

Thermodynamic pitfalls in chromatography revisited: supercritical fluid chromatography

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ABSTRACT

Relationships between solute retention in supercritical fluid chromatography and thermodynamic properties of solute transfer from the mobile to the stationary phase are reviewed and illustrated with statistical thermodynamic calculations on a model system. Attention is paid to the effect of sorption of the mobile phase fluid into the stationary phase. The nearly linear plots of $\ln k'$ vs. $1/T$ at a constant density of the mobile phase fluid ("Van 't Hoff plots") are shown to be of little use in themselves for determining the solute transfer properties. Apparent linearity of these plots results from cancellation of thermodynamic anomalies near the critical point of the mobile phase fluid.

INTRODUCTION

The connection between chromatographic retention and standard thermodynamic properties of sorption was discussed by James *et al.* in a classical but topical paper [1] entitled "Thermodynamic pitfalls in gas chromatography", to which the title of the present contribution makes a deliberate reference. James *et al.* emphasized that, in the equation for the standard molar Gibbs energy of sorption,

$$\Delta G_{sp}^0 = -RT \ln K \quad (1)$$

where R is the molar gas constant and T is the absolute temperature, K is the thermodynamic equilibrium constant given by the ratio of solute activities in the stationary and the mobile phase. The choice of standard states in expressing the activities [2] then determines the physical meaning of ΔG_{sp}^0 and of the derived properties (ΔH_{sp}^0 , ΔS_{sp}^0 , etc.). A clear explanation of this topic has been given by Meyer in two papers concerned

with gas–liquid [3] and gas–solid [4] chromatography.

Chromatographers often yield to temptation to replace the equilibrium constant in eqn. 1 with the chromatographic partition coefficient given by the ratio of solute concentrations in the stationary and the mobile phase. However, such a substitution deprives ΔG_{sp}^0 and the derived properties of their exact meaning because it is then no longer clear what the states of the solute are in both phases to which the sorption properties refer.

In supercritical fluid chromatography (SFC), the standard thermodynamic properties of sorption have not been much used, possibly because the actual physical states of a non-volatile solute in a supercritical mobile phase and in a swollen stationary phase cannot be conveniently related to any sensible choice of standard states for the solute. Instead, thermodynamics of solute retention in SFC have been treated in terms of transfer properties, *i.e.*, the property changes

associated with the transfer of the solute from its actual state in the mobile phase to its actual state in the stationary phase. Similarly as with the standard properties of sorption, the relationships between the transfer properties and the various retention parameters have sometimes been misinterpreted; an example is provided by what is called "Van 't Hoff plots" (see ref. 5 and the citations therein).

The purpose of this contribution is to present a consistent picture of the connections between the thermodynamic properties of solute transfer and the variations of solute retention with temperature and pressure. The discussion will be limited to partition chromatography at infinite dilution of the solute, and it will be illustrated by statistical thermodynamic calculations on a model system typical of open-tubular capillary column SFC. The transfer properties discussed will only be those at the level of the first derivatives of Gibbs energy with respect to temperature and pressure. Determination of higher order transfer properties (*e.g.*, the heat capacity of transfer) from experimental SFC retention data is precluded by insufficient precision of the data and by theoretical problems such as the effects of pressure- or temperature-induced changes in volume and composition of the stationary phase ("swelling").

THEORY

Transfer properties of the solute

Provided that the solute is infinitely diluted by both phases, a transfer property ΔZ_t per mol of the solute may be written as

$$\Delta Z_t = \bar{z}_{1s}^\infty - \bar{z}_{1m}^\infty \quad (2)$$

where \bar{z}_{1s}^∞ and \bar{z}_{1m}^∞ are the respective partial molar thermodynamic properties of the solute (1) at infinite dilution in the stationary (s) and the mobile (m) phases. The definition of ΔZ_t by eqn. 2 does not invoke any standard states.

According to eqn. 2, the Gibbs energy of transfer, ΔG_t , is equal to the difference between the infinite-dilution chemical potentials (= infinite-dilution partial molar Gibbs energies) of

the solute in the stationary and the mobile phases. However, the temperature and pressure in the two phases are the same and, in the centre of a chromatographic band, distribution of the solute between the two phases reflects the thermodynamic equilibrium. Consequently, the two chemical potentials must be the same, and

$$\Delta G_t = 0 \quad (3)$$

As $\Delta G_t = \Delta H_t - T \Delta S_t$, where ΔH_t and ΔS_t are the enthalpy and entropy of transfer, respectively, it follows from eqn. 3 that

$$\Delta S_t = \Delta H_t / T \quad (4)$$

It is useful to concentrate on the enthalpy of transfer and on the volume of transfer, ΔV_t , because these two quantities make important contributions to the temperature and pressure changes in solute retention, respectively. In accordance with eqn. 2,

$$\Delta V_t = \bar{v}_{1s}^\infty - \bar{v}_{1m}^\infty \quad (5)$$

and

$$\Delta H_t = \bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty \quad (6)$$

The infinite-dilution partial molar volume, \bar{v}_{1m}^∞ , and the infinite-dilution partial molar enthalpy, \bar{h}_{1m}^∞ , of the solute in the mobile phase are known to diverge as the temperature and pressure approach the critical point of the mobile phase fluid [6,7]. Near the critical point, \bar{v}_{1m}^∞ is proportional to the isothermal compressibility of the mobile phase fluid, β_{mT} [8–11] and \bar{h}_{1m}^∞ is proportional to the isobaric expansivity of the mobile phase fluid, α_{mP} [11]. The quantities α_{mP} and β_{mT} are defined by

$$\alpha_{mP} = (1/v_3)(\partial v_3 / \partial T)_P \quad (7)$$

and

$$\beta_{mT} = -(1/v_3)(\partial v_3 / \partial P)_T \quad (8)$$

where P is the pressure and v_3 is the molar volume of the pure mobile phase fluid. At the critical point, $\alpha_{mP} \rightarrow +\infty$ and $\beta_{mT} \rightarrow +\infty$. According to the classification presented by Debenedetti and co-workers [12,13], in the solute–mobile phase systems encountered in SFC, $\bar{v}_{1m}^\infty \rightarrow -\infty$ and $\bar{h}_{1m}^\infty \rightarrow -\infty$ at the critical point of the mobile

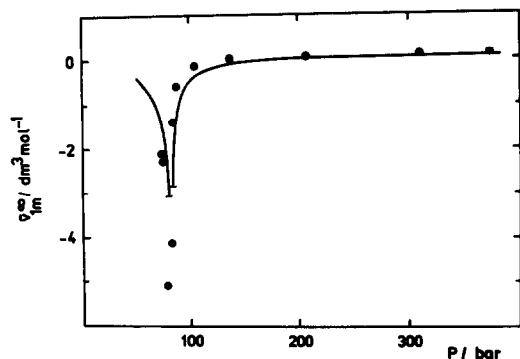


Fig. 1. Infinite-dilution partial molar volume of naphthalene in carbon dioxide at 35.23°C as a function of pressure. Experimental data are from ref. 14.

phase fluid. Large negative values of \bar{v}_{1m}^{∞} and \bar{h}_{1m}^{∞} persist at certain combinations of temperature and pressure in the supercritical region.

Fig. 1 shows the pressure dependence of \bar{v}_{1m}^{∞} for naphthalene in carbon dioxide at 35.23°C. The experimental values were obtained [14] from density measurements of high accuracy. The curve was calculated from a statistical thermodynamic treatment based on the mean-field lattice model designed by Panayiotou and Vera [15]. The details and parameterization of the treatment have been described elsewhere [16,17]. The break in the calculated curve near the minimum in \bar{v}_{1m}^{∞} results from decreased performance of mean-field models near the critical point. Nevertheless, the treatment correctly reproduces the essential features of the pressure course of \bar{v}_{1m}^{∞} .

The behaviour of \bar{h}_{1m}^{∞} in the supercritical region (Fig. 2) is similar to that of \bar{v}_{1m}^{∞} . As the

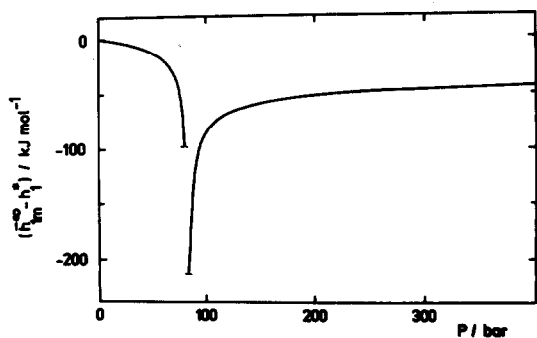


Fig. 2. Difference ($\bar{h}_{1m}^{\infty} - h_1^*$) for naphthalene in carbon dioxide as a function of pressure at 35°C.

statistical thermodynamic model employed cannot yield \bar{h}_{1m}^{∞} directly, the quantity plotted in Fig. 2 is $\bar{h}_{1m}^{\infty} - h_1^*$, where h_1^* is the molar enthalpy of pure naphthalene in an ideal-gas state at 35°C (h_1^* is independent of pressure).

Now let us return to the transfer properties ΔV_t and ΔH_t (eqns. 5 and 6) to consider how these quantities are affected by the large negative values of \bar{v}_{1m}^{∞} and \bar{h}_{1m}^{∞} near the mobile-phase critical point. Under the SFC conditions, an appreciable amount of the mobile phase fluid is sorbed in (or on) the stationary phase (see refs. 18 and 19 for reviews). Nevertheless, the arrangement of molecules in the stationary phase is still largely determined by the principal component of the stationary phase, *e.g.*, by the alkyl chains bonded to the surface of a silica particle in packed-column SFC or by a cross-linked siloxane polymer in open-tubular capillary SFC. Therefore, in the stationary phase there is no divergence in the range of molecular correlations as the temperature and pressure approach the mobile-phase critical point and, thereby, there is no physical reason for the quantities \bar{v}_{1s}^{∞} and \bar{h}_{1s}^{∞} to diverge. Consequently, eqns. 5 and 6 translate the large *negative* values of \bar{v}_{1m}^{∞} and \bar{h}_{1m}^{∞} near the critical point into large *positive* values of ΔV_t and ΔH_t . To illustrate this, Fig. 3 shows the pressure

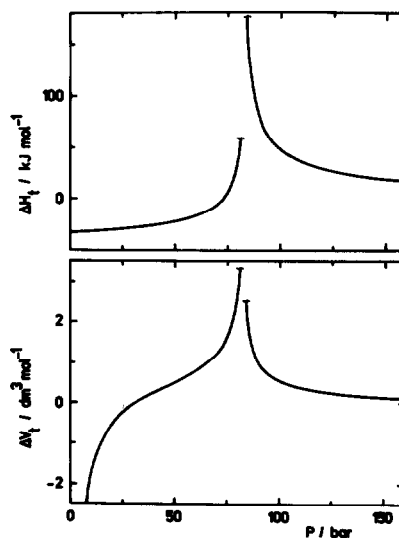


Fig. 3. Enthalpy of transfer and volume of transfer for naphthalene in the PDMS-carbon dioxide system at 35°C as functions of pressure.

courses at 35°C of ΔV_i and ΔH_i for naphthalene in the poly(dimethylsiloxane) (PDMS)–carbon dioxide system calculated with the mean-field lattice model mentioned above. The model takes the “swelling” of the stationary phase into account, and it predicts some variations of \bar{v}_{1s}^∞ and \bar{h}_{1s}^∞ with changing temperature or pressure. Near the critical point of the mobile phase, however, the variations in \bar{v}_{1s}^∞ and \bar{h}_{1s}^∞ are much less significant than those in \bar{v}_{1m}^∞ and \bar{h}_{1m}^∞ , respectively.

Transfer properties versus the effects of pressure and temperature on solute retention

In this section, the title relationships will be illustrated by computer calculations performed for the naphthalene (1)–PDMS (2)–carbon dioxide (3) system. The calculations are based on the statistical thermodynamic treatment mentioned above. It is assumed that a single mechanism of retention is operative, namely partitioning of the solute between the bulk mobile phase and the bulk stationary phase. As the treatment accounts for an appreciable swelling of PDMS by supercritical carbon dioxide [20,21], a reference value of the phase ratio is needed; it is assumed that, at 25°C and zero pressure (*i.e.*, no swelling), the phase ratio V_s/V_m is 0.04, which corresponds to a 50 μm I.D. capillary column containing a 0.5- μm thick film of PDMS. Further, it is assumed that the equilibrium concentration of carbon dioxide in PDMS at a given temperature and pressure is not disturbed by the presence of a trace amount of naphthalene (infinite dilution). The calculations also assume that there is a zero pressure drop along the column, but this assumption does not affect the discussion below. Solute retention will be expressed through the solute capacity factor, k' .

(i) *Pressure dependence of $\ln k'$ at a constant temperature.* Fig. 4 displays three calculated isotherms for $\ln k'$ of naphthalene in the present system. At a subcritical temperature (20°C), the calculated curve shows a discontinuity caused by liquefaction of carbon dioxide. The step decrease in $\ln k'$ reflects a sudden switch from gas chromatography (GC) to liquid chromatography (LC) as the pressure increases. At a temperature (40°C) not far above the critical temperature of

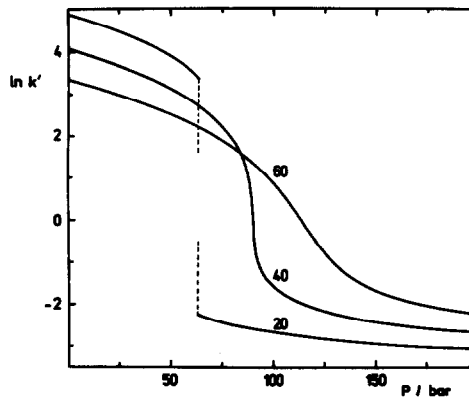


Fig. 4. Pressure dependence of $\ln k'$ for naphthalene in the PDMS–carbon dioxide system. Phase ratio at 20°C and zero pressure: $V_s/V_m = 0.04$. Numbers on the curves indicate the temperature (°C).

carbon dioxide, the discontinuity is replaced by a steep but continuous decrease in $\ln k'$. As the temperature increases, the S-shaped pattern in the isotherms becomes less apparent (60°C).

The slope of a tangent to an isotherm shown in Fig. 4 is given by [22–24]

$$\left(\frac{\partial \ln k'}{\partial P}\right)_T = -\Delta V_i/(RT) - \beta_{mT} - (V_s/V_m)\beta_{sT} - [1/(RT)](\partial \mu_{1s}^\infty/\partial w_{3s})_{T,P}(\partial w_{3s}/\partial P)_{T,\sigma} \quad (9)$$

where V_m and V_s are the volumes of the mobile and the stationary phase in the column, respectively, β_{sT} is the isothermal compressibility of the stationary phase, μ_{1s}^∞ is the infinite-dilution chemical potential of the solute in the stationary phase, w_{3s} is the mass fraction of the mobile phase fluid in the stationary phase and subscript σ denotes saturation of the stationary phase with the mobile phase fluid. The “unpleasant” last term on the right-hand side of eqn. 9 results from the effect of swelling; calculations indicate [17] that this term makes a positive contribution to $(\partial \ln k'/\partial P)_T$ in the present system. Generally, at a given temperature, the relative contribution to $(\partial \ln k'/\partial P)_T$ of the last term in eqn. 9 is minimum at the pressure where β_{mT} is maximum for the given temperature [17]. The term $(V_s/V_m)\beta_{sT}$ is negligible under most conditions.

Therefore, the large negative values of the slope $(\partial \ln k'/\partial P)_T$ near the mobile-phase critical point result from large positive values of β_{mT} and ΔV_t . Hypothetically, at the critical point itself, $(\partial \ln k'/\partial P)_T \rightarrow -\infty$ because $\beta_{mT} \rightarrow +\infty$ and $\Delta V_t \rightarrow +\infty$.

Eqn. 9 may serve as a basis for the determination of ΔV_t and \bar{v}_{1m}^∞ from the pressure course of solute retention at a constant temperature. The most recent applications of SFC for this purpose are those of Shim and Johnston [21,25]. In applying eqn. 9, allowance should be made for the pressure drop along the column [26–28].

Chimowitz and Kelley [22] and Shim and Johnston [25] pointed out that, to avoid the difficult fitting of the $\ln k'$ vs. P curve near the critical point, it is convenient to plot the experimental data as $\ln k'$ vs. $\ln \rho_m$, where ρ_m is the density of the mobile phase fluid. Unlike $(\partial \ln k'/\partial P)_T$, the derivative $(\partial \ln k'/\partial \ln \rho_m)_T$ does not diverge in the near-critical region. From eqn. 9 it follows that

$$\begin{aligned} (\partial \ln k'/\partial \ln \rho_m)_T &= -\Delta V_t/(RT\beta_{mT}) - 1 \\ &- (V_s/V_m)\beta_{sT}/\beta_{mT} - [1/(RT\beta_{mT})] \\ &\times (\partial \mu_{1s}^\infty/\partial w_{3s})_{T,P}(\partial w_{3s}/\partial P)_{T,\sigma} \end{aligned} \quad (10)$$

As the temperature and pressure approach the critical point, β_{mT} and ΔV_t increase and the relative contributions of the β_{sT} - and μ_{1s}^∞ -containing terms in eqn. 10 to $(\partial \ln k'/\partial \ln \rho_m)_T$ decrease [17]. Hypothetically, at the critical point itself, the derivative $(\partial \ln k'/\partial \ln \rho_m)_T$ would be equal to $-\Delta V_t/(RT\beta_{mT}) - 1$. The plot of $\ln k'$ vs. $\ln \rho_m$ is nearly linear, primarily because the ratio $\bar{v}_{1m}^\infty/\beta_{mT}$ is relatively constant in the near-critical region [8–11,14,22].

(ii) *Temperature dependence of $\ln k'$ at a constant pressure.* Fig. 5 shows several calculated isobars for $\ln k'$ of naphthalene in the present system. The break in the 70-bar curve results from vaporization of carbon dioxide which is accompanied by discontinuous decreases in density and solvating power. The break reflects a sudden switch from LC to GC as the temperature increases. In the LC domain, k' increases with increasing temperature at a constant pressure because of a decrease in the

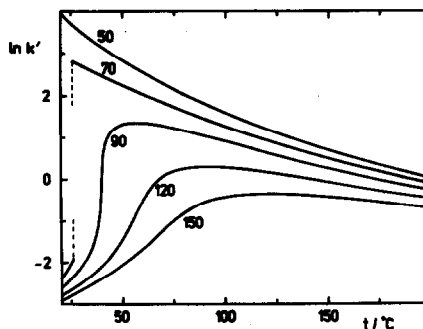


Fig. 5. Temperature dependence of $\ln k'$ for naphthalene in the PDMS-carbon dioxide system. Phase ratio at 20°C and zero pressure: $V_s/V_m = 0.04$. Numbers on the curves indicate the pressure (bar).

solvating power of carbon dioxide. In the GC domain, k' decreases with increasing temperature because of increasing volatility of naphthalene [29]. At supercritical pressures, the isobars become continuous and display maxima [30] that shift to higher temperatures at the pressure increases.

The slope of a tangent to an isobar in Fig. 5 may be written as [23,24]

$$\begin{aligned} (\partial \ln k'/\partial T)_P &= \Delta H_t/(RT^2) + \alpha_{mP} + (V_s/V_m)\alpha_{sP} \\ &- [1/(RT)](\partial \mu_{1s}^\infty/\partial w_{3s})_{T,P}(\partial w_{3s}/\partial T)_{P,\sigma} \end{aligned} \quad (11)$$

where α_{sP} is the isobaric expansivity of the stationary phase. The last term on the right-hand side of eqn. 11 results from the effect of swelling and it makes a negative contribution to $(\partial \ln k'/\partial T)_P$ in the present system. Generally, at a given pressure, the relative contribution to $(\partial \ln k'/\partial T)_P$ of the last term in eqn. 11 is minimum at the temperature where α_{mP} is maximum for the given pressure [17]. Except for the region near the isobar maximum, $\Delta H_t/(RT^2)$ is the major term on the right-hand side of eqn. 11 and the sign of $(\partial \ln k'/\partial T)_P$ is that of ΔH_t . The large positive values of the slope $(\partial \ln k'/\partial T)_P$ near the mobile-phase critical point result from large positive values of α_{mP} and ΔH_t . Hypothetically, at the critical point itself, $(\partial \ln k'/\partial T)_P \rightarrow +\infty$ because $\alpha_{mP} \rightarrow +\infty$ and $\Delta H_t \rightarrow +\infty$.

Eqn. 11 provides a way to determine ΔH_t and \bar{h}_{1m}^∞ from the temperature course of solute retention at a constant pressure. The most recent applications of SFC to this purpose are those of

Shim and Johnston [21,25], who also suggested a convenient mathematical transformation to avoid the difficulties imposed by the divergence of $(\partial \ln k'/\partial T)_P$ near the mobile-phase critical point, namely

$$(\partial \ln k'/\partial T)_P = \alpha_{mP}(\partial \ln k'/\partial \ln \rho_m)_T - T^2[\partial \ln k'/\partial(1/T)]_{\rho_m} \quad (12)$$

The slopes $(\partial \ln k'/\partial \ln \rho_m)_T$ (see above) and $[\partial \ln k'/\partial(1/T)]_{\rho_m}$ (see below) do not diverge near the critical point. In the near-critical region, therefore, the value of $(\partial \ln k'/\partial T)_P$ may be obtained from the experimental data on the "well behaved" quantities $(\partial \ln k'/\partial \ln \rho_m)_T$ and $[\partial \ln k'/\partial(1/T)]_{\rho_m}$ and from α_{mP} calculated from an accurate equation of state for the mobile phase concerned.

(iii) *Temperature dependence of $\ln k'$ at a constant density.* Fig. 6 shows $\ln k'$ for naphthalene calculated as a function of the reciprocal of absolute temperature at a constant density of carbon dioxide. The plots are nearly linear provided that suitable scales have been chosen for both axes. Lauer *et al.* [31] postulated a proportionality between ΔH_t and the slope of a constant-density plot. Thermodynamic analysis [5,17] yields a different expression for the slope, namely

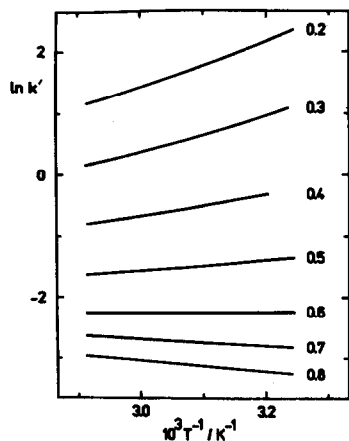


Fig. 6. Dependence of $\ln k'$ for naphthalene in the PDMS-carbon dioxide system on the reciprocal of absolute temperature. Phase ratio at 20°C and zero pressure: $V_s/V_m = 0.04$. Numbers adjacent to the lines indicate the density of carbon dioxide (g/cm^3).

$$\begin{aligned} [\partial \ln k'/\partial(1/T)]_{\rho_m} = & -(\Delta H_t - T\gamma_{mV} \Delta V_t)/R \\ & + T^2(V_s/V_m)(\beta_{sT}\gamma_{mV} - \alpha_{sP}) \\ & + (T/R)(\partial \mu_{1s}^\infty/\partial w_{3s})_{T,P}[(\partial w_{3s}/\partial T)_{P,\sigma} \\ & + \gamma_{mV}(\partial w_{3s}/\partial P)_{T,\sigma}] \end{aligned} \quad (13)$$

where $\gamma_{mV} = \alpha_{mP}/\beta_{mT}$ is the thermal pressure coefficient of the mobile phase fluid. Linearity of the constant-density plots has been interpreted by Martire and Boehm [32] in terms of the unified molecular theory of chromatography, *i.e.*, at a microscopic level. Eqn. 13 supports an alternative, model-independent interpretation at a macroscopic level. It reflects the different nature of constant-density plots compared with those labelling sections (i) and (ii) above. First, the quantities α_{mP} and β_{mT} that diverge at the mobile-phase critical point are absent from eqn. 13 (compare eqns. 9 and 11). Second, it has been shown [8–11] that, although both \bar{v}_{1m}^∞ and \bar{h}_{1m}^∞ diverge at the mobile-phase critical point, the difference $\bar{h}_{1m}^\infty - T\gamma_{mV}\bar{v}_{1m}^\infty$ always remains finite. This particular difference appears in eqn. 11 (see eqns. 5 and 6). In other words, unlike the plots labelling sections (i) and (ii) above, the constant-density plots are *not* sensitive to the near-critical anomalies in \bar{v}_{1m}^∞ and \bar{h}_{1m}^∞ because the anomalies cancel in eqn. 13. The other terms in eqn. 13 do not diverge near the critical point [17]. Therefore, the slope given by eqn. 13 remains relatively constant within narrow temperature intervals and the plot appears to be nearly linear. These considerations also imply that, contrary to popular belief, the constant-density plots themselves are of little use for determination of solute transfer properties.

CONCLUSIONS

Relationships between solute retention in partition chromatography and thermodynamic properties of solute transfer from the mobile to the stationary phase have been reviewed and illustrated by using a statistical thermodynamic model. The model of transfer, ΔV_t , may be obtained from the pressure derivative of $\ln k'$ at a constant temperature, and the enthalpy of transfer, ΔH_t , from the temperature derivative of

In k' at a constant pressure. Near the mobile-phase critical point where the two derivatives diverge, it is convenient to employ the transformations suggested by Chimowitz and Kelley [22] and by Shim and Johnston [25]. The entropy of transfer, ΔS_t , equals $\Delta H_t/T$ because the Gibbs energy of transfer is zero. In reducing the chromatographic data to thermodynamic properties, allowance should be made for the effects of swelling and for the pressure drop along the column. One should also bear in mind that the relationships given above assume infinite dilution of the solute in both phases and the absence of interfacial adsorption of both the solute and the mobile phase fluid. The nearly linear plots of $\ln k'$ vs. $1/T$ at a constant density of the mobile phase fluid ("Van 't Hoff plots") are of little use in themselves for determining the solute transfer properties. The apparent linearity of these plots arises from cancellation of near-critical anomalies in \bar{v}_{1m}^∞ and \bar{h}_{1m}^∞ .

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