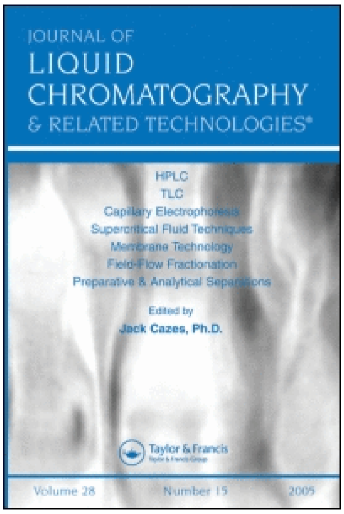

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# Solvent Composition Effects in the Chromatography of Alkaloids in the Systems Water Methanol/Silanized Silica

Edward Soczewinski[a]; Tadeusz Dzido[a]
[a] Department of Inorganic and Analytical Chemistry, Institute of Basic Chemical Sciences Medical Academy, Lublin, Poland

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# SOLVENT COMPOSITION EFFECTS IN THE CHROMATOGRAPHY OF ALKALOIDS IN THE SYSTEMS WATER + METHANOL/SILANIZED SILICA

Edward Soczewinski and Tadeusz Dzido
Department of Inorganic and Analytical Chemistry
Institute of Basic Chemical Sciences
Medical Academy
Staszica 6, 20-081 Lublin Poland

## ABSTRACT

For systems of the type silanized silica/binary aquo-organic solvent, linear log k'vs. % $H_2O$ plots are often obtained, the lines spreading fanwise in the direction of increased concentration of water. An example of such plots for a group of barbiturates is reported. For solutes which have more differentiated structures (especially in terms of the number and type of hydrophilic groups) less regular relationships can be obtained, as illustrated by log k' vs. % $H_2O$ plots of eight alkaloids.

## INTRODUCTION

The retention of solutes chromatographed in systems with nonpolar, chemically bonded stationary phases is usually controlled by addition of polar solvents (methanol, acetonitrile, etc.) to water (1); other methods involve the use of buffer solutions (2) or ion-pairing reagents (1,3). The effect of solvent composition, in these systems, can be frequently described by the semi-empirical equation:

$$\log k' = \text{const.} + (n \bullet \%\ H_2O)$$

An analogous equation was reported much earlier for batch extraction systems (4) and, although it was primarily derived for ideal solvent mixtures (5), it has been shown that it describes, over more or less broad composition ranges, the solvent composition effects in such strongly interacting mixtures as water and dimethyl sulfoxide (6). The linear relationships between log k' ($R_M$ in paper and thin-layer chromatography) and solvent composition have been widely used to determine extrapolated values of $R_M$ for the Hansch analysis of quantitative structure - activity relationships (7).

The equation has also been reported to apply to liquid-solid systems of the type water + methanol/silanized silica, in which hydrophobic interactions, determined by solution phenomena in the mobile phase, play an important role (1,8). For solutes of analogous molecular structure, such as polynuclear hydrocarbons (9,10) or aliphatic alcohols (8), the k' vs. % $H_2O$ lines usually spread fanwise in the direction of increasing concentration of water owing to increasing hydrophobic interactions. Other examples of such relationships are given in Figure 1, in which the data published by Tjaden et al. (11) are plotted in the coordinate system log k' vs. % MeOH; since the solutes from the barbiturate groups have similar structures and differ, primarily, by hydrocarbon radicals, the lines converge to the right with increasing concentration of methanol, in accordance with the observation that $\Delta R_M$ ($CH_2$) diminishes as water is diluted with polar organic solvent (8).

## EXPERIMENTAL

In the present paper we investigated a group of solutes - alkaloids - with greater difference in their molecular structures. The alkaloids were chromatographed using a liquid chromatograph with a pneumatic pump and a variable-wavelength UV detector (VSU-1, Zeiss, Jena, G.D.R.). A stainless steel column, 12 cm x 3.5 mm I.D., was packed with Lichrosorb RP-2, 10 µm (Merck, Darmstadt, F.R.G.) using the slurry technique after Bristow (12). The solutes were injected with a Hamilton syringe (5 µl of 0.2% methanol solutions); the flow rate was 0.5 - 1 ml/min. The dead volume of the column was determined using water as the test solute.

## RESULTS AND DISCUSSION

The experimental results are presented in Figure 2 as log k' vs. % MeOH plots. The plots are straight lines or only slightly curved, and the typical tendency to spreading with increased water content is also apparent; however, the plot of brucine crosses those of cinchonidine and aconitine. Generally, the slopes are more differentiated than in Figure 1.

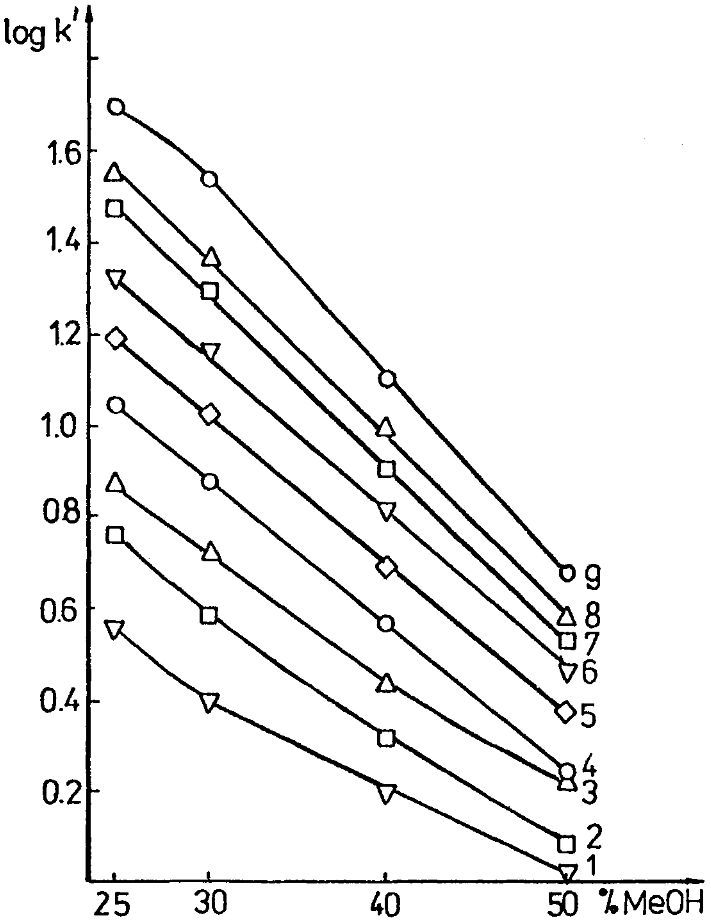

Figure 1. Log k' vs. % MeOH plots, barbiturates: 1-barbital; 2-heptobarbital; 3-allobarbital; 4-brallobarbital; 5-cyclobarbital; 6-hexobartital; 7-heptabarbital; 8-pentobarbital; 9-secobarbital.

Chromatographic System: Water + methanol/silanized silica. For details of experimental technique cf. reference 11.

The experimental results indicate that, for more complex, polyfunctional compounds, the log k' vs. composition plots are less regular than for congeneric solutes like polynuclear hydrocarbons (9,10), homologous series (8) and groups of solutes whose structures differ by nonpolar substituents (alkyl, alkenyl, phenyl, etc.) as in the case of the barbiturates of Figure 1. For congeneric solutes both the slope and the log k' values increase with the hydrophobicity of the nonpolar part of the molecule; this leads to fanwise

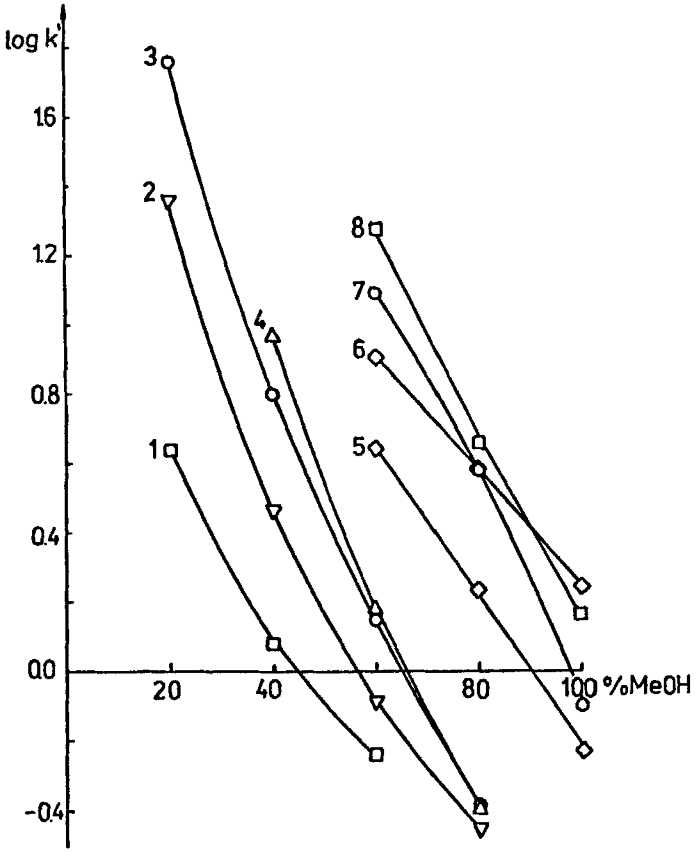

Figure 2. Log k' vs. % MeOH plots of eight alkaloids: 1-caffeine; 2-narceine; 3-colchicine; 4-santonine; 5-codeine; 6-brucine; 7-cinchonidine; 8-aconitine.

Chromatographic System: Water + methanol/octadecyl silica.

spreading of the lines. The introduction of an additional hydrophilic group may weaken the hydrophobic interactions in an individual manner thus causing more diverse log k' vs. composition plots. This is even advantageous from the viewpoint of selectivity. However, crossing of the plots may occasionally cause complications in gradient elution (13).

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