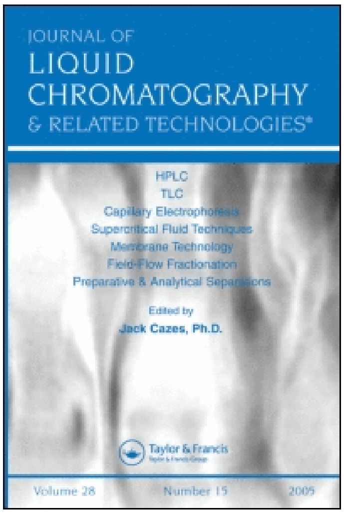

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Role of Interfacial Tension in Reverse Phase Liquid Chromatography

G. K. Vemulapalli[a]; T. Gnanasambandan[a]
[a] Department of Chemistry, University of Arizona, Tucson, Arizona

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ROLE OF INTERFACIAL TENSION IN REVERSE PHASE LIQUID CHROMATOGRAPHY

G.K. Vemulapalli and T. Gnanasambandan, Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

ABSTRACT

A thermodynamic equation relating chromatographic equilibrium constant to the interfacial forces between the stationary phase and the mobile phase is derived from the first principles. Advantages of using this equation in the analysis of bonded phase chromatographic data are discussed.

INTRODUCTION

During the last decade chromatography with chemically bonded phases has evolved into an indispensable technique for chemical separation. It has been widely recognized that both kinetics and equilibrium thermodynamics control chromatographic separation process (1,2). Many attempts have been made to correlate equilibrium constants derived from liquid chromatography with the known solvent-solute interactions (3,4,5). Theoretical attempts have also been made to formulate the equilibrium constant expressions in terms of solvent and solute parameters (6,7,8).

In most of these studies it has been tacitly assumed that the thermodynamic equilibria involved in chromatographic separation are the same as those involved in liquid-liquid partition. However, we should expect interfacial forces to play a crucial role; yet there have been only sketchy discussions on this point

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in liquid chromatographic literature and only empirical correlations between interfacial forces and retention times have been made with ad hoc theoretical machinery. The interfacial forces considered in previous investigations are between two solvents (9) or between solute and a solvent cavity (10). These are not as directly related to chromatographic equilibrium as the interfacial forces between the mobile and the stationary phases considered here.

In the following article we will show how interfacial tension directly enters into the liquid chromatographic equilibrium. We derive a general expression for the equilibrium constant for the distribution of solute between bulk phase, where surface forces may be safely ignored, and an interfacial phase, where surface forces dominate.

Even though the derivation given below is based on familiar theoretical procedures, it is not described in the literature. In tracing the expression for the equilibrium constant back to first principles, we have found that theory gives valuable insights into (a) the role of interfacial tension in the separation process, (b) the composition of the stationary phase and (c) the dependence of selectivity on length of carbon chains in the stationary phase. These are discussed in the last section of the article.

THEORY

Let the subscripts b and s represent bulk and surface phases respectively. The chemical potential of a solute at constant temperature and pressure in the bulk phase is given by

$$d\mu^b = RT\ d\ \ell n\ a^b, \qquad (1)$$

where a^b represents the activity of the solute. The chemical potential of the solute in the surface phase is given by (11)

$$d\mu^s = RT\ d\ \ell n\ a^s + \gamma dA, \qquad (2)$$

since the interfacial tension, γ, is given by

$$\gamma = \left(\frac{\partial \mu}{\partial A}\right)_{T,P,a} , \qquad (3)$$

where A is the area of the interface. In the chromatographic experiments A is usually constant and γ varies with composition of the solution. Hence we need μ as an explicit function of γ. This is accomplished by the following Legendre transformation (12):

$$\hat{\mu} = \mu - A\left(\frac{\partial \mu}{\partial A}\right)_{T,P,a} = \mu - \gamma A \qquad (4)$$

From the above expression it follows that

$$d\hat{\mu}^s = RT\ d\ \ln a^s - A\ d\gamma. \qquad (5)$$

Since surface forces are negligible in the bulk phase,

$$d\hat{\mu}^b = d\mu^b. \qquad (6)$$

The condition for distribution of solute between the two phases is

$$d\hat{\mu}^b = d\hat{\mu}^s, \qquad (7)$$

from which we have

$$RT\ d\ln a^b = RT\ d\ln a^s - A\ d\gamma. \qquad (8)$$

So far no approximations have been made in the derivation. Eq. 8 is valid for any solute distributed between any pair of bulk and surface phases regardless of the nature of intermolecular forces in these phases. To proceed further, we need to know how interfacial tension varies with composition. Prigogine and Defay (13) showed that surface tension (liquid-vapor interface) for a binary solution is accurately given by

$$\sigma_{12} = \sigma_1 X_1 + \sigma_2 X_2 - \beta X_1 X_2 \qquad (9)$$

where the subscripts denote the two components, X, the mole fractions and β, a small constant. In order to avoid unnecessary confusion we shall denote surface tension by σ and interfacial tension by γ. The third term on the right hand side of Eq. 9 is usually small and may be safely ignored when one of the mole fractions is small. Eq. 9 should also apply for interfacial tensions of binary solutions.

In order to be able to integrate Eq. 8 we have to follow a convention regarding standard states. Standard states based on Henry's Law are commonly used for studies of solute distribution between two phases. Integration of Eq. 8 with this convention gives,

$$\frac{1}{X_2^s} \ln \frac{X_2^s}{X_2^b} = \frac{A}{RT} \quad (\gamma_2 - \gamma_1) \,, \qquad (10)$$

where Eq. 9 (with γ in place of σ) is used for the evaluation of the term involving interfacial tension. Subscripts 1 and 2 denote solvent and solute respectively. Note that we have substituted mole fractions for activities. Since

$$(1/X_2^s) \simeq (1 - X_2^s) = \ln X_1^s \qquad (11)$$

and X_1^s is very nearly equal to unity Eq. 10 takes the form:

$$\ln \frac{X_2^s}{X_2^b} = \ln K = \frac{A}{RT} \quad (\gamma_2 - \gamma_1). \qquad (12)$$

It should be noted that a simple expression for equilibrium constant, such as the one given in Eq. 12, does not follow from theory unless the solution is dilute.

DISCUSSION

Eqs. 8 and 12 relate equilibrium constant to other measurable quantities, A and γ. Reliable methods have been devised for estimation of solid-liquid and liquid-liquid interfacial tensions (14,15) since these quantities are significant in the studies of wetting, surface energies of solids and many industrial processes. Thus Eqs. 8 and 12 provide a bridge between liquid chromatography and interfacial studies.

We will now show that Eq. 12 is consistent with experimental observations. According to this equation, ℓnK for a series of compounds (solutes) should vary linearly with their interfacial tensions (γ_2) provided γ_1 and A remain constant (i.e., same solvent and column). Note that γ_2 refers to interfacial tension between the solute and the stationary phase and hence depends on both these phases. (Similarly, γ_1 depends on both the solvent and the stationary phase.) γ_2 values for systems involving the stationary phases of chromatography are not available at present. In order to demonstrate the quantitative validity of Eq. 12, we will use reasonable estimates for γ_2. According to Fowkes (15) interfacial tension between two phases (say a and b) may be estimated from the surface tension of each phase against its own vapor. Fowkes theory has been remarkably successful in predicting interfacial tensions (16). For systems of interest in the present study, his equation has the form:

$$\gamma_2 = \sigma_2 + \sigma_S - 2\sqrt{\sigma_2\sigma_S}\ , \qquad (13)$$

where σ_2 and σ_S are the surface tensions of solute and stationary phases. Since the stationary phase is the same for all solutes in an experiment, we should expect interfacial tensions of solute-stationary phase systems to be proportional to the surface tensions of the solutes. Hence, ℓnK and ℓnk, where k is the capacity factor, should increase with surface tension. Fig. 1 shows that this is indeed the case.

Experimental points (17) in Fig. 1 follow a straight line graph closely indicating that σ_S is relatively small. From the experimental values of capacity factors in Fig. 1, we conclude that $\gamma_2 > \gamma_1$. Even though Eq. 12 relates K, and not k, to interfacial tension, this statement is still correct since $k = K\phi$ where the constant ϕ is the volume ratio (stationary phase to mobile phase) which has been estimated to be less than unity (18). Small interfacial tension between the solvent and the stationary phase results if the stationary phase has solvent molecules incorporated into it. (The more the stationary phase approaches the solvent

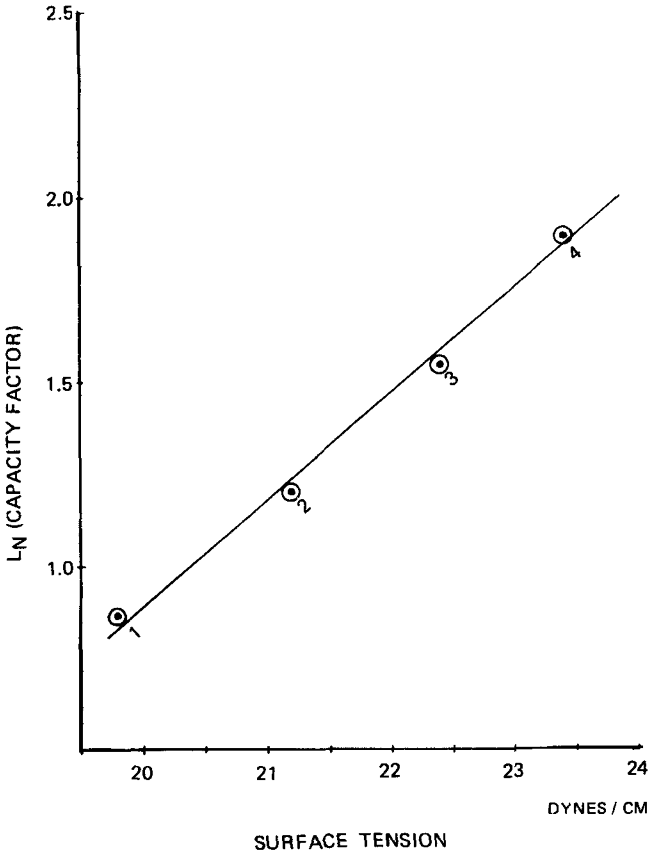

FIGURE 1:

Logarithm of capacity factors (k) as a function of surface tension of solutes. k values are taken from H. Colin and G. Guiochon (Reference 17) solutes 1: n-heptane; 2: n-octane; 3: n-nonane; 4: n-decane. Surface tensions are obtained from CRC Handbook of Physics and Chemistry, 1982.

phase in composition the less would be their interfacial tension.) This conclusion also agrees with the results of previous investigations (19).

It is known experimentally that retention and separation are influenced by chain length of the stationary phase. Practicing chromatographers use this phenomenon in designing appropriate columns for a given system. Attempts have been made to explain the variation of selectivity with chain length by such factors as the surface structure of the stationary phase or steric effects. It should be noted that the mechanisms suggested previously (3,5,6,7,8,9,10) do not explicitly consider the effect of chain length on separation. The theory developed here, however, gives a handle on ths problem through the quantity A in Eq. 12.

Eq. 8 follows from first principles of equilibrium thermodynamics and Eq. 12 has no serious approximations. However, interfacial tensions for materials of chrmoatographic interest are not readily available. Otherwise application of Eq. 12 would be simple and straightforward. We have demonstrated here, with the aid of the available data, the vailidity of Eq. 12. Work in progress is aimed at (i) evaluation of interfacial tensions from experiment and theory and (ii) numerical estimation, with the aid of Eq. 12, of parameters such as the volume ratio and areas of stationary phases.

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