Short Communication

Enthalpy of transfer in supercritical fluid chromatography

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ABSTRACT

The enthalpy of solute transfer from the mobile to the stationary phase in supercritical fluid chromatography has often been calculated from the plot of solute retention against the reciprocal absolute temperature at a constant density of the mobile phase fluid. In this treatment it has been assumed that the enthalpy of solute transfer is directly proportional to the slope of this plot.

In the present report, the above procedure is proven to be incorrect. A thermodynamic analysis shows that the slope of a constant-density plot is related neither to enthalpy nor to internal energy of solute transfer between the two phases.

The temperature dependence of solute retention in supercritical fluid chromatography has been studied at a constant pressure or at a constant density of the mobile phase fluid. The temperature dependence of the logarithm of the solute capacity factor, k, is strongly curved and displays a maximum when observed at a constant pressure [1–4]. On the other hand, the plots of ln k against the reciprocal of absolute temperature, $1/T$, at a constant density of the mobile phase are nearly linear [5]. Several workers [5–9] have employed constant-density plots to calculate the molar enthalpy of transfer of the solute from the mobile to the stationary phase, ΔH_t, according to the equation

$$\Delta H_t = -R[\partial \ln k/\partial(1/T)]_{\rho_m} \tag{1}$$

where R is the molar gas constant and ρ_m is the density of the mobile phase fluid. However, a rigorous thermodynamic support for eqn. 1 has never been presented. Further, Martire and Boehm [10] have related the slope of a constant-density plot to the internal energy of transfer, ΔU_t, rather than to the enthalpy of transfer. Therefore, an attempt to elucidate the actual thermodynamic background of the slope of a constant-density plot appeared worthwhile.

Considering $\ln k$ as a function of the reciprocal of absolute temperature, $1/T$, and of the pressure, P, one may write the total differential of $\ln k$ as

$$d\ln k = \left[\frac{\partial \ln k}{\partial(1/T)}\right]_P d(1/T) + \left(\frac{\partial \ln k}{\partial P}\right)_T dP \tag{2}$$

It follows directly from eqn. 2 that the derivative of $\ln k$ with respect to $1/T$ at a constant density of the mobile phase fluid is given by

$$\left[\frac{\partial \ln k}{\partial(1/T)}\right]_{\rho_m} = \left[\frac{\partial \ln k}{\partial(1/T)}\right]_P + \left(\frac{\partial \ln k}{\partial P}\right)_T \left[\frac{\partial P}{\partial(1/T)}\right]_{\rho_m} \tag{3}$$

Eqn. 3 may be rewritten in a more convenient form:

$$\left[\frac{\partial \ln k}{\partial(1/T)}\right]_{\rho_m} = -T^2(\partial \ln k/\partial T)_P - T^2\gamma_{mV}(\partial \ln k/\partial P)_T \tag{4}$$

where

$$\gamma_{mV} = (\partial P/\partial T)_{\rho_m} \tag{5}$$

is the thermal pressure coefficient [11] of the mobile phase fluid. The derivatives on the right-hand side of eqn. 4 are given by [12]

$$(\partial \ln k/\partial T)_P = (\bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty)/(RT^2) + \alpha_{mP} + (V_s/V_m)\alpha_{sP} + C(\partial x_{3s}/\partial T)_P \tag{6}$$

$$(\partial \ln k/\partial P)_T = (\bar{v}_{1m}^\infty - \bar{v}_{1s}^\infty)/(RT) - \beta_{mT} - (V_s/V_m)\beta_{sT} + C(\partial x_{3s}/\partial P)_T \tag{7}$$

where

$$C = 1/(1 - x_{3s}) - \partial \ln \varphi_{1s}^\infty/\partial x_{3s} \tag{8}$$

$\bar{h}_{1m}^\infty$ and $\bar{h}_{1s}^\infty$ are the infinite-dilution partial molar enthalpies of the solute in the mobile and the stationary phase, respectively, $\bar{v}_{1m}^\infty$ and $\bar{v}_{1s}^\infty$ are the infinite-dilution partial molar volumes of the solute in the two phases, V_m and V_s are the volumes of the two phases in the column, α_{mP} and α_{sP} are the isobaric expansivities of the two phases, β_{mT} and β_{sT} are the isothermal compressibilities of the two phases, x_{3s} is the equilibrium mole fraction of the mobile phase fluid in the stationary phase and φ_{1s}^∞ is the infinite-dilution fugacity coefficient of the solute in the stationary phase.

Substituting from eqns. 6 and 7 into eqn. 4 and employing the identity [11]

$$\alpha_{mP} = \beta_{mT}\gamma_{mV} \tag{9}$$

one obtains

$$\left[\frac{\partial \ln k}{\partial (1/T)}\right]_{\rho_m} = -[\bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty - T\gamma_{mV}(\bar{v}_{1s}^\infty - \bar{v}_{1m}^\infty)]/R + T^2(V_s/V_m)(\beta_{sT}\gamma_{mV} - \alpha_{sP}) -$$

$$CT^2[(\partial x_{3s}/\partial T)_P + \gamma_{mV}(\partial x_{3s}/\partial P)_T] \qquad (10)$$

If the terms containing V_s, V_m and x_{3s} are neglected, one arrives at a final approximate relationship

$$\left[\frac{\partial \ln k}{\partial (1/T)}\right]_{\rho_m} \approx -(\Delta H_t - T\gamma_{mV}\Delta V_t)/R \qquad (11)$$

where ΔH_t and ΔV_t are the molar enthalpy and molar volume of solute transfer from the mobile to the stationary phase, respectively:

$$\Delta H_t = \bar{h}_{1s}^\infty - \bar{h}_{1m}^\infty \qquad (12)$$

$$\Delta V_t = \bar{v}_{1s}^\infty - \bar{v}_{1m}^\infty \qquad (13)$$

The internal energy of solute transfer is given by

$$\Delta U_t = \Delta H_t - P\Delta V_t \qquad (14)$$

The term in parentheses on the right-hand side of eqn. 11 would be equal to ΔU_t if

$$T\gamma_{mV} = P \qquad (15)$$

In general, however, eqn. 15 applies only to an ideal gas. In a supercritical fluid the situation can be very different. For example, in carbon dioxide at 345 K and 150 bar, the Lee–Kesler correlation [13,14] yields $\gamma_{mV} = 1.88$ bar/K, so that $T\gamma_{mV} \approx 650$ bar.

CONCLUSIONS

The plots of ln k against $1/T$ at a constant density of the mobile phase fluid should be interpreted with care. The principal virtue of such plots is their apparent linearity as correctly predicted by the unified molecular theory of chromatography [10]. However, the linearity alone does not imply that the slope of a constant-density plot has a simple physical significance. It appears that the slope of such a plot is related neither to enthalpy nor to internal energy of solute transfer between the two phases. Instead, the slope is a composite parameter given by eqn. 10 or 11.

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