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Publisher *Taylor & Francis*

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Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

Comments on Role of Interracial Tension in Reverse Phase Liquid Chromatography

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To cite this Article Acree Jr., William E.(1985) 'Comments on Role of Interracial Tension in Reverse Phase Liquid Chromatography', *Journal of Liquid Chromatography & Related Technologies*, 8: 9, 1739 – 1742

To link to this Article: DOI: 10.1080/01483918508074091

URL: <http://dx.doi.org/10.1080/01483918508074091>

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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

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

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 . Interestingly, 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°C as experimental conditions were not given.

It should be noted that Schoenmakers (5) recently criticized the mathematical derivation of equation 12 as the authors invoked an incorrect approximation. The earlier criticism 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

$$d\mu^S = RT d \ln a^S + \gamma dA \quad (\text{Eq. 2})$$

mixed both intensive ($d\mu^S$, $RT d \ln a^S$) and extensive (γdA) 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

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

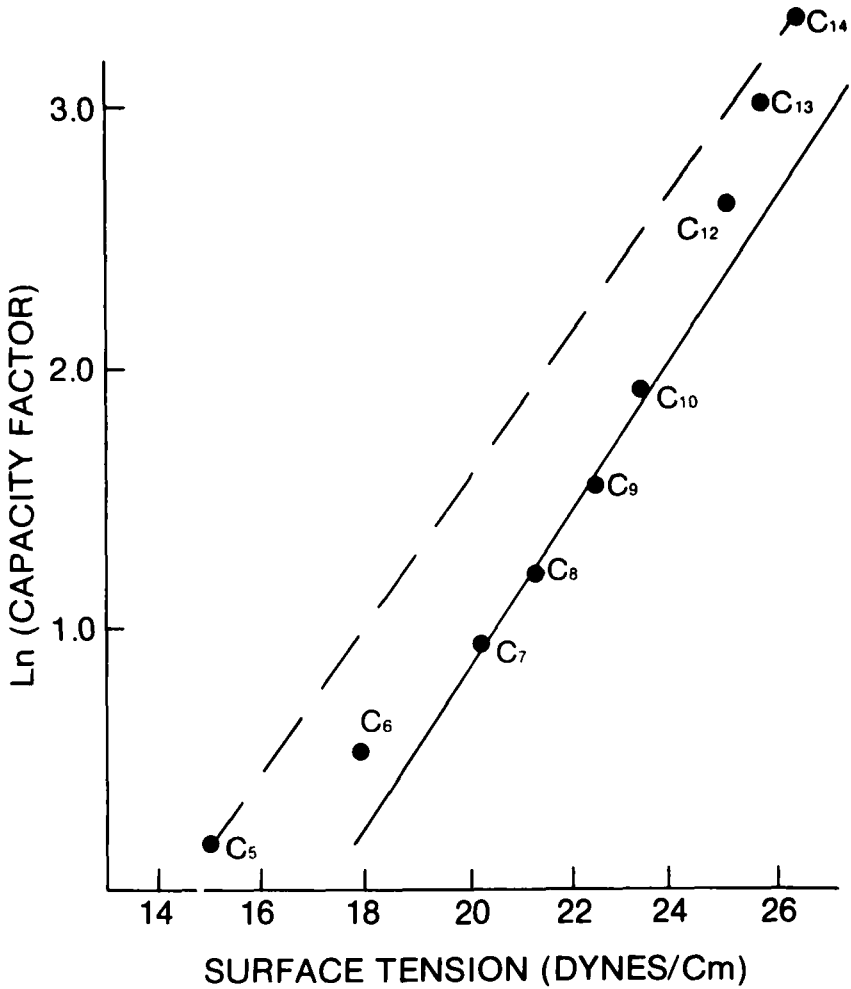


Figure 1. Logarithm of capacity factors as a function of surface tension of solutes.

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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