad (5)$$

where $N_{-h(x)}$ denotes the number of molecules of components other than h th one in

phase x and $N_{i(y)}$ denotes the number of molecules of all of the components in phase y ($y \neq x$). From eqns. 1-5

$$\begin{aligned} \mu_{h(x)}/k_B T = & \ln(\theta_{h(x)}/r_h) + r_h \sum_{i=a}^c \theta_{i(x)}(1 - r_i^{-1}) - \\ & (r_h - 1)\ln(z_x - 1) - r_h \ln q_{h(x)} + (z_e f_x r_h / k_B T) \varepsilon_{hs} + \\ & (z_e f_x r_h / k_B T) \sum_{i=a}^c \theta_{i(m)} \varepsilon_{hi} + [z_e(1 - 2f_x) r_h / k_B T] \sum_{i=a}^c \theta_{i(x)} \varepsilon_{hi} - \\ & [z_e(1 - 2f_x) r_h / 2k_B T] \sum_{i,j=a}^c \theta_{i(x)} \theta_{j(x)} \varepsilon_{ij} \end{aligned} \quad (6)$$

where $h = a, b$ or c , $x = m$ or s , and where $\theta_{i(x)} = r_i N_{i(x)} / M_x$ is the volume fraction of component i in phase x . At equilibrium, each of the components must satisfy the following condition at the operational temperature:

$$\mu_{h(s)}/k_B T = \mu_{h(m)}/k_B T \quad (7)$$

Applying eqns. 6 and 7 to the solute component ($h = a$), one obtains

$$\begin{aligned} \ln[\theta_{a(s)}/\theta_{a(m)}] = & - (r_a - 1)\ln[(z_m - 1)/(z_s - 1)] - \\ & (z_e f_s r_a / k_B T) \varepsilon_{as} - r_a \ln[q_{a(m)}/q_{a(s)}] + \\ & r_a \sum_{i=a}^c [(\theta_{i(m)} - \theta_{i(s)}) (1 - r_i^{-1})] + \\ & [z_e(1 - f_s) r_a / k_B T] \sum_{i=a}^c \theta_{i(m)} \varepsilon_{ai} - \\ & [z_e(1 - 2f_s) r_a / k_B T] \sum_{i=a}^c \theta_{i(s)} \varepsilon_{ai} - \\ & (z_e r_a / 2k_B T) \sum_{i,j=a}^c \theta_{i(m)} \theta_{j(m)} \varepsilon_{ij} + \\ & [z_e(1 - 2f_s) r_a / 2k_B T] \sum_{i,j=a}^c \theta_{i(s)} \theta_{j(s)} \varepsilon_{ij} \end{aligned} \quad (8)$$

The chromatographic distribution coefficient, K , is defined as the ratio of the equilibrium concentration of solute in the stationary phase, $c_{a(s)}$, to that in the mobile phase, $c_{a(m)}$, in the limit of infinite dilution of the solute ($N_a \rightarrow 0$ or $\theta_a \rightarrow 0$). Clearly, in the model system, this ratio is also equal to the ratio of the respective θ_a 's, *i.e.*

$$K = \lim_{N_a \rightarrow 0} (c_{a(s)}/c_{a(m)}) = \lim_{N_a \rightarrow 0} (\theta_{a(s)}/\theta_{s(m)}) \quad (9)$$

Therefore, from eqns. 8 and 9, one obtains

$$\begin{aligned} \ln K_{b+c} = & - (r_a - 1) \ln[(z_m - 1)/(z_s - 1)] - (z_e f_s r_a / k_B T) \epsilon'_{as} + \\ & r_a \sum_{i=b}^c [(\theta_{i(m)} - \theta_{i(s)}) (1 - r_i^{-1})] + [z_e (1 - f_s) r_a / k_B T] \sum_{i=b}^c \theta_{i(m)} \epsilon_{ai} - \\ & [z_e (1 - 2f_s) r_a / k_B T] \sum_{i=b}^c \theta_{i(s)} \epsilon_{ai} - (z_e r_a / 2k_B T) \sum_{i,j=b}^c \theta_{i(m)} \theta_{j(m)} \epsilon_{ij} + \\ & [z_e (1 - 2f_s) r_a / 2k_B T] \sum_{i,j=b}^c \theta_{i(s)} \theta_{j(s)} \epsilon_{ij} \end{aligned} \quad (10)$$

where the subscript $b+c$ in K_{b+c} emphasizes the binary solvent. Also, in eqn. 8, the cell partition function term has been incorporated into the surface interaction term, as follows¹⁴

$$(z_e f_s / k_B T) \epsilon_{hs} + \ln(q_{h(m)}/q_{h(s)}) = (z_e f_s / k_B T) \epsilon'_{hs} \quad (11)$$

thus making ϵ'_{hs} an adhesion free energy per molecular segment in eqns. 10 ($h=a$) and 11.

Eqn. 10 is still incomplete because it does not explicitly take into account the competitive equilibrium involving solvent components b and c , in addition to the solute component (a). Accordingly, setting $\theta_{a(x)} = 0$, applying eqn. 6 for solvent component b ($h=b$, $x=m$ or s) and eqn. 7 ($h=b$) in the form,

$$(r_a / r_b) [(\mu_{b(m)} / k_B T) - (\mu_{b(s)} / k_B T)] = 0 \quad (12)$$

and adding eqns. 10 and 12, one obtains

$$\begin{aligned} \ln K_{b+c} = & \ln K_b + (r_a / r_b) \ln(\theta_{b(s)} / \theta_{b(m)}) + \\ & (z_e r_a / k_B T) [(1 - f_s) \theta_{b(m)} - (1 - 2f_s) \theta_{b(s)} - f_s] [\epsilon_{ab} - \epsilon_{ac} + \epsilon_{bc} - \epsilon_{bb}] \end{aligned} \quad (13)$$

where K_b , the solute distribution coefficient with neat solvent b ($\theta_b \rightarrow 1$; $\theta_c \rightarrow 0$), is given by

$$\begin{aligned} \ln K_b = & [1 - (r_a / r_b)] \ln[(z_m - 1)/(z_s - 1)] + \\ & (z_e f_s r_a / k_B T) (\epsilon'_{bs} - \epsilon'_{as} + \epsilon_{ab} - \epsilon_{bb}) \end{aligned} \quad (14)$$

and where eqn. 11 ($h=b$) has also been applied. In terms of interaction parameters^{15,16}, χ_{ij} , where

$$\chi_{ij} = (z_e / 2k_B T) (2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj}) \quad (15)$$

Eqn. 13 may be written as

$$\ln K_{b+c} = \ln K_b + (r_a/r_b)\ln(\theta_{b(s)}/\theta_{b(m)}) + r_a[(1 - f_s)\theta_{b(m)} - (1 - 2f_s)\theta_{b(s)} - f_s](\chi_{ab} + \chi_{bc} - \chi_{ac}) \quad (16)$$

Similarly, setting $\theta_{a(x)} = 0$, applying eqn. 6 for solvent component c ($h=c$, $x=m$ or s) and eqn. 7 ($h=c$) in the form,

$$(r_a/r_c)[(\mu_{c(m)}/k_B T) - (\mu_{c(s)}/k_B T)] = 0 \quad (17)$$

and adding eqns. 10 and 17, one obtains

$$\ln K_{b+c} = \ln K_c + (r_a/r_c)\ln[(1 - \theta_{b(s)})/(1 - \theta_{b(m)})] + (z_e r_a/k_B T)[(1 - 2f_s)\theta_{b(s)} - (1 - f_s)\theta_{b(m)}][\varepsilon_{ac} - \varepsilon_{ab} + \varepsilon_{bc} - \varepsilon_{cc}] \quad (18)$$

where K_c , the solute distribution coefficient with neat solvent c ($\theta_c \rightarrow 1$; $\theta_b \rightarrow 0$), is given by

$$\ln K_c = [1 - (r_a/r_c)]\ln[(z_m - 1)/(z_s - 1)] + (z_e f_s r_a/k_B T)(\varepsilon'_{cs} - \varepsilon'_{as} + \varepsilon_{ac} - \varepsilon_{cc}) \quad (19)$$

and where eqn. 11 ($h=c$) has also been applied. In terms of interaction parameters (eqn. 15), eqn. 18 may be written as

$$\ln K_{b+c} = \ln K_c + (r_a/r_c)\ln[(1 - \theta_{b(s)})/(1 - \theta_{b(m)})] + r_a[(1 - 2f_s)\theta_{b(s)} - (1 - f_s)\theta_{b(m)}](\chi_{ac} + \chi_{bc} - \chi_{ab}) \quad (20)$$

Letting $z_e = 4$ and $f_s = 1/4$ (*vide supra*), eqns. 13, 14, 18 and 19 become, respectively

$$\ln K_{b+c} = \ln K_b + (r_a/r_b)\ln(\theta_{b(s)}/\theta_{b(m)}) + (r_a/k_B T)(3\theta_{b(m)} - 2\theta_{b(s)} - 1)(\varepsilon_{ab} - \varepsilon_{ac} + \varepsilon_{bc} - \varepsilon_{bb}) \quad (21)$$

$$\ln K_b = [1 - (r_a/r_b)]\ln[(z_m - 1)/(z_s - 1)] + (r_a/k_B T)(\varepsilon'_{bs} - \varepsilon'_{as} + \varepsilon_{ab} - \varepsilon_{bb}) \quad (22)$$

$$\ln K_{b+c} = \ln K_c + (r_a/r_c)\ln[(1 - \theta_{b(s)})/(1 - \theta_{b(m)})] + (r_a/k_B T)(2\theta_{b(s)} - 3\theta_{b(m)})(\varepsilon_{ac} - \varepsilon_{ab} + \varepsilon_{bc} - \varepsilon_{cc}) \quad (23)$$

$$\ln K_c = [1 - (r_a/r_c)]\ln[(z_m - 1)/(z_s - 1)] + (r_a/k_B T)(\varepsilon'_{cs} - \varepsilon'_{as} + \varepsilon_{ac} - \varepsilon_{cc}) \quad (24)$$

where, again, $\theta_{b(x)}$ is the volume fraction of solvent component b in phase x ($x = m$ or s).

In eqns. 22 and 24 (neat solvents) the first term on the r.h.s. stems from the configurational entropy term in $A_x/k_B T$ (eqns. 1 and 4) and the second term reflects the exchange interaction free energy associated with the competitive equilibrium¹³⁻¹⁶. In eqns. 21 and 23 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 associated with the competitive equilibrium¹³⁻¹⁶. Parenthetically, it is noted that for the special case of monomeric solute and solvent molecules ($r_a = r_b = r_c = 1$; $z_e = 6$; $f_s = 1/6$), eqns. 13, 14, 18 and 19 reduce to similar equations derived and discussed previously^{13,14}.

If we now designate component b as the "good" solvent, *i.e.*, the preferentially adsorbed solvent component, and component c as the "poor" solvent, and consider the special case where $\theta_{b(s)} \rightarrow 1$ ($\theta_{c(s)} \rightarrow 0$), eqn. 16 becomes

$$\ln K_{b+c} = \ln K_b - v_{ab} \ln \theta_{b(m)} - r_a(1 - f_s)(1 - \theta_{b(m)})(\chi_{ab} + \chi_{bc} - \chi_{ac}) \quad (25)$$

where $v_{ab} = r_a/r_b$. If, in addition, cancellation of the interaction energy terms (χ_{ij} 's) is assumed, then eqn. 25 reduces to the familiar Snyder-Soczewinski expression¹⁶:

$$\ln K_{b+c} = \ln K_b - v_{ab} \ln \theta_{b(m)} \quad (26)$$

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

Finally, full application of the general set of equations, *i.e.*, eqns. 13 (or 16) and 14, or eqns. 18 (or 20) and 19, requires the adsorption isotherm describing the equilibrium distribution of the solvent components between the mobile and stationary phases. Using eqn. 7 ($h=b$ or c) in the forms

$$(\mu_{b(m)}/k_B T) - (\mu_{b(s)}/k_B T) = 0 \quad (27)$$

$$(r_b/r_c)[(\mu_{c(m)}/k_B T) - (\mu_{c(s)}/k_B T)] = 0 \quad (28)$$

and scaling the system to the smallest molecule by letting $r_c = 1$ (refs. 13 and 15), one obtains from eqns. 6 (with $h=b$ or c , $x=m$ or s , $\theta_{a(x)}=0$), 27 and 28

$$\begin{aligned} & \ln[(1 - \theta_{b(m)})^{r_b}/\theta_{b(m)}] + (r_b - 1)\ln[(z_m - 1)/(z_s - 1)] + \\ & (z_e f_s r_b / k_B T)(\varepsilon_{bs} - \varepsilon_{cs} + \varepsilon_{cc} - \varepsilon_{bc}) + 2r_b(1 - f_s)\chi_{bc}\theta_{b(m)} = \\ & \ln[(1 - \theta_{b(s)})^{r_b}/\theta_{b(s)}] + 2r_b(1 - 2f_s)\chi_{bc}\theta_{b(s)} \end{aligned} \quad (29)$$

where eqn. 11 ($h = b$ or c) has been applied and where, from eqn. 15

$$\chi_{bc} = (z_e/2k_B T)(2\varepsilon_{bc} - \varepsilon_{bb} - \varepsilon_{cc}) \quad (30)$$

UNIFIED THEORY OF FLUID-SOLID CHROMATOGRAPHY WITH A NEAT MOBILE PHASE

In this section we take the final results from the previous section, 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, where the neat mobile phase may be a gas, liquid or supercritical fluid.

It is possible to work with either one of the following two sets of fundamental equations derived in the previous section:

(1) eqns. 14 (for $\ln K_b$), 16 (for $\ln K_{b+c}$, in terms of χ_{ij}) and 29 (mixed-solvent adsorption isotherm);

(2) eqns. 19 (for $\ln K_c$), 20 (for $\ln K_{b+c}$, in terms of χ_{ij}) and 29 (mixed-solvent adsorption isotherm).

These equations are based on a model which considers an energetically homogeneous and planar adsorbent surface, a stationary phase consisting of a monolayer of solvent and solute molecules adsorbed parallel to the surface, and the Bragg-Williams (random-pairing) approximation¹⁸. For reasons soon to become apparent, the second set of basic equations will be utilized here.

Continuing to scale the system by letting $r_c = 1$ (refs. 13 and 15), eqns. 19, 20 and 29 may be manipulated into reduced form by first noting the critical solution condition applicable to the binary-liquid mobile phase¹⁸

$$T^* = 2T\chi_{bc}r_b/(1 + \sqrt{r_b})^2 \quad (31)$$

$$\theta_b^* = (1 + \sqrt{r_b})^{-1} \quad (32)$$

where χ_{bc} is given by eqn. 30, T^* refers to the UCST (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 diagram¹⁸. Introducing reduced variables (subscript R)

$$T_R = T/T^* = (1 + \sqrt{r_b})^2/2r_b\chi_{bc} \quad (33)$$

$$\theta_{b(m),R} = \theta_{b(m)}/\theta_b^* = \theta_{b(m)}(1 + \sqrt{r_b}) \quad (34)$$

and making use of eqn. 33 in eqns. 19, 20 and 29 (with $r_c = 1$ in all), one finds

$$\ln K_c = (1 - r_a)\ln[z_m - 1]/(z_s - 1) + [r_a(1 + \sqrt{r_b})^2f_s/r_bT_R][(\epsilon'_{cs} - \epsilon'_{as} + \epsilon_{ac} - \epsilon_{cc})/(2\epsilon_{bc} - \epsilon_{bb} - \epsilon_{cc})] \quad (35)$$

$$\ln K_{b+c} = \ln K_c + r_a\ln[(1 - \theta_{b(s)})/(1 - \theta_{b(m)})] + [r_a(1 + \sqrt{r_b})^2f_s/r_bT_R][(1 - 2f_s)\theta_{b(s)} - (1 - f_s)\theta_{b(m)}][(\chi_{ac} + \chi_{bc} - \chi_{ab})/2\chi_{bc}] \quad (36)$$

$$\begin{aligned} & \ln[(1 - \theta_{b(m)})^{r_b}/\theta_{b(m)}] + (r_b - 1)\ln[(z_m - 1)/(z_s - 1)] + \\ & [(1 + \sqrt{r_b})^2f_s/T_R][(\epsilon'_{bs} - \epsilon'_{cs} + \epsilon_{bc} - \epsilon_{bc})/(2\epsilon_{bc} - \epsilon_{bb} - \epsilon_{cc})] + \\ & [(1 + \sqrt{r_b})^2(1 - f_s)/T_R]\theta_{b(m)} = \\ & \ln[(1 - \theta_{b(s)})^{r_b}/\theta_{b(s)}] + [(1 + \sqrt{r_b})^2(1 - 2f_s)/T_R]\theta_{b(s)} \end{aligned} \quad (37)$$

By invoking the isomorphism between the critical behavior in a binary liquid system and that in a single-component fluid system³, one may utilize the direct

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. 34 that

$$\theta_{b(m),R} = \rho_{b(m),R} = \rho_{b(m)}/\rho_b^* = \theta_{b(m)}(1 + \sqrt{r_b}) \quad (38)$$

where $\theta_{b(m)}$ is now the volume fraction of space occupied by the hard cores of the molecules in the mobile phase (*i.e.*, the fraction relative to what it would be in a hypothetical close-packed molecular arrangement of these cores, for which $\theta_{b(m)} = 1$), $1 - \theta_{b(m)}$ is the volume fraction of "empty" (unoccupied) space (and similarly for $\theta_{b(s)}$ and $1 - \theta_{b(s)}$ 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 may be replaced by K_0 , the solute distribution coefficient for ideal gas–solid chromatography (GSC) ($\rho_{b(m)} \rightarrow 0$). Lastly, it follows that all interactions involving component c (now representing unoccupied or void space in the model) may be set to zero, *i.e.*, $\epsilon'_{cs} = 0$ and $\epsilon_{ic} = 0$ ($i = a, b, c$). Accordingly, with the aid of eqn. 15, eqns. 35–37 become

$$\ln K_0 = (1 - r_a) \ln[(z_m - 1)/(z_s - 1)] + [r_a(1 + \sqrt{r_b})^2 f_s / r_b T_R] [\epsilon'_{as} / \epsilon_{bb}] \quad (39)$$

$$\ln K = \ln K_0 + r_a \ln[(1 - \theta_{b(s)}) / (1 - \theta_{b(m)})] + [r_a(1 + \sqrt{r_b})^2 / r_b T_R] [(1 - 2f_s)\theta_{b(s)} - (1 - f_s)\theta_{b(m)}] [\epsilon_{ab} / \epsilon_{bb}] \quad (40)$$

$$\ln[(1 - \theta_{b(m)})^{r_b} / \theta_{b(m)}] + (r_b - 1) \ln[(z_m - 1)/(z_s - 1)] - [(1 + \sqrt{r_b})^2 f_s / T_R] [\epsilon'_{bs} / \epsilon_{bb}] + [(1 + \sqrt{r_b})^2 (1 - f_s) / T_R] \theta_{b(m)} = \ln[(1 - \theta_{b(s)})^{r_b} / \theta_{b(s)}] + [(1 + \sqrt{r_b})^2 (1 - 2f_s) / T_R] \theta_{b(s)} \quad (41)$$

where K (replacing K_{b+c}) is the solute distribution coefficient when the mobile-phase density is $\rho_{b(m)}$, which, in turn, is related to $\theta_{b(m)}$ through eqn. 38. Note that eqns. 38–41, which comprise the unified molecular theory, are applicable to gas, liquid and supercritical fluid, single-component mobile phases.

Eqn. 41, which describes the distribution of fluid between the mobile and stationary phases (*i.e.*, the equilibrium adsorption isotherm), is required to determine the equilibrium value of $\theta_{b(s)}$ for a given mobile-phase density, $\rho_{b(m)}$. In eqn. 39 (ideal GSC), the first term on the r.h.s. stems from the change in the configurational entropy of the solute when it is transferred from an ideal-gas mobile phase to a bare, adsorbent stationary phase. The second term reflects the interaction free energy of adsorption of an isolated solute molecule on the surface. In eqn. 40, 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. Note that eqn. 40 may also be written in terms of capacity factors (replacing K and K_0 by, respectively, k' and k'_0) or retention volumes.

At this point, several special cases of eqns. 40 and 41 could be considered. However, with the exception of one such case to be applied in the next section, these are deferred for future study.

Consider a situation where $\theta_{b(s)} \gg \theta_{b(m)} \approx 0$, *i.e.*, where there is an appreciable buildup of the carrier fluid on the adsorbent surface, even at very low mobile-phase densities (or pressures). Accordingly, in this limit, eqns. 40 and 41 become:

$$\ln K = \ln K_0 + r_a \ln(1 - \theta_{b(s)}) + [r_a(1 + \sqrt{r_b})^2 / r_b T_R] [\epsilon_{ab} / \epsilon_{bb}] [(1 - 2f_s) \theta_{b(s)}] \quad (42)$$

$$\ln \theta_{b(m)} = \ln \theta_{b(s)} - r_b \ln(1 - \theta_{b(s)}) - [(1 + \sqrt{r_b})^2 (1 - 2f_s) / T_R] (\theta_{b(s)}) + (r_b - 1) \ln[(z_m - 1) / (z_s - 1)] - [(1 + \sqrt{r_b})^2 f_s / T_R] [\epsilon'_{bs} / \epsilon_{bb}] \quad (43)$$

APPLICATION OF THE UNIFIED THEORY

As an example of its utility, the unified theory is applied here to analyze the GSC retention behavior, at 10°C, of *n*-butane on graphitized carbon black (Carbopack C) modified by adsorption of propane from the carrier-gas stream. Parcher *et al.*¹² and Johnson¹⁹ obtained both retention and adsorption-isotherm data for this system. Although helium was employed as a second fluid component in their studies and, strictly, the model applies to a single-component fluid, the low pressure of carrier gas and the negligible adsorption of helium in their experiments permit application of the present model.

Designating *n*-butane (the solute) as component a and propane as component b, and noting that a value of $r_b = 4.614$ has been determined for carbon dioxide¹, r_i ($i = a$ or b) may be calculated from

$$r_i = r_{CO_2} (V_i / V_{CO_2}) \quad (44)$$

where V is the van der Waals molar volume. The published V data²⁰ and eqn. 44 yield values of $r_a = 11.195$ and $r_b = 8.799$ for the molecular size parameters. From the critical density of propane, $\rho_b^* = 0.217$ g/ml, and eqn. 38, we have

$$\theta_{b(m)} = 1.162 \rho_{b(m)} \quad (45)$$

Since the propane pressure, $P_{b(m)}$, corresponding to monolayer coverage of adsorbed propane is *ca.* 1000 Torr¹², ideal-gas behavior may be safely assumed, with negligible error, to relate $\rho_{b(m)}$ in eqn. 45 to $P_{b(m)}$ (Torr):

$$\theta_{b(m)} = 2.901 \cdot 10^{-6} P_{b(m)} \quad (46)$$

Eqn. 46 establishes the relationship between a model variable and an experimental state variable. With $P_{b(m)} = 1000$ Torr, $\theta_{b(m)} \approx 0.003$, thus justifying the application of eqns. 42 and 43, 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 remaining

molecular parameters in eqn. 41 are $\epsilon_{ab}/\epsilon_{bb}$, which is reasonably assigned a value of 1.000, and f_s , which, as before, is assigned a value of 0.250. Therefore, writing eqn. 42 in terms of standard specific (per unit surface area of adsorbent) retention volumes, V_s^0 , and substituting into it the numerical values determined or assigned above, one obtains

$$\ln V_s^0 = \ln(V_s^0)_0 + 11.195 \ln(1 - \theta_{b(s)}) + 13.071 \theta_{b(s)} \quad (47)$$

Turning to eqn. 43, the applicable adsorption isotherm when $\theta_{b(s)} \gg \theta_{b(m)} \approx 0$, and recalling that $z_m = 6$ and $z_s = 4$, substitution of numerical values yields

$$\ln \theta_{b(m)} = \ln \theta_{b(s)} - 8.799 \ln(1 - \theta_{b(s)}) - 10.274 \theta_{b(s)} + 3.984 - 5.137 (\epsilon_{bs}'/\epsilon_{bb}) \quad (48)$$

where $\theta_{b(m)}$ is related to $P_{b(m)}$ in eqn. 46.

Analysis of the retention volume and adsorption isotherm results^{12,19} using eqns. 47 and 48 gives best-fit values of $\ln(V_s^0)_0 = 1.217$ and $(\epsilon_{bs}'/\epsilon_{bb}) = 2.114$. The excellent fits are evident in Figs. 1 and 2.

The monolayer capacity of adsorbed propane on the Carbpac C used was estimated to be $5.49 \mu\text{mol}/\text{m}^2$ (ref. 12). The $\theta_{b(s)}$ value in our model corresponding to this capacity is 0.562. (Recall that $\theta_{b(s)}$ is the ratio of the monolayer volume physically occupied by the hard cores of adsorbed molecules to the total volume of the monolayer.) This suggests that if the "hard cores" of the propane molecules were close-packed (a physical impossibility, given the prohibitive repulsive forces which would have to be overcome), the monolayer capacity would be $9.77 \mu\text{mol}/\text{m}^2$. Viewed another way, with the estimate of 30.1 \AA^2 for the actual specific surface area of a propane molecule adsorbed on Carbpac C¹², this suggests a realistic hard-core area of 16.9 \AA^2 .

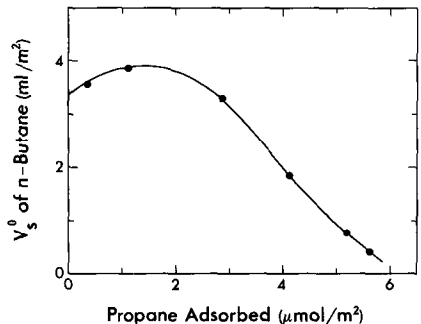
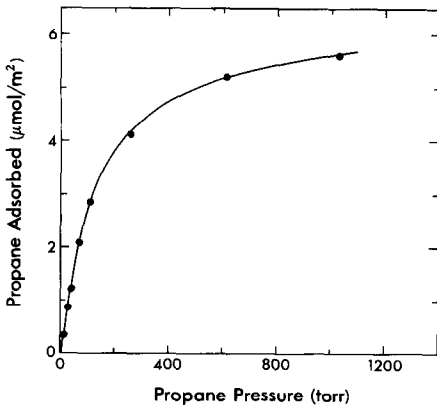


Fig. 1. Adsorption isotherm of propane on Carbpac C at 10°C ^{12,19}. Solid line was calculated from eqns. 46 and 48 with $\epsilon_{bs}'/\epsilon_{bb} = 2.114$.

Fig. 2. Specific retention volume, V_s^0 , of *n*-butane as a function of the amount of propane adsorbed on Carbpac C at 10°C ^{12,19}. Solid line was calculated from eqn. 47 with $\ln(V_s^0)_0 = 1.217$.

The reasonableness and consistency of the model results are further confirmed by evaluation of the specific volume and film thickness of the adsorbed monolayer. Assuming that propane-surface and butane-surface segmental interactions are equivalent, so that $(\epsilon'_{as}/\epsilon_{bb}) = (\epsilon'_{bs}/\epsilon_{bb}) = 2.114$, and, as before, letting $z_m = 6$, $z_s = 4$, $r_a = 11.195$, $r_b = 8.799$, $f_s = 1/4$ and $T_R = 0.766$, eqn. 39 yields a limiting value (zero propane pressure) of $K_0 = 5470$ (dimensionless). Using the fitted value of $(V_s^0)_0 = 3.377 \text{ ml/m}^2$, a specific volume of adsorbed propane of $6.2 \cdot 10^{-4} \text{ ml/m}^2$ is calculated. From the molar volume of liquid propane at 10°C (85.69 ml^{21}) and a monolayer coverage of $5.49 \mu\text{mol/m}^2$, a specific volume of $4.7 \cdot 10^{-4} \text{ ml/m}^2$ is estimated. In addition to the decent agreement between the two independent computations, one should also note the reasonableness of the estimated film thickness of about 5 or 6 Å.

The source of the maximum in Fig. 2 has been analyzed in some detail by Parcher *et al.*¹², who applied a scaled-particle theory in their treatment of the experimental results. The present model provides an explanation which is in full accord with theirs. Briefly, at low propane pressures (low $\theta_{b(s)}$) the third term on the r.h.s. of eqn. 47 ("lateral" interactions between adsorbed propane and butane molecules) dominates and leads initially to an increase in V_s^0 with increasing pressure. At higher propane pressures (higher $\theta_{b(s)}$) the second term, which reflects the availability of unoccupied adsorption sites, dominates and leads to a rapid decrease in V_s^0 with increasing pressure. The maximum occurs at the transition between these two pressure regions, here at $\theta_{b(s)} = 0.144$ (surface coverage of about $1.4 \mu\text{mol/m}^2$). This corresponds to a propane pressure of 45.8 Torr, at which $V_s^0 = 3.89 \text{ ml/m}^2$.

Similar maxima (and, presumably, for a similar reason) have been observed by Semonian and Rogers²² 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, King¹⁰ 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 carbon dioxide-solute lateral interactions was far outweighed by the loss from reduced availability 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 this unified molecular theory of adsorption chromatography.

CONCLUSIONS

The unified theory of adsorption chromatography is compactly expressed by eqns. 39–41, where $\theta_{b(m)}$ is linked to an experimental state variable (reduced density of the mobile phase) by eqn. 38. As in our unified theory of absorption chromatography^{1,2}, these equations 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 to a single (but not trivial) GSC system. As mentioned in the preceding section, additional tests of the theory are clearly in order. Also, as emphasized throughout the derivation, the present model is based on an energetically homogeneous adsorbent and parallel-layer adsorption of the solute and solvent molecules in the assumed monolayer. However, virtually all chromatographic adsorbents have some degree of heterogeneity. There is evidence, for example, that Carboxpack C has a very small

fraction of "high-energy" sites¹², and silica gel is notorious for its heterogeneity. Also, a monolayer picture may not always be adequate, as Findenegg and Löring²¹ have shown in a careful study of propane adsorbed on Graphon (a graphitized carbon black) over a wide temperature range. Thus, a more complete model incorporating a discrete or continuous, energetic distribution of adsorption sites^{14,23} and allowing for multilayer adsorption needs to be explored. (Not included in the data fits via the models in this paper and ref. 12 were the actual, zero-pressure retention volume, where the tiny fraction of high-energy surface sites has its most pronounced effect, and the datum beyond the estimated monolayer coverage, where, in any event, the retention volume becomes impractically low.)

In addition, it is conceivable and, in fact, probable that the orientation of the adsorbed solute and solvent molecules would depend on the chemistry of the molecules and surface, as well as the density of the mobile phase (hence, the surface coverage). A further refinement of the present model would then be to allow for a distribution of molecular orientations in the adsorbed state. To this end, molecular statistics similar to those applied to anisotropic fluids (such as nematic liquid crystals) would have to be applied^{14,15,17}.

Finally, it should be noted that in any application of the results of the present or a modified model to SFSC, it must be kept in mind that the formulated K (or k') is strictly a local value, referring to a given position along the column. A rigorous method needs to be developed to relate the observed retention parameter to appropriate column-averaged quantities for particular inlet and outlet conditions.

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