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SOLVENT COMPOSITION EFFECTS IN LIQUID–SOLID SYSTEMS*

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SUMMARY

It is demonstrated that column chromatographic data reported by Scott and Kucera for systems of the type pentane + polar solvent (S)–silica result in linear plots of log V' *versus* log C_S and are thus in agreement with adsorption models based on the law of mass action. For monofunctional solutes and polar solvents belonging to the same hydrogen-bonding class, the slopes of the lines were close to unity, indicating apparent displacement from the surface in the ratio 1:1.

Scott and Kucera recently reported[1] systematic investigations on solvent composition effects in the liquid chromatography of monofunctional solutes using silica as the adsorbent. It seems worthwhile to discuss their experimental data also from the viewpoint of adsorption models derived by Snyder[2] (Model I) and by ourselves (Model II)[3,4]. These two models have recently been compared by Snyder[5].

In the simplest version of Model II, the capacity factor of a solute adsorbed on silica from solutions of a polar solvent (S) in a non-polar diluent is given by the equation[3,4]

$$k' = \frac{\text{constant}}{X_S} \tag{1}$$

where X_S is the molar fraction of the polar solvent in the mobile phase and the constant is a function of the ratio of solvent volume to adsorbent weight ratio, the specific surface area of the adsorbent and the properties of the solute and solvent. In terms of column chromatographic parameters, the corrected retention volume is given by

$$V' = V - V^0 = k'V^0 = \frac{\text{constant}'}{X_S} \tag{2}$$

$$\log V' = R_M + \log V^0 = \log \text{constant}' - \log X_S \tag{2a}$$

For low concentrations of the polar solvent S, assuming that the molar volumes of the component solvents are comparable, X_S is proportional to molar and weight concentrations; thus, irrespective of the units of the concentration C_S,

$$1/V' = \text{constant}^n \cdot C_S \qquad\qquad (3)$$

When solvent molecules are displaced by the solute in other ratios ($n:1$), eqn. 3 becomes

$$1/V' = \text{constant}'' \cdot C_S^n \qquad\qquad (3a)$$

Eqn. 3 is a simplified version of the following equation derived by Scott and Kucera[1]:

$$1/V' = A + B \cdot C_p \qquad\qquad (4)$$

with C_p expressed in per cent (w/v). In fact, the constant A in eqn. 4 is small in most instances (ref. 1, Tables II and IV). A similar comparison can also be made with Snyder's equation[2].

Scott and Kucera's results are therefore not contradictory with Models I and II. To illustrate this point, the data are re-drawn as log–log plots (Figs. 1–3).
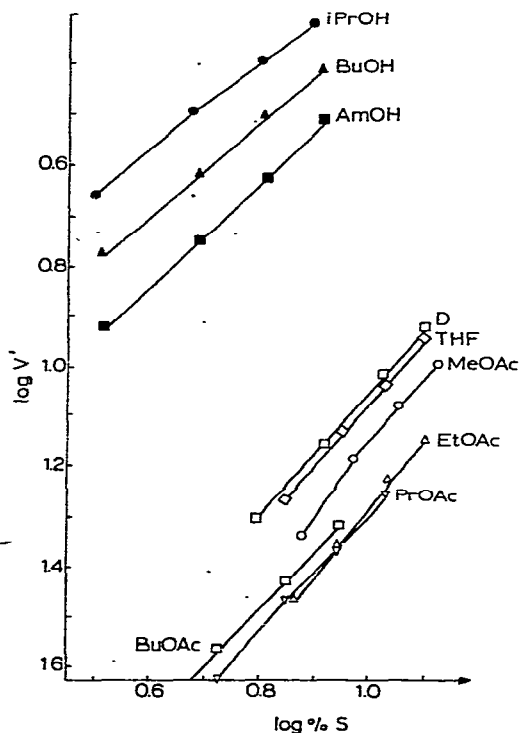

Fig. 1. Log V' versus log % S plots for phenyl methyl carbinol with nine polar solvents (S). From data in ref. 1, Table II (V' values). Slopes: iPrOH, 0.9; BuOH, 0.95; AmOH, 1.05; BuOAc and PrOAc, 1.2; dioxan, tetrahydrofuran and MeOAc, 1.3; EtOAc, 1.4.
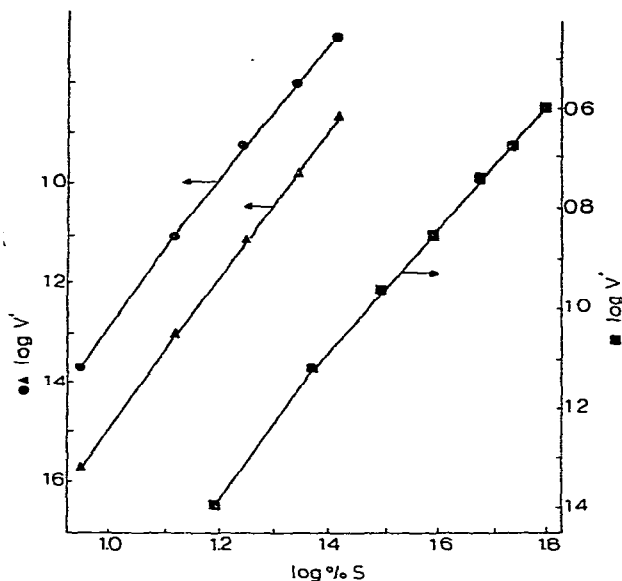
Fig. 2. Log V' *versus* log % S plots for benzyl alcohol (●, slope 1.4) and 3-phenylpropanol-1 (■, slope 1.5) with the polar solvent tetrahydrofuran, and desoxycorticosterone alcohol (▲, slope 1.25) with the polar solvent isopropanol. From data in ref. 1, Table I.
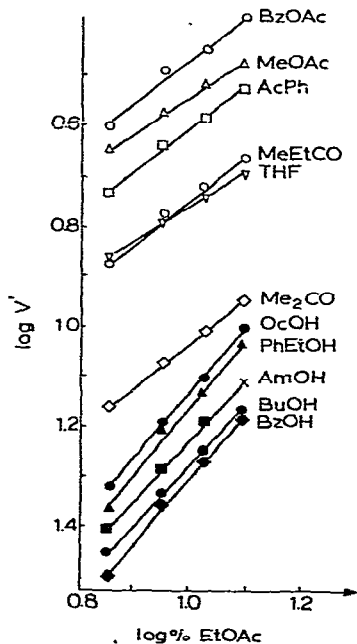

Fig. 3. Log V' *versus* log % EtOAc plots for eleven solutes (Bz = benzyl; Ac = acetate; THF = tetrahydrofuran; PhEtOH = α-phenylethanol; AcPh = acetophenone; MeEtCO = methyl ethyl ketone; etc.). From data in ref. 1, Table IV. ×, Calculated from $1/V'$ value. Slopes: MeOAc, 0.7; THF, 0.75; BzOAc, AcPh, MeEtCO and Me₂CO, 0.9; BuOH, 1.2; AmOH, 1.25; OcOH and BzOH, 1.3; PhEtOH, 1.4.

As $V' = k'V^0$, and the concentration scales are proportional for the systems considered, it follows from both models[5] that

$$\log(1/V') = a + n \log C_S \tag{5}$$

where a and n are constants, the slope n denoting the average number of solvent molecules displaced from the adsorbent surface by a single solute molecule (negligible secondary effects are assumed).

The agreement of all experimental relationships with eqn. 5 can be considered very good in most instances. The slopes of the straight lines and their relative positions permit us to formulate tentative conclusions about the molecular mechanism of adsorption.

In Model I, the slope n is expressed as the ratio of the molecular areas of the solute (A_s) and solvent (n_b) at the adsorbent surface. For proton-donor associated solvents, secondary solvent effects may complicate the sense of the slope. In Model II, for monofunctional solutes and solvents, the slope should be 1.0; however, its value can be higher if the solute molecules are large enough to displace vicinal solvent molecules[4] (Fig. 4b), or if the polar group of the solute is competitively solvated by the polar solvent (ref. 6, Fig. 1).
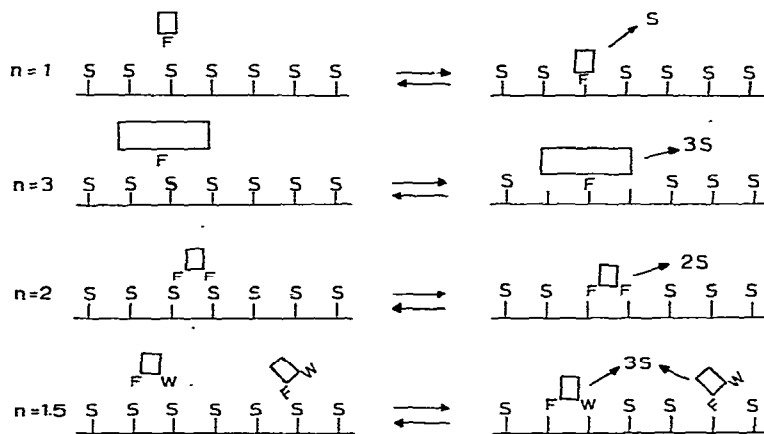

Fig. 4. Model of adsorption of solutes with strongly (F) and weakly (W) interacting polar groups.

The slopes of the straight lines are given in the legends of the figures; in several instances the first point, which corresponds to the lowest concentration of the polar solvent (and highest retention volume), does not lie on the straight line drawn through the remaining points.

The relationship between the molecular structures of the adsorbed molecules and the slope of the log V' versus log C_S lines can be summarized as follows. For solutes and solvents belonging to the same class[7] (adsorption of solutes of class AB from solvents of class AB and solutes of class B from solvents of class B), in most instances the slopes are in the range 0.8–1.0, indicating an apparent exchange in the 1:1 ratio. For solutes and solvents of different types (B and AB), the slopes are

higher, usually in the range 1.1–1.3. Similar or even identical slopes for solutes with different molecular sizes but analogous steric situations of the hydrogen-bonding group seem to indicate the vertical orientation of the molecules on the surface. Some of the presumed configurations of the adsorbed molecules are shown in Fig. 5, taking into account that hydrogen bonds are strongest for linear arrangement of the OH ← N or OH ← O groups so that tetrahedral configurations of hydrogen bonds and chemical bonds should be favoured for primary, secondary and tertiary amines and oxygen compounds and flat triangular configurations for compounds of the pyridine type. In spite of some freedom of rotation around the Si–O and OH ← N axes, the orientation of an adsorbed molecule should thus be determined by the optimal directions of the bonds and by its interactions with vicinal adsorbed molecules and with the surface network of the adsorbent. It should be noted that a vertical orientation corresponds to the formation of a maximal number of hydrogen bonds between the compounds and the surface silanol groups and to displacement of a minimal number of solvent molecules from the surface monolayer by a single solute molecule.
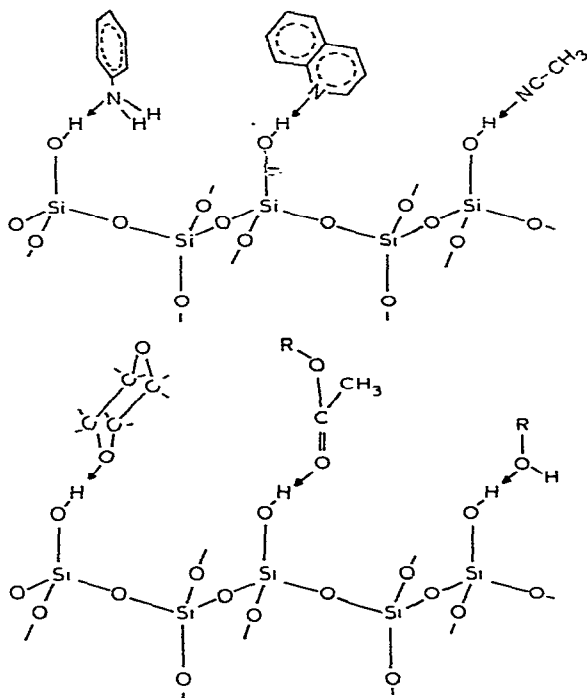

Fig. 5. Presumable orientation of adsorbed molecules of solutes and solvents.

The interpretation of the experimental data from the viewpoint of the presumed molecular adsorption mechanism should be considered as a working hypothesis that requires verification by other methods. The logarithmic plots, used so far in investigations of solution equilibria which obey the law of mass action (solvation, complex formation and more complex processes such as extraction and ion exchange[8]), also

seem to be useful in adsorption equilibria[9], due account being taken of complicating effects. It should be mentioned that a quantitative description of solvent composition effects has a fundamental significance in gradient elution chromatography[10]; in their theoretical study of this technique, Jandera and co-workers[11,12] recently reported further examples of linear log k' *versus* log C_S relationships.

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