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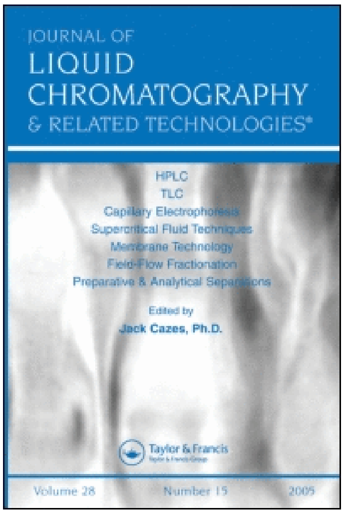

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Unified Theory of Absorption Chromatography: Gas, Liquid, and Supercritical Fluid Mobile Phases

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

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ABSTRACT

Based on a simple theoretical model which exploits the isomorphism pervading critical phenomena, a general equation is derived for the solute capacity factor, k', in a chromatographic system where the stationary phase is an absorbent and the mobile-phase fluid may be an ideal gas, moderately nonideal gas, supercritical fluid or liquid. This comprehensive equation is in the form $\ell nk' = \ell nk_0' + F(T_R,\rho_R)$, where T_R and ρ_R are the reduced temperature and reduced density of the mobile phase and where $\ell nk_0'$, the stationary-phase contribution, corresponds to ideal gas-liquid chromatography ($\rho_R = 0$) and $F(T_R,\rho_R)$, the mobile-phase contribution (eqn. 14), is a quadratic function of ρ_R and a linear function of T_R^{-1} and solute carbon number (homologous solute series). The limitations and advantages, molecular interpretation, predictions, practical implications and applications, and general utility of this unified theory are discussed, with special emphasis on supercritical fluid chromatography (and extraction).

INTRODUCTION

In many areas of the physical sciences, researchers have been attempting to develop unified theories in the form of master equations to describe, compactly and quantitatively, related physical phenomena. For example, the isomorphism among various types of critical phenomena has been identified and treated (1), suggesting some quantitative universal laws. Also, the quest for a unified theory to describe the effects of different force fields continues in physics. However, with one notable exception, unified approaches have been lacking in the area of chromatography, despite their conceptual and practical advantages.

In a classic paper presented at the Brighton chromatography symposium in 1964 (2), Giddings observed that "logically, it would seem, there ought to be only one theory, or at least one true theory, of chromatography", and he proceeded to address the dynamics of zone evolution in the form of "grand chromatographic equations" to describe packed and capillary column efficiencies with gas, liquid and supercritical fluid mobile phases. Some twenty years have passed without a similar effort to describe the equilibrium or peak-retention properties. This "40 year anniversary" issue provides an opportune forum to do so.

Starting with a previously derived equation for the solute partition coefficient in the case of a binary liquid mobile phase and an absorbent (liquid-like) stationary phase that are completely immiscible, and exploiting the isomorphism between the upper critical solution temperature (U.C.S.T.) in a binary liquid system and the liquid-gas critical point in a single-component fluid system (1), a general equation is derived for the solute partition coefficient in a chromatographic system where the stationary phase is an absorbent and the mobile phase is a single-component ideal gas, moderately nonideal gas, supercritical fluid or even a liquid. Given the more advanced state of theory and theoretical treatments of experimental data in gas and liquid chromatography, this unified theory should find its widest application in supercritical fluid chromatography (SFC), as will be illustrated.

THEORY

Let us consider the distribution of solute (component a; e.g., an alkyl benzene) between two completely immiscible liquid phases constituting a conventional (reversed-phase) liquid-liquid chromatographic (LLC) system: a stationary phase (component d; e.g., a high molecular weight alkane) and two mixed solvents, a "good" solvent (component b; e.g., methanol) and a "poor" solvent (component c; e.g., water). In our previous theoretical work in liquid chromatography based on cell or lattice models (3-5), we have ultimately shown that the solute partition coefficient, K_{b+c}, in such a mixed-solvent system is given by

$$\ell nK_{b+c} = \theta_b \ell nK_b + \theta_c \ell nK_c - \theta_b \theta_c r_a \chi_{bc} \tag{1}$$

where θ_i is the volume fraction of mobile-phase solvent i, K_b and K_c are the partition coefficients with, respectively, neat b and neat c as the mobile phases, where

$$\ell nK_b = r_a(r_d^{-1}-r_b^{-1}) + r_a(\chi_{ab}-\chi_{ad}) \tag{2}$$

$$\ell nK_c = r_a(r_d^{-1}-r_c^{-1}) + r_a(\chi_{ac}-\chi_{ad}) \qquad (3)$$

and where r_i is the number of segments in molecule i (proportional to its van der Waals volume) and χ_{ij}, the interaction parameter, is given by

$$\chi_{ij} = (z/k_BT)[\varepsilon_{ij} - (\varepsilon_{ii}+\varepsilon_{jj})/2] \qquad (4)$$

where z is the lattice coordination number, k_B is the Boltzmann constant, T is the experimental temperature and ε_{ij} (< 0) is the attractive interaction energy between two adjacent non-bonded segments on molecules i and j. Scaling the system to the smallest molecule by letting $r_c = 1$, inserting eqn. 2 and 3 into eqn. 1, and collecting terms (with $\theta_c = 1 - \theta_b$), one obtains the familiar quadratic form (4):

$$\begin{aligned}\ell nK_{b+c} &= \ell nK_c + r_a(1-r_b^{-1})\theta_b \\ &\quad + r_a(\chi_{ab}-\chi_{ac}-\chi_{bc})\theta_b + r_a\chi_{bc}\theta_b^2. \qquad (5)\end{aligned}$$

Eqn. 1 and 5, which may be written in terms of the respective capacity factors, k', instead of K, are also applicable to chemically-bonded stationary phases in the "collapsed-chain limit" (4), and require that both the uptake of mobile-phase solvent by the stationary phase and the contribution of interfacial adsorption to solute retention are negligible (3-5). In eqn. 5, the entire stationary-phase contribution is contained in ℓnK_c, the remaining terms being solely mobile-phase ones (6).

Eqn. 5 may be manipulated into reduced form by first noting the critical solution conditions (7), applicable here to the mobile phase (b+c):

$$T_{(cr)} = 2\ T\ r_b \chi_{bc}/(1+\sqrt{r_b}\,)^2 \tag{6}$$

$$\theta_{b(cr)} = (1+\sqrt{r_b}\,)^{-1} \tag{7}$$

where $T_{(cr)}$ refers to the U.C.S.T. (above which the b+c solvent system is homogeneous over the entire composition region) and $\theta_{b(cr)}$ refers to the critical volume fraction of "good" solvent, i.e., the composition corresponding to $T_{(cr)}$ in the T-θ_b phase diagram. Introducing reduced variables (subscript R),

$$T_R = T/T_{(cr)} = (1+\sqrt{r_b}\,)^2/2r_b\chi_{bc} \tag{8}$$

$$\theta_R = \theta_b/\theta_{b(cr)} = \theta_b(1+\sqrt{r_b}\,) \tag{9}$$

substituting eqn. 8 and 9 into eqn. 5, eqn. 8 into eqn. 3, and applying eqn. 4, one finds (6)

$$\begin{aligned} \ell nK_{b+c} &= \ell nK_c + (r_a/r_b)(\sqrt{r_b}-1)\theta_R + (r_a/r_b)(\theta_R^{\,2}/2T_R) \\ &\quad + (r_a/r_b)(\sqrt{r_b}+1)[(\varepsilon_{ab}-\varepsilon_{ac}-\varepsilon_{bc}+\varepsilon_{cc})/(2\varepsilon_{bc}-\varepsilon_{bb}-\varepsilon_{cc})](\theta_R/T_R) \end{aligned} \tag{10}$$

$$\begin{aligned} \ell nK_c &= (r_a/r_b)[(r_b/r_d) - r_b] \\ &\quad + (r_a/r_b)(\sqrt{r_b}+1)^2[(\varepsilon_{ac}-1/2\varepsilon_{cc}-\varepsilon_{ad}+1/2\varepsilon_{dd})/(2\varepsilon_{bc}-\varepsilon_{bb}-\varepsilon_{cc})]/T_R \end{aligned} \tag{11}$$

By invoking the isomorphism between the critical behavior in a binary liquid system and that in a single-component fluid system

(1), 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. Accordingly, replacing θ_R by $\rho_R = \rho/\rho_{cr}$, the reduced density of the single-component fluid (whence, $T_R = T/T_{cr}$ becomes the usual reduced temperature of the fluid), replacing K_c by K_o, the solute partition coefficient as $\rho_R \rightarrow 0$ (representing ideal gas-liquid chromatography, GLC), and letting $\varepsilon_{ic} = 0$ (i = a, b, c), i.e., recognizing that interactions involving unoccupied or void space are zero, eqn. 10 and 11 yield (6)

$$\ell nK = \ell nK_o + F(T_R,\rho_R) \tag{12}$$

$$\ell nK_o = (r_a/r_b)[(r_b/r_d) - r_b] + (r_a/r_b)(1+\sqrt{r_b}\,)^2[(\varepsilon_{ad}/\varepsilon_{bb}) - (\varepsilon_{dd}/2\varepsilon_{bb})]/T_R \tag{13}$$

$$F(T_R,\rho_R) = (r_a/r_b)[(\sqrt{r_b}-1)(\rho_R) - (\sqrt{r_b}+1)(\varepsilon_{ab}/\varepsilon_{bb})(\rho_R/T_R) + (\rho_R{}^2/2T_R)] \tag{14}$$

where K (replacing K_{b+c}) is the solute partition coefficient when the mobile-phase reduced density is ρ_R. The entire stationary-phase contribution to solute retention is contained in ℓnK_o and the mobile-phase contribution is given by $F(T_R,\rho_R)$. Consistent with the assumptions made in deriving eqn. 1 and 5 (hence, eqn. 12-14), since the phase ratio, $\Phi = V_s/V_m$, is assumed to be independent of θ_R (hence, ρ_R), eqn. 12 may be written in terms of the respective k' volumes:

$$\ell nk' = \ell nk'_o + F(T_R,\rho_R) \qquad (15)$$

where $k' = K\,\Phi$ and $k'_o = K_o\Phi$.

Finally, let us consider the temperature and density derivatives of $\ell nk'$. Neglecting the temperature dependence of Φ, from thermodynamics and eqn. 13 one obtains

$$R[d\ell nk'_o/dT^{-1}] \approx R[d\ell nK_o/dT^{-1}] = \Delta\overline{H}^{\infty}_{a(d)} - RT = \Delta\overline{E}^{\infty}_{a(d)} =$$

$$RT_{cr}(r_a/r_b)(1+\sqrt{r_b'})^2[(\varepsilon_{ad}/\varepsilon_{bb}) - (\varepsilon_{dd}/2\varepsilon_{bb})] \qquad (16)$$

where $\Delta\overline{E}^{\infty}_{a(d)}$ and $\Delta\overline{H}^{\infty}_{a(d)}$ (both > 0) are, respectively, the partial molar internal energy and enthalpy of solute transfer, at infinite dilution, from the pure stationary liquid to an ideal-gas mobile phase ($\rho_R = 0$). Similarly, from eqn. 14:

$$R[\partial F(T_R,\rho_R)/\partial T^{-1}]_{\rho_R} = -\Delta\overline{E}^{\infty}_{a(b)} =$$

$$-RT_{cr}(r_a/r_b)[(\sqrt{r_b'}+1)(\varepsilon_{ab}/\varepsilon_{bb})(\rho_R) - (\rho_R{}^2/2)] \qquad (17)$$

where $\Delta\overline{E}^{\infty}_{a(b)}$ (> 0) is the partial molar internal energy of solute transfer, at infinite dilution, from the actual mobile phase at ρ_R to an ideal-gas mobile phase. Therefore, from eqn. 15-17:

$$R[\partial\ell nk'/\partial T^{-1}]_{\rho_R} \approx R[\partial\ell nK/\partial T^{-1}]_{\rho_R} =$$

$$\Delta\overline{E}^{\infty}_{a(d)} - \Delta\overline{E}^{\infty}_{a(b)} = \Delta\overline{E}^{\infty}_{a(d\rightarrow b)} \qquad (18)$$

where $\Delta\overline{E}^{\infty}_{a(d\rightarrow b)}$ reflects the actual chromatographic process at ρ_R, i.e., solute transfer from the stationary liquid phase (d) to the actual mobile phase (b), and is the slope of a $R\ell nk'$ vs. T^{-1} plot at fixed ρ_R. Note that if a ρ_R value is reached where $\Delta\overline{E}^{\infty}_{a(d\rightarrow b)} = 0$, then $\ell nk'$ is predicted to be independent of temperature for the particular chromatographic system at that density.

Neglecting the mobile-phase density dependence of Φ, eqn. 12-15 give:

$$[\partial \ell nk'/\partial \rho_R]_{T_R} \approx [\partial \ell nK/\partial \rho_R]_{T_R} = [\partial F(T_R,\rho_R)/\partial \rho_R]_{T_R} =$$

$$(r_a/r_b)[\sqrt{r_b} -1) - (\sqrt{r_b} +1)(\varepsilon_{ab}/\varepsilon_{bb})/(T_R) + (\rho_R/T_R)] \qquad (19)$$

Setting eqn. 19 equal to zero, one predicts the following condition for the existence of a minimum in a $\ell nk'$ vs. ρ_R plot at fixed T_R:

$$(\rho_R)_{min} = (\sqrt{r_b} +1)(\varepsilon_{ab}/\varepsilon_{bb}) - (\sqrt{r_b} -1)T_R > 0. \qquad (20)$$

Note that for a given mobile phase (b), the position of the minimum, $(\rho_R)_{min}$, is predicted to depend only on the chemical nature of the solute (through ε_{ab}) and thus should be approximately the same for a given class of solutes and shift to higher values for more polarizable and/or polar solutes.

DISCUSSION

The fundamental equations comprising the unified theory are eqn. 12-15. They describe solute retention with an absorbent (liquid-like) stationary phase and a single-component mobile fluid phase which may be a gas, liquid or supercritical fluid. They are in the form of separable and additive stationary-phase and mobile-phase contributions to solute retention. They clearly reveal that the natural mobile-phase state variables are temperature and density (viz., the reduced variables, T_R and ρ_R). Details of the dependence of solute retention on temperature at fixed density and on density at fixed temperature, as derived from eqn. 12-15, are given by eqn. 16-20.

The apparent restrictions (some being interrelated) on these equations are: (a) the contribution to solute retention from interfacial adsorption is negligible; (b) the mobile phase and stationary phase are virtually immiscible over the operating T_R, ρ_R range; (c) the phase ratio is virtually independent of T_R and ρ_R; (d) the stationary-phase contribution to solute retention (ℓnK_o or $\ell nk'_o$) is independent of ρ_R. Although these may appear to be severe limitations, we have shown, for example, in the case of alkane solutes, supercritical CO_2 as the mobile phase and polysiloxanes as the stationary phase (systems for which condition a is satisfied), that even though conditions b, c and d are not fully satisfied individually, these equations still provide an excellent description of the SFC data, as a result of compensating (and essentially cancelling) effects (8). For instance, although the stationary phase tends to swell somewhat as CO_2 density (or pressure) increases at fixed temperature (leading to longer retention and a larger phase ratio, V_s/V_m), this is counterbalanced by the effect of external pressure *per se* (leading to shorter retention and a smaller phase ratio).

In ideal and moderately nonideal GLC, restrictions b and d are of no real consequence, and small corrections for the thermal expansion of the stationary phase (in restriction c) are easily handled (9, 10). In LLC (including chemically-bonded-phase systems), the situation depends on the amount of uptake of the mobile-phase solvent by the stationary phase (and vice versa when the stationary phase is not immobilized), but the unified theory may be readily modified to take into account these second-order effects (4,5,8). In both GLC (9-11) and LLC (3-5) (and, presumably, SFC), the contribution to retention from interfacial adsorption (restriction a) may be important, depending on the chemical nature of the chromatographic system. Theoretical models incorporating concurrent adsorption and absorption effects have been developed for GLC (9-11) and LLC (4,5). In a future study, the present unified theory will be extended to treat adsorbent stationary phases, as well as concurrent adsorption and absorption contributions to solute retention.

Returning to eqn. 12-15, note first that r_a/r_b is a linear function of solute carbon number (n_a) for a homologous solute series. Accordingly, $\ell nk'$ (or ℓnK) is a linear function of both n_a and the reciprocal of the reduced temperature (T_R), and a quadratic function of the mobile-phase reduced density (ρ_R). Note also that the quadratic dependence of $\ell nk'_{b+c}$ (or ℓnK_{b+c}) on θ_b or θ_R, eqn. 5 or 10, is mirrored by the quadratic dependence of $\ell nk'$ (or ℓnK) on ρ or ρ_R, indicating that reducing retention via replacing "poor" solvent by "good" solvent in LC with binary liquid mobile phases through increasing θ_b is formally equivalent to doing it by replacing "holes" or void space by molecules or occupied space in dense-gas GC or SFC with a single-component mobile phase through increasing ρ. This suggests that what has been learned about solvent-gradient elution in LC should find application to density-gradient elution in SFC.

The stationary-phase contribution to solute retention, $\ell nk'_o$ the capacity factor at $\rho_R = 0$, may be obtained directly from ideal GLC (effectively, at very low column pressures) or by extrapolation to zero density (or column pressure) using moderately nonideal GLC (9,10). As is well-known (9,10) and can be seen from eqn. 13, $\ell nk'_o$ increases with increasing solute molecular volume (6), increasing strength of solute-stationary liquid segmental attractive interactions (ε_{ad}), decreasing strength of mutual stationary liquid segmental attractive interactions (ε_{dd}), and decreasing temperature.

The mobile-phase contribution to solute retention, $F(T_R,\rho_R)$, is given by eqn. 14. The first term in the square brackets arises from configurational entropy, is independent of temperature, and leads to an increase in solute retention with increasing ρ. The second and usually dominant term stems from attractive solute-mobile phase segmental interactions (ε_{ab}) and leads to a decrease in solute retention with increasing ρ, more so for larger ε_{ab} and at lower temperatures. The third term reflects mutual mobile-phase segmental attractive interactions (which, in effect, act as solute-mobile phase repulsive interactions), becomes more important at higher ρ values, and leads to an increase in solute retention with increasing ρ, more so at lower temperatures. Note that the possibility of a minimum in $\ell nk'$ vs. ρ at fixed T is predicted at a mobile-phase density where the first and third terms begin to overcome the second term (see eqn. 19 and 20).

The dependence of $\ell n k'$ on reciprocal temperature at fixed mobile-phase density is described by eqn. 16-18. For a given chromatographic system they predict a positive slope at $\rho = 0$, becoming increasingly less positive with increasing ρ (as has been observed in SFC (8)), and the possibility of a zero slope ($\ell n k'$ independent of T) at some sufficiently high ρ, where the solute would show no energetic preference toward either of the two phases. They also predict that plots of $\ell n k'$ vs. T^{-1} at fixed ρ should be continuous as one passes from the supercritical fluid region through the critical isotherm and into the liquid region of the mobile phase (provided, of course, no phase boundary is crossed), as has been observed experimentally (12).

To assess quantitatively the effect of mobile-phase density on solute retention, let us first rearrange eqn. 15:

$$\ell n(k'/k'_o) = F(T_R,\rho_R) \qquad (21)$$

where $F(T_R,\rho_R)$, which reflects the "solvent strength", is given by eqn. 14 and where eqn. 21 describes solute retention (k') relative to the ideal GLC value (k'_o). To apply eqn. 14 and 21, the critical temperature and density of the mobile phase are required. To use an SFC example, T_{cr} = 304.2 K and ρ_{cr} = 0.468 g/cm^3 for CO_2. The reduced state variables, T_R and ρ_R, may then be determined from the experimental conditions, leaving only three molecular parameters, r_a/r_b, r_b and $\varepsilon_{ab}/\varepsilon_{bb}$ with which to contend.

The parameter r_a/r_b may be conveniently and accurately estimated from the ratio of the respective van der Waals volumes (13). By analyzing SFC data for _n_-alkane solute/CO_2 mobile phase/cross-linked SE-54 stationary phase systems, reported at several temperatures and densities (14,15), best-fit values of $r_b = 4.61$ and $\varepsilon_{ab}/\varepsilon_{bb} = 0.884$ have been determined (8), the latter value indicating slightly weaker alkane-CO_2 segmental attractive interactions relative to CO_2-CO_2 ones. Inserting these values into eqn. 14 and 21, one obtains the following general expression for _n_-alkane solute + CO_2 mobile-phase systems (with _any_ absorbent stationary phase):

$$\ell n(k'/k'_o) = (r_a/r_b)[1.148(\rho_R) - 2.784\ (\rho_R/T_R) + 0.500(\rho_R{}^2/T_R)] \qquad (22)$$

Other solutes or solute classes may be similarly characterized, requiring only the assignment of $\varepsilon_{ab}/\varepsilon_{bb}$.

The quantitative predictive ability of eq. 22 has been successfully tested with immobilized Carbowax 400 as the stationary phase (6,8). Moreover, the validity of this theoretical approach has been demonstrated by determining $\varepsilon_{ab}/\varepsilon_{bb}$ for n-alkane solute + supercritical ethane mobile-phase systems. The determined value, 1.04, is close to the expected value, 1.00 (8).

Methylene group selectivity, relative to such selectivity under ideal GLC conditions ($\rho \rightarrow 0$), can be examined using eqn. 22.

With $r_a/r_b = 1.388 + 0.519\, n'_a$ (13), where n'_a is the number of methylene carbons in the n-alkane solute, eqn. 22 gives:

$$[\partial \ln(k'/k'_o)/\partial n'_a]_{\rho_R} = 0.596(\rho_R) - 1.446(\rho_R/T_R) + 0.260(\rho_R{}^2/T_R). \qquad (23)$$

Therefore, in supercritical CO_2 at 49.3°C ($T_R = 1.06$), the methylene group selectivity (slope of the $\ln k'$ vs. n'_a plot at fixed T and ρ) is predicted to become less positive (relative to the slope of the $\ln k'_o$ vs. n'_a plot at the same T) by the following decrements: 0.340, 0.541 and 0.601 units at, respectively, ρ = 0.25, 0.50 and 0.75 g/cm^3 ($\rho_R = \rho/0.468$). This trend of decreasing selectivity with increasing CO_2 density has been observed experimentally (8).

Letting $r_b = 4.61$ in eqn. 20, the following positions of retention minima are predicted for CO_2 mobile-phase systems:

$$(\rho_R)_{min} = 3.148(\varepsilon_{ab}/\varepsilon_{bb}) - 1.148\, T_R. \qquad (24)$$

For n-alkane solutes ($\varepsilon_{ab}/\varepsilon_{bb} = 0.884$), eqn. 24 predicts a minimum at $\rho = 0.75$ g/cm^3 at 40°C, shifting to $\rho = 0.68$ g/cm^3 at 80°C, where the higher thermal energy is more effective in overcoming solute-mobile phase attractive interactions (see eqn. 19 and earlier discussion). For the more polarizable naphthalene as the solute ($\varepsilon_{ab}/\varepsilon_{bb} = 0.973$ (8)), eqn. 24 predicts a minimum at ρ = 0.88 g/cm^3 at 40°C, corresponding to a CO_2 pressure of 250 bar, which is the approximate column pressure at which Christensen (16) observed common retention minima for several polycylic aromatic hydrocarbon solutes.

Using a simple thermodynamic argument, an interesting relationship with practical implications can be developed between the dependence of solute retention in SFC and solute solubility in supercritical fluid extraction (SFE) on T_R and ρ_R of the supercritical fluid (SF). Continuing to assume that the stationary-phase contribution to solute retention is independent of ρ_R and is entirely contained in $\ell n k'_o$, then from eqn. 21

$$\ell n(k'_o/k') = \ell n(c_{a(b)}/c^o_{a(b)}) = - F(T_R,\rho_R) \qquad (25)$$

where $c^o_{a(b)}$ and $c_{a(b)}$ refer to the concentration of solute in the SF mobile phase (b) at $\rho_R = 0$ and $\rho_R > 0$, respectively. If it is also assumed, in a parallel manner, that the thermodynamic properties of the SFE matrix (e.g., a pure compound being solubilized or a mixture containing a compound being extracted by the SF) are relatively insensitive to ρ_R, and if compounds which are but sparingly soluble in the SF are considered (17), then the solubility enhancement factor (18-20), $E = c_{a(b)}/c^o_{a(b)}$, in SFE should be approximately equal to k'_o/k'; i.e., from eqn. 25:

$$\ell n E \approx \ell n(k'_o/k') = - F(T_R,\rho_R) \qquad (26)$$

where $F(T_R,\rho_R)$ is given by eqn. 14.

Equation 26 implies that information obtained by SFC through studying the effects of temperature and density on solute retention (to determine $F(T_R,\rho_R)$) should be useful in assessing the solubility enhancement in SFE of the same solute or class of solutes, provided the concentration of solute in the latter is sufficiently low (17). By extension, it also suggests the use of SFC as a "pilot plant" for SFE, wherein the potential of different SF and modifiers ("entrainers" in SFE) may be rapidly and economically screened. It should be noted that Giddings and co-workers (18,19) were the first to explore the similarities between solubility enhancement in SFE and migration enhancement in SFC.

Equation 19 and 26 predict that, for a given solute + SF system, solubility maxima in SFE should be observed at approximately the same SF density as retention minima in SFC (see eqn. 20), a prediction lacking a definitive experimental test. That solubility maxima exist in SFE is well-known (19,20), and the rationale offered for their appearance (20) is quite similar in spirit to the theoretical analysis presented earlier to explain SFC retention minima. In qualitative agreement with eqn. 24 (written now in terms of $(\rho_R)_{max}$), it has been observed (19) that Carbowax-1000 and -4000 (same $\varepsilon_{ab}/\varepsilon_{bb}$) have a solubility maximum at virtually the same SF CO_2 density and that the maximum for octadecanol (smaller $\varepsilon_{ab}/\varepsilon_{bb}$ than the previous compounds, since it mainly reflects methylene-CO_2 interactions) occurs at a much lower CO_2 density. Also, the solubility maximum for hydrocarbon solute + SF CO_2 clearly shifts toward lower density at higher temperature (21), as predicted (vide supra).

Finally, from a more detailed derivation and exposition of this unified theory presented elsewhere (8), it has been shown that eqn. 12-15 may be represented in terms of macroscopic properties instead of molecular parameters (22), as follows

$$\ln k' = \ln k'_o + [(2B_{ab}-\overline{V}^{\infty}_{a(d)})/V_{cr}]\rho_R + (V^*_a/V^*_b)(\rho_R{}^2/2T_R) \qquad (27)$$

where B_{ab} is the (temperature-dependent) solute-mobile phase interaction second virial coefficient (9,10,23), $\overline{V}^{\infty}_{a(d)}$ is the infinite-dilution solute partial molar volume in the stationary liquid (approximately equal to the liquid molar volume of the pure solute), V_{cr} is the critical volume of the mobile-phase fluid and $V^*_a/V^*_b = r_a/r_b$ is a ratio of the van der Waals molar volumes. For sufficiently low (but not negligible) ρ_R where one may neglect the $\rho_R{}^2$ term, letting $\rho \approx \langle P\rangle M/RT$, where $\langle P\rangle$ is the average mobile-phase column pressure and M is the molecular weight of the mobile phase, eqn. 27 yields:

$$\ln k' = \ln k'_o + [(2B_{ab}-\overline{V}^{\infty}_{a(d)})/RT]\langle P\rangle \qquad (28)$$

which is the familiar result for solute retention in moderately nonideal GLC (9).

As should be evident from the fact that eqn. 12-15 were derived starting with LC equations and from the aforementioned continuity in $\ln k'$ vs. T^{-1} plots at fixed ρ (12), it is also possible to show in more detail (8) that the familiar LLC result for solute retention with a single-component liquid mobile phase (3) is embodied in the unified theory.

CONCLUDING REMARKS

The conceptual advantages, convenience and utility of the proposed unified theory have been demonstrated. Namely, solute retention behavior in ideal gas, moderately nonideal gas, supercritical fluid and liquid mobile phases can be uniformly treated, interpreted and compared within a single theoretical framework.

It is hoped that this paper will stimulate the reader to reflect on and develop other principles and/or equations unifying different chromatographic or, more broadly, separations methods. Given the conceptual and practical advantages to be gained, it would indeed be unfortunate if another twenty years passed without significant effort in this direction.

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REFERENCES AND NOTES

1. Griffiths, R.B.; Wheeler,J.C. Phys. Rev. A **1970**, 2, 1047.

2. Giddings, J.C. In "Gas Chromatography 1964"; Goldup, A., Ed.; Elsevier: Amsterdam, **1965**; pp. 3-24.

3. Locke, D.C.; Martire, D.E. Anal. Chem. **1967**, 39, 921; Martire, D.E.; Locke, D.C. Anal. Chem. **1971**, 43, 68.

4. Martire, D.E.; Boehm, R.E. J. Phys. Chem. **1983**, 87, 1045.

5. Jaroniec, M.; Martire, D.E. J. Chromatogr. **1986**, 351, 1.

6. Note that the formulations for ℓnK_c (eqn. 3 and 11) and ℓnK_o (eqn. 13) are strictly applicable to translationally and rotationally (internal and external) unrestricted stationary liquids. To account explicitly for the effects of molecular restriction due to immobilization and/or cross-linking of the stationary phase, which are entropic in origin, the first r.h.s. term in each of these equations would have to be

modified, but would, nevertheless, remain proportional to r_a (4). This limitation, of course, does not preclude use of the unified theory to describe the dependence of solute retention on the mobile-phase state variables.

7. Hill, T.H. "An Introduction to Statistical Thermodynamics"; Addison-Wesley: Reading, MA, **1960**; chaps. 20 and 21.

8. Martire, D.E.; Boehm, R.E. J. Phys. Chem. **1987**, 91, 0000 (in press), and references cited therein.

9. Laub, R.J.; Pecsok, R.L. "Physicochemical Applications of Gas Chromatography"; John Wiley and Sons: New York, **1978**.

10. Conder, J.R.; Young, C.L. "Physicochemical Measurement by Gas Chromatography"; John Wiley and Sons: New York, **1979**.

11. Martire, D.E. In "Progress in Gas Chromatography"; Purnell, J.H., Ed.; John Wiley and Sons: New York, **1968**; pp. 93-120.

12. Lauer, H.H; McManigill, D.; Board, R.D. Anal. Chem. **1983**, 55, 1370.

13. Bondi, A. J. Phys. Chem. **1964**, 68, 441.

14. Wright, B.W.; Kalinoski, H.T.; Smith, R.D. Anal. Chem. **1985**, 57, 2823.

15. Yonker, C.R.; Smith, R.D. J. Chromatogr. **1986**, 351, 211.

16. Christensen, R.G. J. High Resolut. Chromatogr. Chromatogr. Comm. **1985**, 8, 824.

17. Note that the theory may be readily extended to include solutes at higher concentrations in SFE and to derive a more general equation than eqn. 26 to link SFC and SFE (8).

18. Giddings, J.C.; Myers, M.N.; King, J.W. J. Chromatogr. Sci. **1969**, 7, 276.

19. Czubryt, J.J.; Myers, M.N.; Giddings, J.C. J. Phys. Chem. **1970**, 74, 4260.

20. Schneider, G.M. Ber. Bunsenges. Phys. Chem. **1984**, 88, 841.

21. Giddings, J.C., private communication (unpublished data), December, **1986**.

22. Actual B_{ab} data are available for a limited number of systems, but primarily for low molecular weight (volatile) solutes (23). In principle, B_{ab} may be estimated from pure-component properties (9,10), but the additional estimate of critical

properties would be required for high molecular weight (nonvolatile) solutes. Accordingly, while such an eventuality does seem unlikely, it remains to be determined whether eqn. 27 proves to be as useful and accurate as the form in terms of molecular parameters that has been applied here and elsewhere (8).

23. Dymond, J.H.; Smith, E.B. "The Virial Coefficients of Pure Gases and Their Mixtures"; Clarendon Press: Oxford, U.K., 1980.