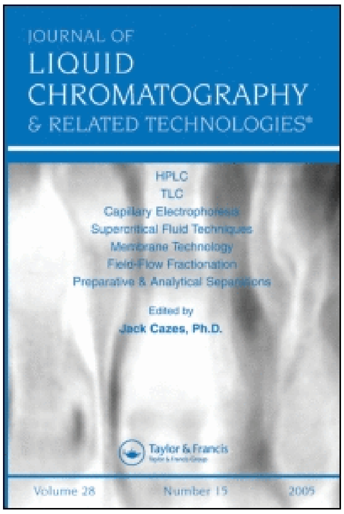

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DETERMINATION OF ASSOCIATION EFFECTS IN TLC DATA FOR DIFFERENT SOLUTES CHROMATOGRAPHED IN METHANOL-ACETONE ON SILICA GEL

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ABSTRACT

The TLC data for different solutes chromatographed in methanol-acetone mobile phase on silica gel at 293 K are analysed by means of the theoretical equations discussed in the previous paper (1). This analysis shows that for the above systems the solute-solvent and solvent-solvent association and the composition of the surface phase play an important role. The composition of the surface phase has been determined by utilizing the excess adsorption data of methanol from acetone on silica gel.

INTRODUCTION

In the previous paper (1) a model of liquid adsorption chromatography, involving solute-solvent and solvent-solvent association in the mobile phase, energetic heterogeneity of the adsorbent surface, and differences in molecular sizes of solutes and solvents, has been proposed. The general equation for the capacity ratio of the s-th solute chromatographed in binary mobile phase is a complex function of mole fractions of the solvents in the mobile and surface phases. This function contains the following parameters : ratio of molecular sizes of solute and solvent, equilibrium constant describing formation of the complexes between solute and solvent molecules, parameter defining the number of solvent molecules associating with one solute molecule, equilibrium constant describing association of solvent molecules, parameter defining the number of solvent molecules forming a molecular complex, equilibrium constants characterizing interactions of solutes and solvents with the adsorbent surface, and parameter characterizing energetic heterogeneity of the adsorbent surface. In many chromatographic systems only some parameters are important, whereas, the influence of other parameters on the capacity ratio or R_M-value may be neglected.

In this paper the simplified models of liquid adsorption chromatography will be applied to interpret the TLC data for different solutes chromatographed in methanol-acetone on silica gel at 293 K. For these data the effects connected with nonideality of the mobile phase are greater than the heterogeneity effects. Therefore, analysing the above data we shall use the models, which involve solvent-solvent and solute-solvent specific interactions in the mobile phase.

EXPERIMENTAL

Chemicals

Acetone and methanol (puriss. grade) were obtained from Polskie Odczynniki Chemiczne (Gliwice,Poland). The silica gel H (Type 60) was from E.Merck (Darmstadt, FRG).

TLC measurements

The TLC measurements were made under thermostatted conditions at 293 K. Silica gel H was the adsorbent, and methanol-acetone was the eluent.The adsorbent layers were 0.3 mm thick and were activated for 2h at 408 K. The chromatograms were developed by the ascending technique to a distance of 16 cm. The spots were visualized using the universal reagent (2). The R_F-values were converted into R_M -values using the equation of Bate-Smith and Westall (3). The R_M-values have been measured for the following solutes: 2-nitro-p-toluidine, 4-nitro-o-toluidine, 5-nitro-o-toluidine, N-phenyl-1-naphthalenamine, fluorenone, 2,3-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, naphthalene, o-nitrophenol, and p-nitrophenol at $x_1 = 0$, 0.1 , 0.3 , 0.5 , 0.7 , 0.9 and 1.0 , where x_1 is the mole fraction of methanol in the mobile phase.

Measurements of excess adsorption data

The excess adsorption isotherm for methanol-acetone mixture on silica gel H was measured at 293 K. The silica gel used was the same as in the TLC measurements.

A binary solution of known composition was prepared for each experimental point.The amounts of liquid and adsor-

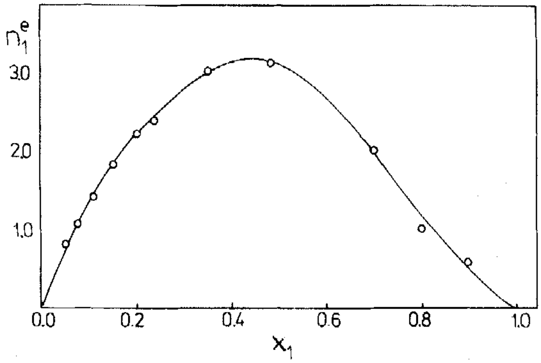

FIGURE 1 . The excess adsorption isotherm of methanol from acetone on silica gel at 293 K.

bent were measured gravimetrically. Equilibrium was obtained by shaking the flask with the adsorbent and liquid mixture in a water bath for 24h. Compositions of binary liquid mixtures were measured with a gas chromatograph, type Chromatron GCHF 18.3 , with a thermal conductivity detector. Hydrogen, purified by using a filter containing molecular sieve 5A pellets, was used as the carrier gas at flow-rate of 50 cm^3/min. A column, 100 cm x 4 mm I.D., containing the partition packing (10% silicone oil on Polysorb) was used. The chromatographic measurements were performed at 353 K.

The excess isotherm of methanol from acetone on silica gel at 293 K was calculated using the procedure described in (4) and it is shown in Figure 1 .The surface phase capacity n^s ,evaluated by the method of Schay and Nagy (5), is equal to 6.15 mmole/g.

RESULTS AND DISCUSSION

The R_M-values for toluidine, naphthalene and phenol derivatives chromatographed in methanol-acetone silica gel at 293 K change little with the increasing of methanol concentration in the mobile phase.The values of R_M for solutes chromatographed in pure methanol and and acetone are similar. Moreover,the absolute value of R_M for a solute in acetone is smaller than that for methanol.For ten solutes investigated the smallest absolute value of R_M in acetone is equal to 0.23 ,however, the highest absolute value of R_M in methanol is equal to 0.45 .The curves R_M vs. x_1 ,where x_1 is the mole fraction of methanol in the mobile phase, are weakly decreasing functions or they show a small minimum.

Firstly, the experimental dependences R_M vs. x_1 for different solutes have been analysed by applying the linear relationship of Soczewiński (6) :

$$R_M = R_{M1} - r \log x_1 \qquad (1)$$

where R_{M1} is the R_M- value for a given solute chromatographed in the pure methanol, and r is the ratio of molecular sizes of the solute and solvent.Equation 1 has been derived by applying the following assumptions : ideality of both phases, energetic homogeneity of the adsorbent surface, equality of molecular sizes of both solvents, and competitive character of adsorption of solutes and solvents. Moreover,this equation is valid for solvents showing great difference in the elution strengths.Then the mole fraction of the more efficient eluting solvent in the surface phase is close to unity. All experimental dependences 1 show deviations at low concentrations of x_1, because equation 1 predicts the non-physical value of R_M at $x_1 = 0$. Figure 2 shows the dependence R_M vs. log x_1 for a selected solute (the dashed line with the black circles), which is non-linear. The dependences R_M vs. log x_1 for other solutes investigated are also non-linear. Thus, equation 1 does not fulfil the above TLC data.

Figure 2 also presents the experimental dependence for a selected solute (the solid line with the white circles) plotted according to the linear relationship (7):

$$R_M = R_{M1} + r \log (y_1/x_1) \qquad (2)$$

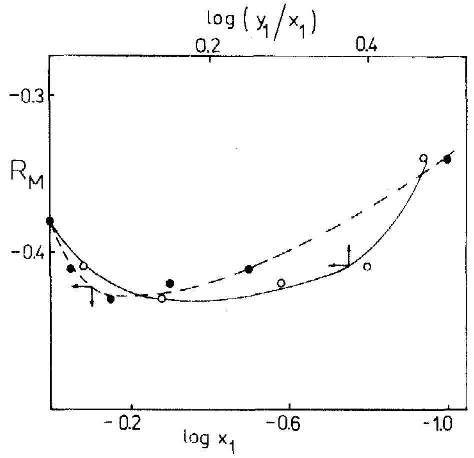

FIGURE 2 . The dependences R_M vs. log x_1 (the dashed line) and R_M vs. log (y_1/x_1) (the solid line) for 2,3-dihydroxynaphthalene in methanol-acetone on silica gel at 293 K.

where y_1 is the mole fraction of methanol in the surface phase.Equation 2 takes into account changes of the surface phase composition to dependence on the mobile phase composition.The mole fraction y_1 ,appearing in equation 2 ,may be calculated from the excess adsorption isotherm (c.f., Figure 1) according to the following equation :

$$y_1 = n_1^e/n^s + x_1 \tag{3}$$

where n_1^e is the adsorption excess of the more efficient eluting solvent, and n^s is the total number of moles in the surface phase.

It follows from Figure 2 that equation 2 also does not fulfil the above TLC data.

Next, we applied a model involving solvent-solvent and solute-solvent association in the mobile phase for analysing the TLC data measured for methanol-acetone mobile phase and silica gel. According to this model we have (1,8):

$$G(x_1) = 1/K + [(L-2M)/K]\, x_1 \tag{4}$$

where

$$G(x_1) = (y_1\, 10^{-R_M})/x_1$$

and K , L , M are the equilibrium constants characterizing the competitive character of the solute adsorption, formation of two-molecular solute-solvent associates and formation of two-molecular associates consisting from molecules of 1-st solvent,respectively. Equation 4 has been derived by assuming that two-molecular associates consisted from molecules of the solute and 1-st solvent form in the mobile phase, molecules of solutes and solvents have identical molecular sizes, and adsorbent surface is energetically homogeneous.

Equation 4 and its simpler form, i.e.,

$$G'(x_1) = 10^{-R_M}/x_1 = 1/K + [(L-2M)/K]\, x_1 \qquad (5)$$

have been used to describe the TLC data measured in methanol-acetone on silica gel. Figure 3 presents the dependences 4 and 5 for a selected solute chromatographed in methanol-acetone on silica gel.

The plots for other solutes are analogous to those presented in Figure 3 .Table 1 contains the values of R_{M1} and

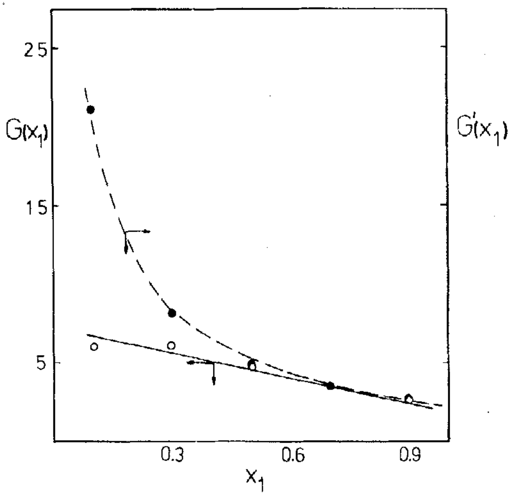

FIGURE 3 . The dependences $G(x_1)$ vs. x_1 (the solid line) and $G'(x_1)$ vs. x_1 (the dashed line) for 2,3-dihydroxynaphthalene chromatographed in methanol-acetone on silica gel at 293 K.

TABLE 1

Parameters characterizing the TLC systems investigated.

Solute	R_{M1}	R_{M2}	K	(L-2M)
p-nitrophenol	-0.40	-0.28	0.15	-2.51
o-nitrophenol	-0.35	-0.23	0.17	-3.77
naphthalene	-0.38	-0.31	0.13	-2.17
2,3-dihydroxynaphthalene	-0.38	-0.31	0.14	-2.22
2,7-dihydroxynaphthalene	-0.41	-0.30	0.14	-2.22
N-phenyl-1-naphthalen-amine	-0.45	-0.39	0.12	-1.73
2-nitro-p-toluidine	-0.36	-0.34	0.13	-2.13
4-nitro-o-toluidine	-0.39	-0.37	0.13	-1.89
5-nitro-o-toluidine	-0.37	-0.33	0.14	-2.00
fluorenone	-0.30	-0.26	0.15	-3.34

R_{M2} for all solutes and the parameters K and (L-2M) calculated from the linear plots 4 .It follows from Figure 3 that the experimental points plotted according to equation 5 show deviations at low concentrations of methanol in the mobile phase,however, the dependence plotted according to equation 4 is linear (the solid line). The slopes of the dependences 4 for all solutes studied are negative ; it means that the effects connected with association of the more polar solvent (methanol) are greater than the effects of solute-solvent association. Since,the slopes are similar for all solutes investigated ,the average slope may be used to characterize the specific interactions between molecules of methanol.

Concluding, we can draw that in the case of TLC data for toluidine,naphthalene and phenol derivatives chromatographed in methanol-acetone on silica gel two factors are important :

- specific interactions between molecules of methanol in the mobile phase,
- specific interactions of solute molecules with methanol molecules in the mobile phase,and
- change of the surface phase composition to dependence on the mobile phase composition.

The effects connected with nonideality of the surface phase, energetic heterogeneity of the adsorbent surface, and molecular sizes of solutes and solvents play smaller role in the chromatographic process.

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