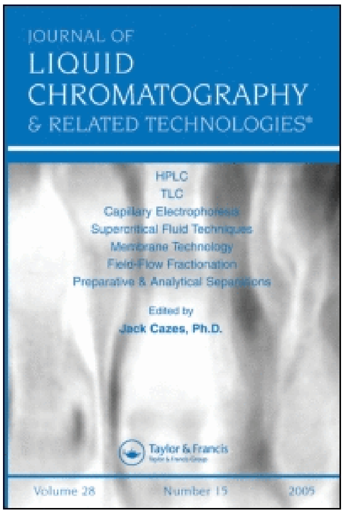

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PARTITION COEFFICIENTS AT INFINITE DILUTION FROM FLORY-HUGGINS THEORY

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ABSTRACT

An expression relating partition coefficients at infinite dilution to Flory-Huggins interaction parameters has been derived. The equation has been successfully applied to the partitioning of alcohols between water and cellulose acetate. The solvent-solute interaction parameter has a dominant effect on partition coefficients. For the systems studied, solvent-polymer interactions appear to be negligible.

INTRODUCTION

Liquid chromatography (LC) is an established tool for the rapid and accurate determination of the partition coefficient between solid and a fluid phase. Such partition coefficients are useful in characterizing membrane materials, since the partitioning of a solute between a liquid phase and a membrane phase is an important factor that determines membrane selectivity in a variety of processes. Transport through these membranes is often related to the preferential sorption of one permeant by the membrane. Solubility parameters are sometimes used to predict partition coefficients and to assist in selecting a membrane material appropriate to a given separation task [1].

Modified Flory-Huggins theory with concentration dependent binary interaction parameters can be used to describe the thermodynamics of ternary systems containing a polymer [2,3]. In this paper, modified Flory-Huggins theory is used to predict the partition coefficients of alcohols at infinite dilution between a water phase and a membrane phase containing cellulose acetate.

THEORY

Equilibrium between a liquid solution and a swollen polymer can be described by the equation [4]:

$$\Delta\mu_i + V_i P_e = \Delta\mu_i^o, \tag{1}$$

where $\Delta\mu_i$ is the chemical potential of component i. Components are numbered as follows: 1 stands for solvent, 2 for solute, and 3 for polymer. The superscript ^{o} denotes the polymer-free (liquid) phase and the term $V_i P_e$ represents the elastic contribution to the chemical potential of component i in the polymer-rich (solid) phase.

The Gibbs free energy of mixing of a ternary phase is given by the equation [2]

$$\frac{\Delta G_{mix}}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_2) n_1 \phi_2 + g_{13}(\phi_3) n_1 \phi_3 + g_{23}(\phi_3) n_2 \phi_3 + g_T n_1 \phi_2 \phi_3, \tag{2}$$

where the g_{ij} are concentration dependent binary interaction parameters and g_T is a concentration dependent ternary interaction parameter. The variables ϕ_i and n_i are the volume fraction and number of moles of component i, respectively, and u_2 is the volume fraction of solute defined on a polymer-free basis:

$$u_2 = \frac{\phi_2}{\phi_1 + \phi_2} \quad . \tag{3}$$

Differentiation of equation (2) with respect to n_i gives the chemical potential of component i as a function of composition:

$$\frac{\Delta\mu_1}{RT} = \ln \phi_1 + 1 - \phi_1 - s\phi_2 - t\phi_3 + (g_{12}\phi_2 + g_{13}\phi_3)(\phi_2 + \phi_3)$$
$$- s g_{23}\phi_2\phi_3 - u_1u_2\phi_2 \frac{dg_{12}}{du_2} - \phi_1\phi_3^2 \frac{dg_{13}}{d\phi_3} - s\phi_2\phi_3^2 \frac{dg_{23}}{d\phi_3} \qquad (4)$$
$$+ \frac{\partial}{\partial n_1}(n_1\phi_2\phi_3 g_T)$$

and

$$\frac{\Delta\mu_2}{RT} = \ln \phi_2 + 1 - \phi_2 - \frac{1}{s}\phi_1 - \frac{t}{s}\phi_3 + (\frac{1}{s} g_{12}\phi_1 + g_{23}\phi_3)(\phi_1 + \phi_3)$$
$$- \frac{1}{s} g_{13}\phi_1\phi_3 + \frac{1}{s} u_1u_2\phi_1 \frac{dg_{12}}{du_2} - \phi_2\phi_3^2 \frac{dg_{23}}{d\phi_3} - \frac{1}{s}\phi_1\phi_3^2 \frac{dg_{13}}{d\phi_3} \qquad (5)$$
$$+ \frac{\partial}{\partial n_2}(n_1\phi_2\phi_3 g_T)$$

where $s = V_1/V_2$ and $t = V_1/V_3$ are ratios of the molar volumes of the pure components. Since the molar volume of the polymer is much larger than that of either the solvent and solute, terms containing t can be dropped out in further analysis. Chemical potentials in the limit of infinite dilution of solute are obtained by taking the limit of equations (4) and (5) as $\phi_2 \to 0$:

$$\left.\frac{\Delta\mu_1}{RT}\right|_{\phi_2 \to 0} = \ln \phi_1 + \phi_3(1 + \phi_3 g_{13} - \phi_1\phi_3 \frac{dg_{13}}{d\phi_3}) \qquad (6)$$

and

$$s\left.\frac{\Delta\mu_2}{RT}\right|_{\phi_2 \to 0} = s \ln \phi_2 + \phi_1(s - 1) + s\phi_3 + g_{12}\phi_1 + s g_{23}\phi_3$$
$$- \phi_1\phi_3(g_{13} + \phi_3 \frac{dg_{13}}{d\phi_3}) + g_T\phi_1\phi_3. \qquad (7)$$

Chemical potentials of solvent and solute in the polymer-free phase at infinite dilution of solute are given by the equations

$$\left.\frac{\Delta\mu_1^0}{RT}\right|_{\upsilon_2\to 0} = 0 \tag{8}$$

and

$$s\left.\frac{\Delta\mu_2^0}{RT}\right|_{\upsilon_2\to 0} = s\ \ln \upsilon_2 + s - 1 + g_{12}, \tag{9}$$

where the υ_i are volume fractions in the polymer-free phase.

From equation (1) and equations (6)-(9), the partition coefficient of the solute at infinite dilution, K, is given by the relationship

$$s\ \ln \frac{\phi_2}{\upsilon_2} = s\ \ln K = (1 - \phi_1)(g_{12} + g_{13} - \phi_1 g_T - sg_{23}) + \ln \phi_1. \tag{10}$$

The interaction parameters in equation (10) are to be evaluated when the solute is infinitely dilute. The ternary interaction parameter, g_T, expresses deviations from the assumption that all binary contributions to the free energy of mixing are additive, and is poorly understood at present. To fit preferential sorption data in dilute polymer solutions, Pouchly and Zivney assumed that in the limit of infinite dilution of polymer [5]

$$\left. g_T \right|_{\phi_3\to 0} = \alpha' g_{12}, \tag{11}$$

where α' is a constant characteristic of the system under consideration.

In the case of infinitely dilute solute, it is reasonable to assume that ternary contributions to the free energy of mixing are determined primarily by the components in excess, the solvent and polymer. Therefore, in the limit of infinitely dilute solute, g_T will be expressed as

$$\left. g_T \right|_{\phi_2\to 0} = \alpha g_{13}, \tag{12}$$

Substituting equation (12) into equation (10) yields the relationship

$$s \ln K = (1-\phi_1)g_{12} + (1-\phi_1)[g_{13}(1-\alpha\phi_1)-sg_{23}] + \ln \phi_1. \tag{13}$$

Equation (13) suggests that the s-weighted logarithm of the partition coefficient is linearly related to the solvent-solute interaction parameter g_{12}. An increase in g_{12} corresponds to a decrease in the miscibility of the solvent and solute, and should be accompanied by an increase of the partition coefficient. Such behavior is consistent with the observations of many researchers that the solubility of an organic solute in a membrane is inversely related to the water solubility of the solute [6].

The solvent-solute interaction parameter, g_{12}, is related to the solute activity coefficient at infinite dilution, γ_2^∞, through the equation

$$g_{12}\Big|_{\phi_2\to 0} = s(\ln \gamma_2^\infty + \ln s - 1 + \frac{1}{s}). \tag{14}$$

Equation (14) is derived in the Appendix of this paper. The parameters g_{13} and g_{23} are functions of the volume fraction of polymer in the system, ϕ_3. The relationship between g_{i3} and the Flory-Huggins interaction parameter χ_{i3} is expressed by the equation [7]

$$\chi_{i3} = g_{i3} - (1 - \phi_3)\frac{dg_{i3}}{d\phi_3} \tag{15}$$

To calculate g_{i3}, the Flory-Huggins parameter must be measured over the range of compositions of interest; equation (15) must then be integrated numerically. If the Flory-Huggins parameter is assumed to be constant, which is often a good assumption for concentrated polymer solutions, then $g_{i3} = \chi_{i3}$, and g_{i3} can be determined from a single measurement, such as swelling, sorption, or inverse gas chromatography.

DISCUSSION

The correlation derived above was tested using partition coefficients measured at infinite dilution for alcohols partitioning between water and cellulose acetate (CA) [8]. These partition coefficients, shown in Table 1, were obtained from LC experiments using two CA columns. Column 1 was prepared with bulk polymer; Column 2 was prepared with precipitated polymer. Activity coefficients at infinite dilution were used with equation (14) to obtain g_{12}; the activity coefficients were calculated at 25 °C using Pierotti's correlation [9], and are also presented in Table 1. Correlation errors in γ_2^∞ are less than 8 % [9,10]. Molar volumes were calculated from pure component densities.

The quantity s ln K is shown as a function of g_{12} for both columns in Figure 1. Correlation of s ln K as a function of g_{12} yields the following results :

$$\text{Column 1 : } s \ln K = 0.726\, g_{12} - 0.7849 \qquad r2=0.999 \qquad (16)$$

$$\text{Column 2 : } s \ln K = 0.815\, g_{12} - 0.8805 \qquad r^2=0.991 \qquad (17)$$

There is a strong linear relationship between s ln K and g_{12}. It is significant that the correlation holds for a set of solutes that

Table 1. Solvent-solute interaction parameters and partition coefficients for alcohols in water and cellulose acetate

Alcohol	s	γ_2^∞	g_{12}	K Column 1	K Column 2
Methanol	0.445	1.53	0.384	0.315	0.262
Ethanol	0.308	3.38	0.704	0.407	0.364
1-Propanol	0.241	11.4	1.003	0.794	0.777
1-Butanol	0.197	42.8	1.223	1.658	1.680
1-Pentanol	0.167	168.	1.390	3.655	3.946
2-Propanol	0.235	6.54	0.866	0.540	0.535
2-Methyl- 2-propanol	0.191	10.1	0.934	0.606	0.662

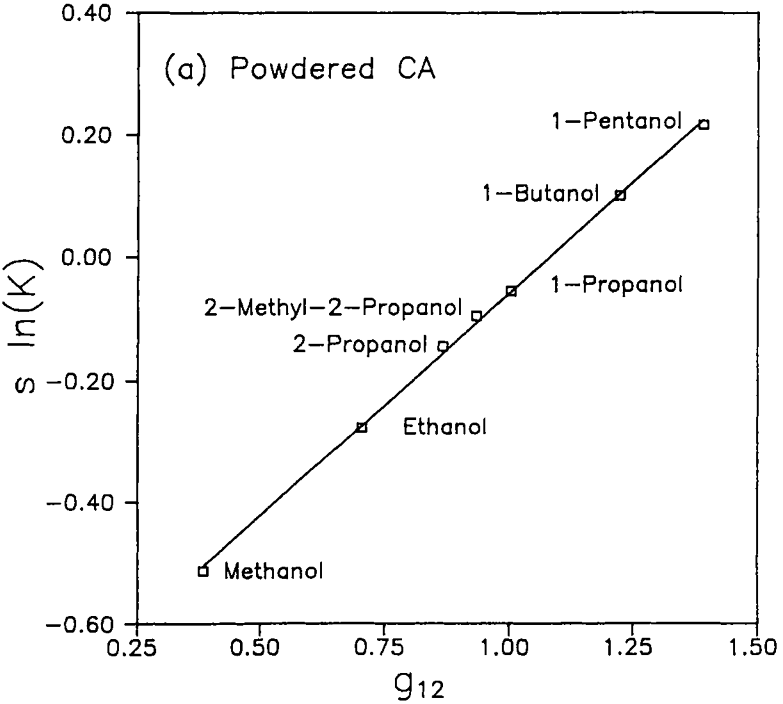

Figure 1. Regression results for partitioning of alcohols between water and (a) powdered cellulose acetate (b) reprecipitated cellulose acetate.

(continued)

includes primary alcohols, a secondary alcohol, 2-propanol, and a tertiary alcohol, 2-methyl-2-propanol. The correlation of s ln K with g_{12} is not restricted to a homologous series of alcohols.

The success of these correlations given in equations (16) and (17) indicates that the product s g_{23} is constant for a given column. The ratio of molar volumes, s, significantly decreases as the molecular weight of the alcohol increases; the same trend can be expected for the parameter g_{23} because of increasing physicochemical similarity between the solute and the polymer. For

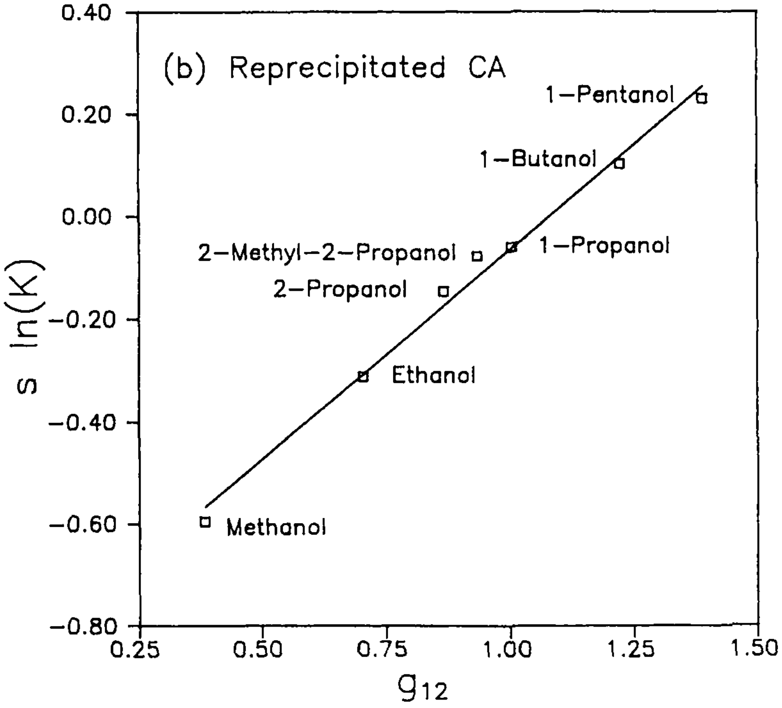

Figure 1B

reasons to be given presently, the value of g_{23} obtained from liquid chromatography experiments does not necessarily correspond to the value given by other techniques. In particular, for alcohols partitioning between water and CA, it is plausible to assume that g_{23} is zero regardless of solute. This assumption is supported by both thermodynamic and kinetic arguments.

On a microscopic level, swollen cellulose acetate is likely to have a heterogeneous structure, with regions inaccessible to water near polymer microcrystallites [11], and water-rich regions penetrating into the polymeric structure. Nishi and coworkers [12] suggest that ethanol molecules in dilute aqueous solutions tend to form a polymeric structure stabilized by a surrounding water shell. If alcohol molecules enter primarily through the water-rich region of swollen cellulose acetate, this water shell can shield the alcohol molecules from the polymer on the time scale characteristic of an LC experiment. In this situation, the observed value of g_{23} does not reflect the effects of direct interactions between the polymer and the solute.

From the regression slopes, the volume fraction of water in cellulose acetate is 0.274 for Column 1 and 0.185 for Column 2. These values are slightly higher than those obtained from sorption experiments [8] (0.240 for Column 1 and 0.167 for Column 2). This result is consistent with the assumption that some regions are not accessible to water.

Using the regression results, the Flory-Huggins solvent-polymer interaction parameter χ_{13} can be found from the relationship [13]:

$$\chi_{13} = - \frac{\ln \phi_1 + 1 - \phi_1}{(1 - \phi_1)^2} . \tag{18}$$

Using equation (18), χ_{13} is calculated to be 1.1 for Column 1 and 1.3 for Column 2. The value of 1.3 for Column 2, which was made from precipitated polymer, agrees closely with the independently reported value of $\chi_{13} = 1.4$ for CA membranes [13]. Assuming χ_{13} and g_{13} are not strongly concentration dependent at high polymer concentrations, $g_{13} \approx \chi_{13}$, and, from equation (13), $\alpha = 1.3$ for both columns. This constant value of α, independent of solute, suggests that the ternary contribution to the free energy of mixing is primarily entropic. This contribution arises from the reduction of free volume when mixing the polymer and low molecular weight species. If this is the case, the ternary contribution will be proportional to the volume of the system and not to the number of molecules of solute. This volume is constant for a given column regardless of the solute, resulting in a constant ternary contribution for a given column.

CONCLUSIONS

A correlation for partition coefficients at infinite dilution as functions of Flory-Huggins interaction parameters has been developed. The correlation has been successfully tested on alcohols partitioning between water and cellulose acetate. A linear relationship exists between s ln K and the solvent-solute interaction parameter, g_{12}; the slope of the regression line is related to the water content of the polymer. The solute-polymer interaction parameter appears to be zero regardless of alcohol. This conclusion is supported on the basis of nonrandom structure on the microscopic level, where solute molecules are effectively isolated from polymer molecules. The ternary interaction parameter, g_T, is independent of solute, suggesting its origin as an entropic effect.

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APPENDIX

The excess free energy of mixing, ΔG^E, for a binary system can be written either using activity coefficients:

$$\frac{\Delta G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2, \tag{A.1}$$

or using the defining equation for g_{12} [5]:

$$\frac{\Delta G^E}{RT} = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + g_{12} x_1 \phi_2 \tag{A.2}$$

Combining equations (A.1) and (A.2) and converting from mole fractions to volume fractions,

$$g_{12} = \frac{1}{\phi_2} \ln \gamma_1 + \frac{s}{\phi_1} \ln \gamma_2 - \frac{1}{\phi_2} \ln (\phi_1 + s\phi_2) - \frac{s}{\phi_1} \ln \left(\frac{\phi_1}{s} + \phi_2 \right) \tag{A.3}$$

In the limit of pure solvent, $\phi_2 \rightarrow 0$, the relationship between g_{12} and the activity coefficient of the solute at infinite dilution is obtained from equation (A.3) as:

$$g_{12} \Big|_{\phi_2 \rightarrow 0} = s(\ln \gamma_2^\infty + \ln s - 1 + \frac{1}{s}). \tag{A.4}$$

SYMBOLS

g_{ij}	Concentration dependent binary interaction parameters [dimensionless]
g_T	Concentration dependent ternary interaction parameter [dimensionless]
ΔG_{mix}	Free energy of mixing [J]
n_i	Number of moles of component i [mol]
r	Correlation coefficient [dimensionless]
R	Gas constant [J $mol^{-1}K^{-1}$]
s	Ratio of molar volumes of pure solvent and solute [dimensionless]
t	Ratio of molar volumes of pure solvent and polymer [dimensionless]
T	Temperature [K]
u_2	Volume fraction of solute defined on a polymer-free basis [dimensionless]
V_i	Molar volume of pure component i [dimensionless]

V_iP_e	Elastic contribution to chemical potential of component i [J mol^{-1}]
α	Constant in equation (12) [dimensionless]
α'	Constant in equation (11) [dimensionless]
γ_2^∞	Solute activity coefficient at infinite dilution [dimensionless]
ϕ_i	Volume fraction of component i in membrane phase [dimensionless]
χ_{ij}	Flory-Huggins interaction parameters [dimensionless]
μ_i	Chemical potential of component i [J mol^{-1}]
υ_i	Volume fraction of component i in polymer-free phase [dimensionless]

Subscripts

1	Solvent
2	Solute
3	Polymer

Superscript

°	Polymer-free phase

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