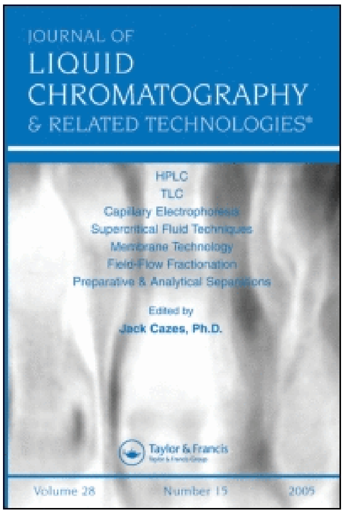

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Letter to the Editor

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LETTER TO THE EDITOR

Sir,

In a recent paper in your Journal (1) Vemulapalli and Gnanasambandan present an equation that relates chromatographic retention with the interfacial tensions of the solute and the solvent each in combination with the stationary phase. This equation is quite remarkable, as it suggests that

a) the interaction between the solute and the solvent plays no part in the retention mechanism and
b) the interfacial adsorption mechanism leads to a linear adsorption isotherm and hence symmetrical peaks, at least for dilute solutions.

These remarkable features caused me to take a closer look at the derivation of the retention equation. Besides the possible errors introduced by substituting an approximate equation for the surface tension of binary mixtures for the interfacial tension and extrapolation of the magnitude of the constants in this equation, the derivation seems to be reasonably sound until after eq. (10) is obtained.

In going from eq. (10) to eq. (12) a factor $(1/X^s{}_2)$ is ignored. This is explained from eq. (11), which reads

$$(1/X^s{}_2) \quad (1-X^s{}_2) = \ln\ (X^s{}_1).$$

Since the authors state (correctly) that $X^s{}_1$ is nearly equal to unity and since $X^s{}_2 + X^s{}_1 \square 1$, this equation seems rather odd. E.g., if we taken $X^s{}_2$ to be 0.01, it reads

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$$100 \quad 1 = -0.01 \; .$$

This, of course, is an absurd statement. Moreover, its function in the derivation is unclear. However, it is used to omit the factor $(1/X^s{}_2)$, which is both large and variable from the final equation.

The evidence supplied for the final result is minimal. Four datapoints from a literature source merely indicate that retention increases with surface tension of the pure solute (no further information about the chromatographic system given !) and an inaccurate and incomplete reference to the observed variation of retention with stationary phase chainlength is of hardly any value.

Therefore, I must conclude that the cited paper is erroneous, and, moreover, that it should not have been published.

Nov. 1, 1983

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(1) G.K. Vemulapalli and T. Gnanasambandan,
Journal of Liquid Chromatography 6 (10) (1983) 1777.