Comments on Role of Interracial Tension in Reverse Phase Liquid Chromatography

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COMMENTS ON ROLE OF INTERFACIAL TENSION IN REVERSE PHASE LIQUID CHROMATOGRAPHY

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ABSTRACT

A polemic is given on the article of G. K. Vemulapalli and T. Gnanasambandan (J. Liq. Chromatogr., 1983, 6(10), 1777).

Recently Vemulapalli and Gnanasambandan (1) presented an equation

$$\ln K = (A/RT) (\gamma_2 - \gamma_1) \qquad \text{(Eq. 12)}$$

that relates the chromatographic retention, K, with the interfacial surface tensions of the solute, γ_2, and solvent, γ_1, each in combination with the stationary phase. To support their derived expression, the authors demonstrated that the retention data of n-heptane, n-octane, n-nonane and n-decane, determined by Colin and Guiochon (2), is linear when plotted

against the surface tension of the pure solute, σ_2. Interest-
ingly, Colin and Guiochon report experimental data for nine
different solutes ranging from n-pentane to n-tetradecane.
As shown in Figure 1, a plot including all nine solutes is
not linear. Surface tensions of n-alkane solutes were taken
from published data (3,4) and chromatographic data were
assumed to be at $25^{\circ}C$ as experimental conditions were not given.

It should be noted that Schoenmakers (5) recently criti-
cized the mathematical derivation of equation 12 as the
authors invoked an incorrect approximation. The earlier criti-
cism failed to note that Vemulapalli and Gnanasambandan selected
only four of nine data points (no justification being given for
exclusion of the remaining five solutes) and that equation 2
of the original manuscript

$$d\mu^S = RT \; d \ln a^S + \gamma \, dA \qquad (Eq. 2)$$

mixed both intensive ($d\mu^S$, $RT \, d \ln a^S$) and extensive ($\gamma \, dA$)
thermodynamic properties. The chemical potential of a solute
in a surface phase is expressed in terms of the partial molar
surface area of the solute, A_2, rather than the total surface
area, A (6,7). One would not necessarily expect identical
A_2-values for a series of n-alkanes ranging from n-pentane to
n-tetradecane. Furthermore, the definition of the interfacial
surface tension

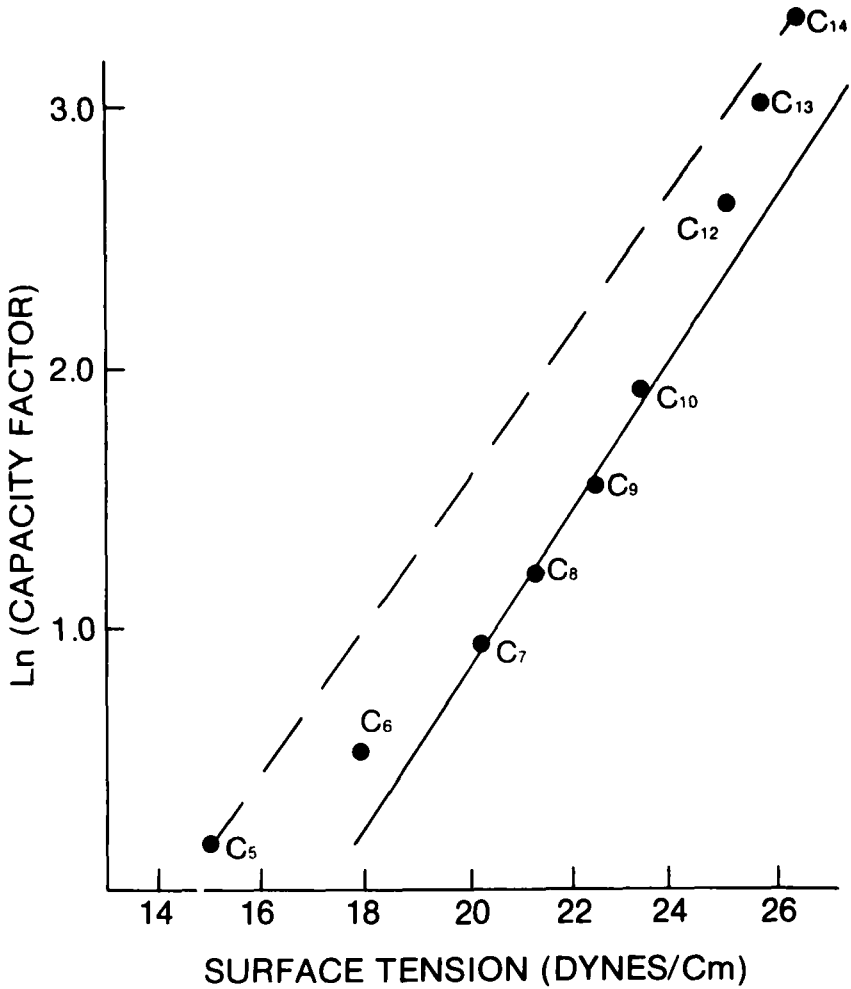$$\gamma = (\partial\mu/\partial A)_{T,P,a} \qquad (Eq. 3)$$

Figure 1. Logarithm of capacity factors as a function of surface tension of solutes.

is incorrect and should be written as the partial derivative

of the Gibbs free energy with respect to area.

Based on the number of errors and limited comparison

between theory and experimental values, I find that I too must

side with Schoenmakers in stating that the original paper

should never have been published.

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