MECHANISM OF SOLUTE RETENTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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Introduction

Retention in supercritical fluid chromatography (SFC) is determined by solute solubility in the fluid and solute interaction with the stationary phase. The functional relationship between retention and pressure at constant temperature has been described by Van Wasen and Schneider (1). The trend in retention is shown to depend on the partial molar volume of the solute in the mobile and stationary phase coupled with the isothermal compressibility of the fluid mobile phase.

The solubility of the solute in a fluid has been discussed by Gitterman and Procaccia (2) and solute solubility has been described over the entire region of pressures of interest. The combination of solute solubility in a fluid with the equation for retention as a function of pressure derived by Van Wasen and Schneider allows one to determine the effect of solubility on solute retention.

The purpose of this work was to determine the relationship between solubility and retention. A thermodynamic model was developed which predicts the trend in retention as a function of pressure, given the solubility of the solute in the fluid mobile phase. From this model, solute retention behavior can be examined by theory and experiment in order to gain some insight into the complicated dependence of retention on the thermodynamic and physical properties of the solute and the fluid, providing a basis for consideration of more subtle effects unique to SFC.

Theory

In SFC, the basic assumption of infinitely dilute solutions of the solute in the mobile and stationary phases is valid. The concentration of the solute in these phases respectively is $C_i = X_i/V_m$, where X_i is the mole fraction of solute (i) and V_m is the molar volume of the pure mobile or stationary phase (1). Solute retention is calculated from a dimensionless retention factor, k, where,

$$k = (C_i^{stat}/C_i^{mob}) \cdot (V^{stat}/V^{mob}) \qquad 1)$$

C_i^{stat} and C_i^{mob} are the concentration of solute (i) in the stationary and mobile phases respectively, V^{stat} and V^{mob} are the volumes of the stationary and mobile phase. Substituting for concentration into equation 1,

$$k = (X_i^{stat}/X_i^{mob}) \cdot (V_m^{mob}/V_m^{stat}) \cdot (V^{stat}/V^{mob}) \qquad 2)$$

Taking the natural logarithm of both sides of equation 2 one obtains,

$$\ln k = \ln (X_i^{stat}/X_i^{mob}) + \ln (V_m^{mob}\ V^{stat}/V_m^{stat}\ V^{mob}) \qquad 3)$$

At equilibrium, the solute chemical potential in the respective phases are equal $\mu_i^{stat} = \mu_i^{mob}$ (3). Therefore,

$$\mu_i^{stat} = \mu_i^{mob} = \mu_i^{stat\,\infty} + RT\ \ell n X_i^{stat} = \mu_i^{mob\,\infty} + RT\ \ell n\ X_i^{mob} \qquad 4)$$

where μ_i^{∞} is the chosen standard state of infinite dilution of solute (i) in the two phases. Rearranging equation 4,

$$\ell n\ (X_i^{stat}/X_i^{mob}) = (\mu_i^{mob\,\infty} - \mu_i^{stat\,\infty})/RT \qquad 5)$$

Substituting equation 5 into 3,

$$\ell nk = (\mu_i^{mob\,\infty} - \mu_i^{stat\,\infty})\ /\ RT + \ell n\ (V_m^{mob}\ V^{stat}/V_m^{stat}\ V^{mob}) \qquad 6)$$

An assumption can be made that the second term on the right-hand side (RHS) of equation 6 is independent of pressure except for V_m^{mob}, the molar volume of the fluid mobile phase. Therefore differentiation of equation 6 with respect to pressure at constant temperature yields,

$$(\partial \ell nk/\partial P)_T = 1/RT\ [(\partial \mu_i^{mob\,\infty}/\partial P)_T - (\partial \mu_i^{stat\,\infty}/\partial P)_T] + (\partial \ell n\ V_m^{mob}/\partial P)_T \qquad 7)$$

The partial molar volume of a solute is defined as $(\partial \mu_i/\partial P)_T$ (3) and on rearranging the second term on the RHS of equation 7 one obtains the isothermal compressibility of the fluid mobile phase (4). Thus on substitution equation 7 reduces to,

$$(\partial \ell nk/\partial P)_T = 1/RT\ [\bar{V}_i^{mob\,\infty} - \bar{V}_i^{stat\,\infty}] - K \qquad 8)$$

where $\bar{V}_i^{mob\,\infty}$ and $\bar{V}_i^{stat\,\infty}$ are the partial molar volume of the solute (i) in the mobile and stationary phases at infinite dilution respectively and K is the isothermal compressibility of the fluid mobile phase. Equation 8 is the same as obtained by Van Wasen and Schneider (1) in their derivation of the trend in retention as a function of pressure for SFC.

The solubility of a solid in a supercritical fluid has been described by Gitterman and Procaccia (2). The region of interest chromatographically will be for infinitely dilute solutions whose concentration is far removed from the lower critical end point (LCEP) of the solution. Therefore the solubility of the solute in a supercritical fluid at infinite dilution can be approximated as,

$$(\partial \ell n X_i^{mob}/\partial P)_T = 1/RT\ [V^S - \bar{V}_i^{mob\,\infty}] \qquad 9)$$

where V^s is the molar volume of the pure solid solute. This is the same as equation 2.5 in Gitterman and Procaccia (2), describing solute solubility for dilute solutions far from criticality. Solving equation 9 for $\bar{V}_i^{mob}$.

$$\bar{V}_i^{mob} = -RT\ (\partial \ln X_i^{mob}/\partial P)_T + V^s \qquad 10)$$

Equation 10 can be substituted into equation 8 and upon rearrangement,

$$(\partial \ln k/\partial P)_T = (V^s - \bar{V}_i^{stat})/RT - (\partial \ln X_i^{mob}/\partial P)_T - K \qquad 11)$$

Equation 11 should be the relationship between retention-solubility and pressure at constant temperature for infinitely dilute solutions. The RHS of equation 11 consists of three terms, the first term will be a constant whose value depends on the partial molar volume of the solute in the stationary phase. The second term can be determined experimentally from bulk solubility measurements of the solute in the supercritical fluid mobile phase. The last term, the solvent isothermal compressibility, can be reasonably predicted from a two-parameter, cubic equation of state (EOS) such as the Redlich-Kwong EOS or the Peng-Robinson EOS (5,6).

The fluid mobile phases isothermal compressibility was determined using the Redlich-Kwong EOS to evaluate the derivative $(\partial\ V_m^{mob}/\partial P)_T$ in equation 12,

$$(\partial \ln V_m^{mob}/\partial P)_T = (1/V_m^{mob}) \cdot (\partial\ V_m^{mob}/\partial P)_T = -K \qquad 12)$$

From the Redlich-Kwong EOS,

$$(\partial V_m^{mob}/\partial P)_T = \frac{V_m^{mob}\ T^{0.5}\ (b^2 - (V_m^{mob})^2)}{P\ T^{0.5}(3\ (V_m^{mob})^2 - b^2) - RT^{3/2}\ (2V_m^{mob} + b) + a} \qquad 13)$$

where R is the gas constant, P is pressure, and T is temperature in K. The constants a and b of the Redlich-Kwong EOS are,

$$a = 0.4278\ R^2\ T_c^{2.5}/P_c \qquad 14a)$$

$$b = 0.0867\ RT_c/P_c \qquad 14b)$$

where P_c and T_c are the critical pressure and temperature of the fluid. The molar volume of the fluid was determined by the Peng-Robinson EOS, thus allowing one to solve for the isothermal compressibility of the fluid.

Therefore from equation 11, the trend in retention as a function of pressure at constant temperature can be determined and it is related to the solubility of the solute in the supercritical fluid, the isothermal compressibility of the solvent and the partial molar volume of the solute in the stationary phase at infinite dilution.

Experimental

The experimental apparatus and technique has been described in detail elsewhere (7,8). The retention factors of selected solutes under isothermal conditions at various pressures were obtained using capillary columns coated with a cross-linked phenyl polymethylphenylsiloxane stationary phase with carbon dioxide as the fluid mobile phase. A Varian 8500 syringe pump was operated under computer control providing accurate, pulsefree control of the fluid pressure. The retention times of the solute as a function of pressure were determined by a reporting integrator with an accuracy of a tenth of a second. Solubility data for the solutes in CO_2 was obtained from the literature ((9) and references therein).

Results and Discussion

Solute retention as a function of pressure has been determined experimentally for a wide number of solutes over a range of temperatures and pressures (1,10-12). The trend in retention of a solute with pressure can be predicted from the simple thermodynamic model upon which equation 11 is predicted. Experimental data for the retention of naphthalene in CO_2 at 35°C over a pressure range was reported by Van Wasen and Schneider (12). The solubility of naphthalene in CO_2 is given by McHugh and Paulaitis at 35°C, 55.0°C, 60.4°C, and 64.9°C (13). This data allows the trend in retention to be predicted from the calculation of the slope of $(\partial \ln k/\partial P)_T$ for naphthalene at 35°C in CO_2.

A plot of $\ln X_i^{mob}$ versus pressure in shown in Figure 1 based on the data from McHugh and Paulaitis (13). The slope $(\partial \ln X_i^{mob}/\partial P)_T$ at 35°C was obtained by interpolation between the data points, also the data range was extended to lower pressures than given in reference (13) by fitting the data using the method outlined by Reid et al. (14). This allowed the modeling of the trend in retention for a wider range of pressure. The fluids isothermal compressibility can be easily calculated for any temperature and pressure range of interest. The solute partial molar volume in the stationary phase was assumed constant and independent of pressure (15). Available data suggests that for a highly cross-linked stationary phase coated in a capillary column solvation is very small or negligible (16), therefore V^{stat} and V_i^{stat} would be independent of pressure. The above simplifying assumptions allow one to calculate the trend in solute retention based on the solubility of the solute in the mobile phase. Figure 2 shows the fit of equation 11 to the experimental data of Van Wasen and Schneider (12). The partial molar volume of the solute naphthalene in the stationary phase was determined to be ~180 cm^3/mole, this gave the best fit to the experimental data (naphthalene's molar volume is ~130.8 cm^3/mole). The simple thermodynamic model fits the retention data very satisfactorily. More experimental data for CO_2 in coated capillary columns is being undertaken in our laboratory at the present time but preliminary results with the model are promising.

On closer examination of equation 11, one can deduce that as the isothermal compressibility of the solvent becomes less important (temperature and pressure further removed from the critical temperature and pressure), $(\partial \ln k/\partial P)_T$ is proportional to the solubility of the solute in the fluid phase. Therefore, if solubility is found to be a linear function of density than retention will mirror this behavior and also be a linear function of density. Further, the farther one is from the critical pressure and temperature of the solvent the more likely one obtains a constant slope ($(\partial \ln k/\partial P)_T$ = constant).

Conclusion

The simple thermodyanamic relationship developed in this work has been shown to adequately describe the features of solute retention as a function of pressure at constant temperature for supercritical fluid chromatography. The importance of this model is the relationship drawn between solute solubility in the fluid mobile phase to the trend in solute retention. The trend in solute retention is demonstrated to be dependent on isothermal compressibility, solubility in the fluid and the partial molar volume of the solute in the stationary phase. The dependence of $\bar{V}_i^{stat\infty}$ on pressure is being examined and will be discussed in a future work. This change and further experimental investigations over the relevant ranges of temperature and pressure are in progress and will serve to guide future experimental and theoretical developments.

Acknowledgments

The authors acknowledge the financial support of the U.S. Department of Energy, Office of Basic Energy Science, under Contract DE-AC06-76RLO 1830.

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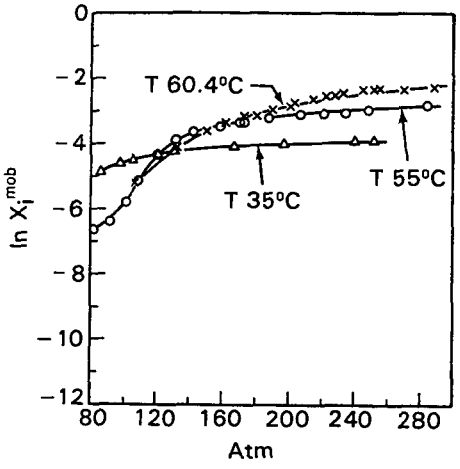

Figure 1. Plot of ln X_i^{mob} against pressure in atmospheres at 35°C, 55°C, and 60.4°C. Data from McHugh and Paulaitis (13).

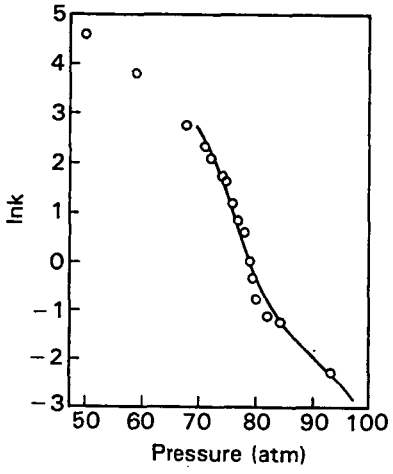

Figure 2. Experimental data for naphthalene with CO_2 (ref. 12) at 35°C and theoretical model (solid line).