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ADSORPTION FROM MULTI-COMPONENT LIQUID MIXTURES ON TO HETEROGENEOUS SOLID SURFACES: THE ROLE OF ADSORPTION OF WATER ON SILICA IN LIQUID–SOLID ADSORPTION CHROMATOGRAPHY*

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SUMMARY

The water content in mixed solvents that are used as mobile phases in liquid–solid adsorption chromatography on silica surfaces has been reported to play a special role in controlling the retention of solutes. The phenomena reported in the literature were investigated by a theoretical treatment: *a priori* calculations of the activity coefficients allow the influence of non-ideal mixing in the mobile phase to be estimated. Following a concept of "competitive adsorption within a multi-layer model", the water coverage at the surface was calculated as a function of its bulk phase concentration, and the concentration range of water in the bulk phase was calculated where multi-layer adsorption of water on the surface takes place. Subtracting the influence of solute activity coefficients from measured capacity factor data, the competitive behavior of the three solvent components with respect to the solute was studied and the competitive adsorption constants were approximately evaluated by regression. Finally, the possible influence of the water content on the surface phase activity coefficients is discussed, assuming a geometric arrangement of oriented adsorbates.

INTRODUCTION

Of various column packings used in liquid adsorption chromatography (LSC), silica gels are commonly applied. Very often the separation is optimized by using mixed mobile phases, where the solvents that are mixed contain a certain small amount of water. Because of the unusual adsorption of water on silica surfaces, this small concentration of water in the mobile phase assumes great importance. Mixing various solvents results in an accompanying change in the water concentration and especially water activity in the mobile phase. This change is usually not controlled, although it may have a significant effect on the behaviour of the capacity factors of the solutes.

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* Dedicated to Prof. J. F. K. Huber on the occasion of his 60th birthday.

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Paanakker *et al.*[1] were one of the first groups to carry out a systematic study of the effects of water concentration in the mobile phase. Their experiments revealed a phenomenon that has not been explained up to now, namely that the capacity ratio measured at very low water concentrations decreased with increasing concentration of water in the mobile phase, whereas at high water concentrations an opposite trend in the behaviour of the capacity ratio was observed. This trend can hardly be explained on the basis of most of the existing and commonly applied theories of LSC processes[2–6], all of which predict a decrease in capacity factors with increasing concentration of the more active solvent ("moderator"). These experimental data of Paanakker *et al.*[1] are the subject of the investigations reported in this paper. The special approach in this paper is the application of *a priori* calculations in order to separate the different contributions to the partition coefficients in liquid–solid adsorption systems.

The effects recognized so far as the most important in adsorption from solution can be summarized as (i) the competitive adsorption of the solvent components and the solute (including the influence of the different surface areas occupied by the adsorbed molecules), (ii) the non-ideal mixing behaviour in the mobile phase with respect to all components, (iii) the non-ideal mixing in the surface phase, (iv) the formation of adsorbed multilayers and (v) the energetic heterogeneity of the surface.

Some of the equations developed so far take into account many of these effects. The important contribution of the activity coefficients of the solutes in the mobile phase, $\gamma_i^{(L)}$, to the capacity factor, κ_i, has been pointed out by several workers[1,2,7–12]. However, only limited data are currently available. For *n*-heptane–2-propanol mobile phase systems this contribution has been experimentally quantified for several solutes by Slaats *et al.*[8] by applying headspace gas chromatography.

The importance of activity coefficients in the surface phase, which ought to account for the non-ideal mixing between neighbouring adsorbates, has been mentioned by several workers[12,13]. All calculations made so far in this field have shown that the activity coefficients in the surface phase obtained by regression analysis are very different from those calculated or measured in the liquid bulk phase[12,13]. Hence the activity coefficients of solutes in the adsorbed phase could only be used in combination with a best-fit parameter. Lane[14] obtained similar results. This has two main reasons: first, the heterogeneity of surfaces can be accounted for formally by "activity coefficients"[13], although these "activity coefficients" do not describe the non-ideality of mixing. Therefore, if the heterogeneity of the surface is not taken into account explicitly in an accurate way, the activity coefficients in the surface phase obtained from regression will reflect both the non-ideal mixing in the surface phase and a correction due to the improper description of surface heterogeneity. The second reason is more fundamental. Adsorption on a surface is connected with a loss of freedom of motion and an orientation of the adsorbed molecules. This orientation is well known to occur with surfactants and with other compounds consisting of a polar and a non-polar part on interfaces. It might well be significant also for the adsorption of dipolar molecules on a polar surface from a non-polar bulk phase.

Multilayer-type adsorption of mixed solvents cannot be properly described and predicted by most of the equations used commonly in chromatographic data reduction[2–4,6]. The influence of the energetic heterogeneity of surfaces on adsorption from solution has been investigated extensively by many scientists[10,11,15–17]. Some of the chromatographic data mentioned here have already been investigated using an approximate solution to this heterogeneity problem[18].

In this work we studied the influence of non-ideal mixing in the bulk phase by analysing the activity coefficients of the solutes and the solvent components in the mobile phase. These activity coefficients were obtained by *a priori* calculations. In this way it is possible to separate this contribution clearly from the other contributions mentioned above. Because many of these contributions produce a similar type of dependence of the capacity factor on the mobile phase composition, it would be difficult otherwise to distinguish between these different effects on the basis of curve-fitting capacity factor data only, even using high-precision data.

As a second problem, the importance of multilayer formation by water in liquid adsorption chromatography was investigated by evaluating the concentration range where the multilayer formation of water is expected to take place in adsorption from ternary mixtures. For this purpose the adsorption isotherm of water is assumed to be analogous to that measured by Souteyrand *et al.*[19], who used various less polar binary solvents. Again, a knowledge of the activity coefficients of the solvent components in the mobile liquid phase is needed.

The competitive adsorption between solvent components and solutes (this contribution is obtained after dividing the measured capacity factors by the calculated activity coefficients) in a concept of multilayer adsorption is illustrated and quantified for several solutes.

The possible importance of surface phase activity coefficients, and how they are influenced by the absorbed water, is discussed in a qualitative way by using model calculations. As the physical systems mentioned are very complicated, many simplifying assumptions have to be introduced into our theoretical interpretation in order to make the problem tractable. As it cannot be excluded that surface heterogeneity may also contribute to the mentioned phenomenon, a preliminary investigation of the influence of surface heterogeneity in these systems will be presented in the near future.

THEORETICAL

The chromatographic capacity factor, κ_i, is interrelated to the partition coefficient, ${}^xK_i$, by the equation

$$\kappa_i = {}^xK_i \, q \, [\bar{v}^{(\mathrm{L})}/\bar{v}^{(\sigma)}] \tag{1}$$

where q is the phase ratio and $\bar{v}$ is the mean molar volume of the phase indicated by the superscript. For the description of the dependence of the partition coefficient, ${}^xK_i$, on the mixture composition we use the equation according to Rudziński and co-workers[10,18,20,21], which is based on the assumption of monolayer-type competitive adsorption from a multi-component solution on to a heterogeneous solid surface and which accounts for non-ideal mixing in the bulk and in the surface phase:

$${}^xK_i = [x_i^{(\sigma)}/x_i^{(\mathrm{L})}] = \frac{\gamma_i^{(\mathrm{L})}/\gamma_i^{(\sigma)}}{\sum\limits_{n=1}^{N} K_{ni}\,[x_n^{(\mathrm{L})}\gamma_n^{(\mathrm{L})}/\gamma_n^{(\sigma)}]^{\alpha_{in}\rho_{in}}} \tag{2}$$

Where γ represents the activity coefficients, describing the deviation from ideal mixing behaviour in the bulk (L) and in the surface (σ) phase, respectively, x denotes the molar fractions and K_{ni} the equilibrium constant for the exchange reaction, where compound n displaces compound i from the solid surface. Further α_{in} is the ratio of the surface areas occupied by molecules i and n and ρ_{in} is an appropriate surface heterogeneity parameter.

Adsorption of solvent components

Dealing with solvent components, one may ignore to a certain extent the usually smaller influence of different surface areas occupied by different solvent molecules, and the influence of surface phase activity coefficients of solvents. Neglecting in this instance also the influence of surface heterogeneity on the adsorption of the solvent components, eqn. 2 can be reduced to

$$\frac{x_i^{(\sigma)}}{x_i^{(\mathrm{L})}} = \frac{\gamma_i^{(\mathrm{L})}}{\sum\limits_{n=1}^{N} K_{ni}\, x_n^{(\mathrm{L})}\, \gamma_n^{(\mathrm{L})}} \tag{3}$$

For the particular case of a ternary mixture of solvents, eqn. 3 becomes

$$x_3^{(\sigma)} = \frac{x_3^{(\mathrm{L})}\, \gamma_3^{(\mathrm{L})}}{\sum\limits_{n=1}^{3} K_{n3}\, x_n^{(\mathrm{L})}\, \gamma_n^{(\mathrm{L})}} \tag{4}$$

and after some rearrangement we obtain

$$\frac{x_3^{(\sigma)}}{1 - x_3^{(\sigma)}} = x_3^{(\mathrm{L})}\, \gamma_3^{(\mathrm{L})}\, [K_{13}\, x_1^{(\mathrm{L})}\gamma_1^{(\mathrm{L})} + K_{23}\, x_2^{(\mathrm{L})}\gamma_2^{(\mathrm{L})}]^{-1} \tag{5}$$

This equation allows one to estimate the surface coverage of the strongest adsorbed solvent (3) as a function of the concentration of all other components, if one knows the adsorption equilibrium constants, K_{13} and K_{23}, and if the activity coefficients can be obtained as function of the composition. The activity coefficients in the mobile phase can be calculated according to refs. 22–24 or by the method described in the Appendix.

As mentioned before, eqn. 5 is based on the concept of competitive adsorption of solutes in a monolayer fashion. However, if more than one adsorbed layer is formed on the surface (as described for the adsorption of water on silica[1,19]), then eqn. 5 does not give the correct adsorption isotherm of water in the first layer. The competitive influence of the second modifier (2) would be overestimated by this equation, as it neglects the energy gain by adsorption of the modifier (2) in the second layer on the water molecules adsorbed in the first layer. Any rigorous treatment by equations properly extended for the description of multilayer adsorption requires a knowledge of the competitive adsorption constants in each layer, involving a large number of unknown parameters. For evaluating the concentrations of the solvent components in the first layer, a simpler and more practicable treatment is proposed.

For this purpose we assume that the contribution of the modifier (2) can be described approximately by substituting the equilibrium constant K_{23} in eqn. 5 by an effective constant K_{23}', which is expected to be much smaller than the original constant K_{23}. To analyse the adsorption of the solvents in the first layer, the following equation is then used:

$$x_3^{(L)} = \frac{x_3^{(\sigma)}}{1 - x_3^{(\sigma)}} \cdot \frac{1}{\gamma_3^{(L)}} [K_{13}\, x_1^{(L)}\gamma_1^{(L)} + K_{23}' x_2^{(L)}\gamma_2^{(L)}] \qquad (6)$$

If one assumes that multilayer formation during the adsorption of water (3) ["additive" to the adsorption of the other polar modifier (2) instead of "pure competitive"] allows one to neglect completely the influence of the second modifier (2) on the surface concentration of water in the first layer, eqn. 6 can be reduced to

$$x_3^{(L)} = \frac{x_3^{(\sigma)}}{1 - x_3^{(\sigma)}} \cdot \frac{1}{\gamma_3^{(L)}} \cdot K_{13}\, x_1^{(L)}\, \gamma_1^{(L)} \qquad (7)$$

Eqn. 6 or 7 allows one to calculate the water concentration in the bulk phase which corresponds to a distinct surface coverage of water, and *vice versa*. The approximate knowledge of the surface coverage of water calculated in this way facilitates a realistic understanding of the role of water and allows one to establish approximately the water content, where a second layer of water is starting to be built up.

Adsorption of solutes

Investigating the adsorption of solutes, we return to eqn. 2. In this instance the subscript i indicates the solute. Again, the activity coefficients of the solutes and the solvent molecules in the mobile phase, $\gamma_i^{(L)}$ and $\gamma_n^{(L)}$, respectively, can be quantified by several equations that are obtained from molecular thermodynamics[25–27]. One of these methods is described in the Appendix. The activity coefficients in the surface layer cannot be easily calculated. The magnitude and the possible influence of this contribution are discussed in a qualitative way later. Assuming that the adsorbed molecules are oriented perpendicular to the surface, the parameter α_{in}, *i.e.*, the ratio of the surface areas occupied by different adsorbates can be set approximately to unity. The validity of this assumption is discussed later. The influence of surface heterogeneity is expected to contribute significantly at very low concentrations of water on the surface. Its possible role at higher concentrations will be investigated in a later paper. Within the following calculations, ρ is set equal to 1.

Separating the influence of bulk phase activity coefficients of the solute from the contributions of competitive adsorption on the surface, one obtains the following equation:

$$\ln [\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}] = \ln [q/v^{(\sigma)}] - \ln \gamma_i^{(\sigma)} - \ln \left[\sum_{n=1}^{N} K_{ni}\, x_n^{(L)}\gamma_n^{(L)} \right] \qquad (8)$$

Assuming the first two terms on the right-hand side to be not much affected by the solvent composition [this is discussed later for $\ln \gamma_i^{(\sigma)}$], eqn. 8 for a ternary mobile phase becomes

$$\ln [\kappa_i/\gamma_i^{(L)}v^{(L)}] = C_0 - \ln [K_{1i}\, a_1^{(L)} + K_{2i}\, a_2^{(L)} + K_{3i}\, a_3^{(L)}] \quad (9)$$

where C_0 is a constant.

An investigation of the dependence of ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ on the activities of the solvent components allows one to calculate the constants for the competitive adsorption of solvent components relative to the solute, K_{1i}, K_{2i} and K_{3i}.

Remembering that eqn. 2 is based on the concept of competitive adsorption within a monolayer model, eqn. 9 is valid only for monolayer-type adsorption. How-

TABLE I

CAPACITY RATIOS OF SEVERAL SOLUTES AS A FUNCTION OF THE PERCENTAGE OF 1-BUTANOL AND WATER IN ISOOCTANE MEASURED BY PAANAKKER *et al.*[1]

This Table is a condensed copy of Table I in the paper by Paanakker *et al.*[1].

1-Butanol		*Water (ppm)*	*Anthracene*	*Acetophenone*	*Benzyl alcohol*
(v/v)	*x*				
0.1	0.0018	14	0.43	6.99	
		26	0.31	5.69	
		40	0.25	4.67	
0.3	0.0053	17	0.30	2.56	
		25	0.29	2.28	
		38	0.28	1.95	
0.4	0.0072	15	0.27	2.21	28.85
		25	0.26	1.95	25.66
		42	0.26	1.73	21.93
0.5	0.0090	14	0.25	2.08	20.43
		41	0.24	1.89	17.19
1.0	0.0179	49	0.20	1.28	11.01
		60	0.19	1.23	10.14
		95	0.18	1.15	10.20
		142	0.20	1.24	10.75
2.5	0.0441	118	0.18	1.00	4.35
		204	0.19	0.94	4.46
		258	0.22	0.94	4.72
		310	0.22	0.92	4.76
3.5	0.0613	107	0.17	0.87	3.35
		201	0.18	0.97	3.55
		305	0.17	0.98	3.62
		365	0.17	0.98	3.64
5.0	0.0865	98	0.16	0.68	2.32
		245	0.17	0.70	2.41
		394	0.18	0.71	2.44
7.5	0.1274	90	0.17	0.67	1.62
		200	0.17	0.67	1.60
		435	0.18	0.65	1.54
10.0	0.1670	106	0.16	0.63	1.23
		238	0.16	0.58	1.12
		348	0.17	0.56	1.11
		646	0.16	0.58	1.11
		979	0.18	0.62	1.18

ever, introducing "effective" constants, K_{1i}', K_{2i}' and K_{3i}', instead of K_{1i}, K_{2i} and K_{3i}, respectively, one obtains the following equation:

$$\ln\left[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}\right] = C_0 - \ln\left[K_{1i}'a_1^{(L)} + K_{2i}'a_2^{(L)} + K_{3i}'a_3^{(L)}\right] \tag{10}$$

which can be used for the correlation of adsorption data when more than one adsorbed layer is formed *and* when "additive" adsorption of the solute (and solvent components) on the solvent molecules which are already adsorbed can be observed or expected.

Specification of the investigated data set

The liquid–solid adsorption systems investigated in this work consist of ternary mixed mobile phases composed of 2,2,4-trimethylpentane (isooctane), 1-butanol and small amounts of water and a silica surface (silica gel Si 60 from E. Merck) as stationary support. The solutes selected for a theoretically treatment in this paper are anthracene, acetophenone and benzyl alcohol. The composition of the phase systems and the chromatographic capacity factor data for this investigation are quoted from the paper of Paanakker *et al.*[1]. Their data are collected in a condensed form in Table I.

RESULTS AND DISCUSSION

Influence of non-ideal mixing in the liquid bulk phase

The activity coefficients, $\gamma^{(L)}$, of the solvent components, isooctane, 1-butanol and water, and of several solutes were calculated by us for the mixed mobile phases used in the investigations of Paanakker *et al.*[1] (Table I). Activity coefficients were calculated by use of the NRTL equation of Renon and Prausnitz[23] and/or by using the "solution of groups" model[25,26], which is described in more detail in the Appendix. It is important to note that these methods allow *a priori* calculations, where no curve fitting procedure has to be applied to the data investigated here.

Solvent components. The activity coefficients of the solvent components calculated by use of the NRTL equation[23] are reported in Table II. These data show that the activity coefficient of butanol, $\gamma_{\mathrm{BuOH}}^{(L)}$, varies with increasing butanol concentration from about 44 to 3.7, that is, by one order of magnitude. The differences in the water content at parts per million levels do not affect the butanol activity coefficient much.

The activity coefficient of water, $\gamma_{\mathrm{water}}^{(L)}$, varies from about 2100 to about 35 for the investigated mixtures, that is, by two orders of magnitude. The large decrease in the activity coefficients of water is caused by an increase in the butanol concentration. While the molar fraction of water changes from 0.00013 to 0.0083 in the investigated phase systems (a factor of 65), the activity of water is observed to vary significantly less (by a factor of 4–8). It is important for chromatographic purposes that even large variations in the water content, induced by the increased solubility of water with increasing alcohol concentration, lead to much less dramatic variations in the activity of water, which is the decisive variable according to eqns. 6 and 9.

Solutes. The activity coefficients of solutes in the described solvent systems were calculated by use of the "solution-of-groups" model. As this model is restricted

TABLE II

MOBILE PHASE ACTIVITY COEFFICIENTS, $\gamma_n^{(L)}$, AND ACTIVITIES, $a_n^{(L)}$, OF THE THREE SOLVENT COMPONENTS AT DIFFERENT MIXTURE COMPOSITIONS

The data were calculated by use of the NRTL equation[23]

$x_1^{(L)}$	$x_2^{(L)}$	$x_3^{(L)}$	$\gamma_1^{(L)}$	$\gamma_2^{(L)}$	$\gamma_3^{(L)}$	$a_1^{(L)}$	$a_2^{(L)}$	$a_3^{(L)}$
0.9981	0.0018	0.000128	1.000	43.8	2116	0.998	0.079	0.271
0.9980	0.0018	0.000238	1.000	43.6	2084	0.998	0.079	0.496
0.9978	0.0018	0.000366	1.000	43.3	2046	0.998	0.078	0.749
0.9945	0.0053	0.000155	1.001	39.6	1794	0.995	0.214	0.279
0.9944	0.0053	0.000229	1.001	39.4	1776	0.995	0.213	0.406
0.9944	0.0053	0.000347	1.001	39.2	1747	0.995	0.212	0.607
0.9927	0.0072	0.000137	1.001	37.6	1651	0.994	0.270	0.226
0.9926	0.0072	0.000228	1.001	37.4	1632	0.994	0.269	0.373
0.9924	0.0072	0.000384	1.001	37.2	1598	0.994	0.267	0.613
0.9909	0.0090	0.000128	1.001	35.8	1528	0.992	0.321	0.195
0.9906	0.0090	0.000374	1.001	35.4	1480	0.992	0.318	0.554
0.9817	0.0179	0.000445	1.005	28.1	1022	0.987	0.503	0.455
0.9816	0.0179	0.000545	1.005	28.0	1010	0.987	0.501	0.551
0.9812	0.0179	0.000863	1.005	27.7	973	0.987	0.495	0.840
0.9808	0.0179	0.001290	1.006	27.2	927	0.987	0.487	1.196
0.9548	0.0441	0.001059	1.022	15.8	402	0.976	0.699	0.426
0.9541	0.0441	0.001830	1.023	15.5	376	0.976	0.684	0.689
0.9536	0.0441	0.002314	1.023	15.3	361	0.976	0.675	0.836
0.9531	0.0441	0.002779	1.024	15.1	347	0.976	0.667	0.965
0.9377	0.0613	0.000953	1.036	11.8	258	0.972	0.726	0.246
0.9369	0.0613	0.001789	1.037	11.6	242	0.972	0.712	0.434
0.9360	0.0613	0.002713	1.038	11.4	227	0.972	0.698	0.615
0.9355	0.0613	0.003245	1.039	11.3	218	0.972	0.689	0.708
0.9126	0.0865	0.000863	1.059	8.3	150	0.966	0.721	0.129
0.9113	0.0865	0.002155	1.061	8.1	138	0.966	0.704	0.299
0.9100	0.0865	0.003462	1.062	8.0	129	0.966	0.688	0.445
0.8718	0.1274	0.000781	1.102	5.38	76.1	0.961	0.643	0.059
0.8709	0.1274	0.001733	1.103	5.32	73.0	0.961	0.635	0.127
0.8688	0.1274	0.003763	1.106	5.19	67.0	0.961	0.618	0.252
0.8321	0.1670	0.000899	1.149	3.94	46.4	0.956	0.657	0.042
0.8310	0.1670	0.002016	1.151	3.90	44.7	0.956	0.650	0.090
0.8301	0.1670	0.002945	1.152	3.87	43.4	0.956	0.644	0.128
0.8275	0.1670	0.005455	1.156	3.79	40.0	0.956	0.630	0.218
0.8248	0.1670	0.008246	1.161	3.71	36.7	0.956	0.615	0.303

to "monofunctional" compounds, and as for the region of strong dilution an especially optimized set of group-interaction parameters is needed[27], the number of solutes for which we can offer reliable calculation results is limited. Fig. 1 shows calculated activity coefficients for anthracene, acetophenone and benzyl alcohol at various molar fractions of 1-butanol in the mobile phase. The corresponding data are given in Table III, from which the effect of water at ppm concentrations on the solute activity coefficients is observed to be very small, *i.e.*, less than 0.5%.

Subtracting the effect of mobile phase non-ideality from the total retention behaviour yields ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$. This term reflects the phenomena of adsorption due to exchange reactions on the surface or in the adsorbed layers according to eqn. 9.

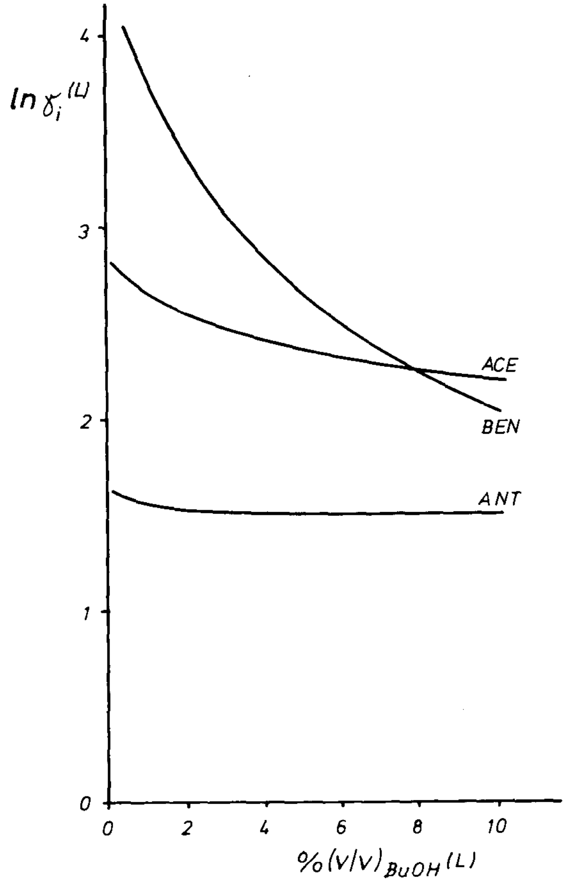

Fig. 1. Dependence of the mobile phase activity coefficients of anthracene, acetophenone and benzyl alcohol at infinite dilution on the composition of the mobile phase, calculated by means of the ASOG equation. Additional data are given in Table III.

For the three solutes anthracene, acetophenone and benzyl alcohol, Fig. 2 shows the dependence of this contribution ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ on the logarithm of the modifier (butanol) activity.

The small influence of the variation of water content in the mobile phase on the activity coefficient of the solutes justifies the interpretation of ln κ_i *vs.* ln a_{water} plots at constant butanol concentration directly, instead of using ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ *vs.* ln a_{water} plots. ln κ_i *vs.* ln a_{water} plots were presented by Paanakker *et al.*[1]; They show a flattening of the descending ln κ_i curves and sometimes a subsequent increase beyond a certain water concentration (and above a certain butanol concentration) for most of the solutes. This phenomenon is not yet completely understood.

Multilayer adsorption of solvent components

Experimental data on multilayer adsorption on silica in alkane–water and alkane–alcohol–water mixtures. Prior to any calculation and for assuming reasonable

TABLE III

MOBILE PHASE ACTIVITY COEFFICIENTS AT INFINITE DILUTION, $\gamma_i^{(L)\infty}$, FOR THE THREE SOLUTES ANTHRACENE, ACETOPHENONE AND BENZYL ALCOHOL AT DIFFERENT MIXTURE COMPOSITIONS CALCULATED BY USE OF THE ASOG EQUATION (SEE APPENDIX)

The ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ data were obtained dividing the measured capacity factors[1] by the calculated activity coefficients and the mean molar volume of the mobile phase. These values are used for Fig. 2 and for the determination of the adsorption constants in Table VI.

x_2	x_3	γ_{Ant}	γ_{Ace}	γ_{Ben}	$\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}$		
					Anthracene	*Acetophenone*	*Benzyl alcohol*
0.0018	0.000128	5.02	16.55		0.0143	0.0705	
0.0018	0.000238	5.00	16.45		0.0104	0.0577	
0.0018	0.000366	4.98	16.38		0.0084	0.0476	
0.0053	0.000155	4.96	16.01		0.0101	0.0267	
0.0053	0.000229	4.96	15.97		0.0098	0.0239	
0.0053	0.000347	4.95	15.92		0.0095	0.0205	
0.0072	0.000137	4.93	15.74	57.1	0.0092	0.0235	0.0844
0.0072	0.000228	4.93	15.70	56.4	0.0088	0.0208	0.0761
0.0072	0.000384	4.92	15.64	55.4	0.0088	0.0185	0.0662
0.0090	0.000128	4.91	15.49	54.2	0.0085	0.0225	0.0631
0.0090	0.000374	4.89	15.40	52.7	0.0082	0.0205	0.0546
0.0179	0.000445	4.78	14.37	41.5	0.0070	0.0150	0.0445
0.0179	0.000545	4.78	14.35	41.2	0.0067	0.0144	0.0413
0.0179	0.000863	4.77	14.30	40.4	0.0063	0.0135	0.0423
0.0179	0.001290	4.77	14.24	39.6	0.0070	0.0146	0.0456
0.0441	0.001059	4.59	12.38	24.3	0.0067	0.0137	0.0305
0.0441	0.001830	4.59	12.33	23.7	0.0070	0.0129	0.0319
0.0441	0.002314	4.60	12.31	23.5	0.0081	0.0130	0.0341
0.0441	0.002779	4.60	12.28	23.2	0.0081	0.0127	0.0348
0.0613	0.000953	4.53	11.58	19.0	0.0064	0.0129	0.0301
0.0613	0.001789	4.54	11.54	18.7	0.0068	0.0144	0.0325
0.0613	0.002713	4.54	11.50	18.4	0.0064	0.0146	0.0337
0.0613	0.003245	4.55	11.48	18.2	0.0064	0.0146	0.0342
0.0865	0.000863	4.49	10.72	14.3	0.0062	0.0110	0.0280
0.0865	0.002155	4.50	10.67	14.1	0.0065	0.0113	0.0297
0.0865	0.003462	4.51	10.63	13.8	0.0069	0.0116	0.0305
0.1274	0.000781	4.48	9.74	10.1	0.0067	0.0121	0.0282
0.1274	0.001733	4.49	9.71	10.0	0.0067	0.0122	0.0281
0.1274	0.003763	4.51	9.66	9.85	0.0070	0.0119	0.0275
0.1670	0.000899	4.52	9.05	7.83	0.0064	0.0125	0.0282
0.1670	0.002016	4.53	9.02	7.78	0.0063	0.0115	0.0258
0.1670	0.002945	4.54	9.00	7.73	0.0067	0.0112	0.0258
0.1670	0.005455	4.57	8.93	7.62	0.0063	0.0116	0.0261
0.1670	0.008246	4.60	8.86	7.51	0.0070	0.0125	0.0281

numerical values for the constants in eqn. 6, experimental evidence[1,19] is emphazised concerning multilayer formation in alkane (or chloroalkane)–water and in alkane–alcohol–water systems adsorbed on silica.

Experimental adsorption isotherms of water from non-polar and less polar alkanes or chloroalkanes (class N solvents) on silica were investigated by Souteyrand *et al.*[19]. They found that at higher water concentrations the formation of at least a

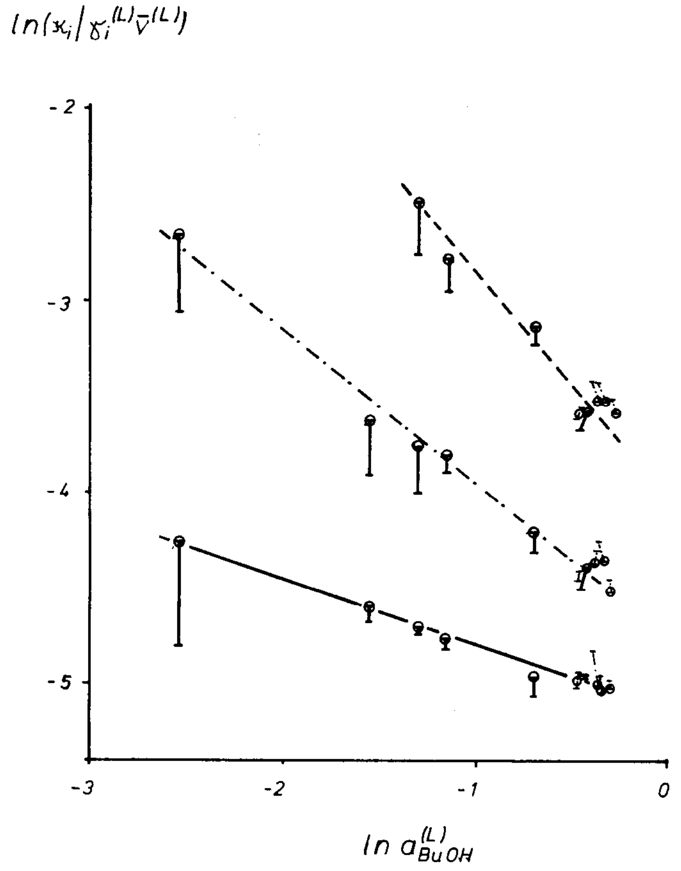

Fig. 2. Dependence of ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ on the activity of 1-butanol in the mobile phase. The ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ values are taken from Table III. The bars represent the variation in the water activity within experiments. The circles indicate those data which are measured at water concentrations near to the corresponding calculated $x_{\text{water}}^{(L)*}$ value. The lines connect points of about equal water activity (a_{water} = 0.27). ———, Anthracene; —·—·—, acetophenone; — — —, benzyl alcohol.

double layer of water has to be presumed. For the solvents methylenechloride and chloroform it was observed that the formation of a second layer of water on silica starts at that molar fraction of water in the mobile phase where the monolayer model would indicate an adsorption degree of 75%, *i.e.*, $x_{\text{water}}^{(\sigma)}/[1-x_{\text{water}}^{(\sigma)}] = 3$. (We shall assume in our following calculation that the ratio 3 can be applied also to solvents other than methylenechloride and chloroform and for solvent mixtures.) The values of the equilibrium constant for the competitive adsorption between the non-polar solvent and water was reported to be 1/22.

Mobile phase systems of the type alkane–alcohol–water and their adsorption on silica were investigated by Paanakker *et al.*[1]. From the shape of the adsorption isotherm of 1-butanol in a binary mixture with isooctane on silica, monolayer adsorption is concluded for 1-butanol. This conclusion, based on the shape of the isotherm, is in agreement with the amount of solvents adsorbed. With silica Si 60, the isotherm reaches a plateau, *i.e.*, the surface is covered by a more or less complete layer of butanol, at $x_{BuOH}^{(L)} = 0.014$ (ref. 1). Using isooctane–1-butanol solvent mixtures with a certain controlled content of water, the adsorption isotherm of the moderators was found to be basically unchanged. Paanakker *et al.*[1] concluded that water did not compete with these moderators in the concentration range investigated.

Based on these experimental data reported in the literature, the following assumptions are made for a quantitative treatment of the adsorption of solvent components from the mobile phase isooctane–1-butanol–water on silica.

Depending on the water content in the mixture, the moderator 1-butanol is adsorbed either on the silica surface or on the water molecules which are strongly bonded to the silanol groups. The equilibrium constant, K_{23}', in eqn. 6, which describes the removal of water from the surface by 1-butanol, is assumed to be much smaller than would be expected for a pure (monolayer-type) competitive adsorption of solvents. It is assumed to be of the order of K_{13}, the octane–water adsorption equilibrium constant, or can even be ignored.

Beyond a certain concentration of water in the mobile phase, the adsorption of water itself exeeds a monolayer and the formation of a second layer of water is started. By analogy with the results of Souteyrand *et al.*[19], we assume in our following calculations that this formation of a second layer of water starts at a water concentration in the mobile phase where the monolayer model would indicate a 75% coverage of the surface. 1-Butanol is then also adsorbed on this second layer of water.

Calculation of water coverage on the surface. Using eqn. 6, one can calculate the water coverage in the first surface layer which corresponds to a certain concentration of water in the mobile phase, and *vice versa*. The activity coefficients of the solvent components needed in this calculation are given in Table II. The equilibrium constant, K_{13}, in eqn. 6, has been taken to be 1/22, the value reported by Souteyrand

TABLE IV

WATER CONCENTRATION IN THE MOBILE PHASE, $x_{water}^{(L)*}$, AT WHICH A SECOND LAYER OF WATER STARTS TO BUILD UP AT THE SURFACE, CALCULATED ACCORDING TO EQNS. 6 AND 7

$K_{13} = 1/22$. A: $K_{23}' = 0$. B: $K_{23}' = 0.045$, 0.10 and 0.20.

$x_{BuOH}^{(L)}$	*A*		*B*		
	$x_{water}^{(L)*}$	Vol. $ppm_{water}^{(L)*}$	Vol. $ppm_{water}^{(L)*}$		
			$K_{23}' = 0.045$	$K_{23}' = 0.10$	$K_{23}' = 0.20$
0.0018	0.000064	7	8	8	10
0.0053	0.000076	8	10	12	16
0.0072	0.000082	9	11	14	20
0.0090	0.000089	10	13	17	24
0.0179	0.00013	15	22	31	47
0.0441	0.00033	37	63	95	153
0.0613	0.00053	60	104	157	254
0.0865	0.00094	107	187	282	456
0.1274	0.00180	208	354	529	849
0.1670	0.00328	387	642	947	1507

et al.[19]. For the effective constant, K_{23}', different values were investigated, *viz.*, 0, 1/22, 1/10 and 1/5.

By doing these calculations, the water concentration in the mobile phase, $x_{\mathrm{water}}^{(\mathrm{L})*}$, which corresponds to an adsorption degree of 75% and at which the formation of a second layer of water is assumed to begin can be calculated. The results are given in Table IV. Those in Table IVA were obtained by the approximation which neglects completely the competitive adsorption of 1-butanol in the first layer (*i.e.*, $K_{23}' = 0$) and which is expressed by eqn. 7. Table IVB presents the results of model calculations using three different values for the equilibrium constant K_{23}' in eqn. 6, namely 1/22, 1/10 and 1/5. A value of 1/22 means an equally strong competitive effect of 1-butanol and isooctane with respect to water. A value of 1/5 means that K_{23}' has about the same magnitude as K_{12}. The value of 1/10 lies in between. These values for K_{23}' refer to the different adsorption models, *i.e.*, "additive" adsorption of water and alcohol at very small values of K_{23}' (*i.e.*, the alcohol is easily adsorbed on the water molecules), or competitive adsorption of water for high values of K_{23}' (the alcohol and water compete for the adsorption sites on the surface, assuming more or less a monolayer model). The assumption of an "additive" adsorption of water, however, is to be preferred in the light of the earlier experimental evidence[1]. Hence the results for K_{23}' values of 0 (Table IVA) or 1/22 (Table IVB) are assumed to be the most probable.

The water concentration in the mobile phase at which the second water layer starts, $x_{\mathrm{water}}^{(\mathrm{L})*}$, is an important value in the discussion of the predominant adsorption mechanism. Beyond this concentration, the effects of surface heterogeneity, which are of great importance at lower water concentrations on the solid surface, might not play a dominant role in the changes in capacity factors with variation in

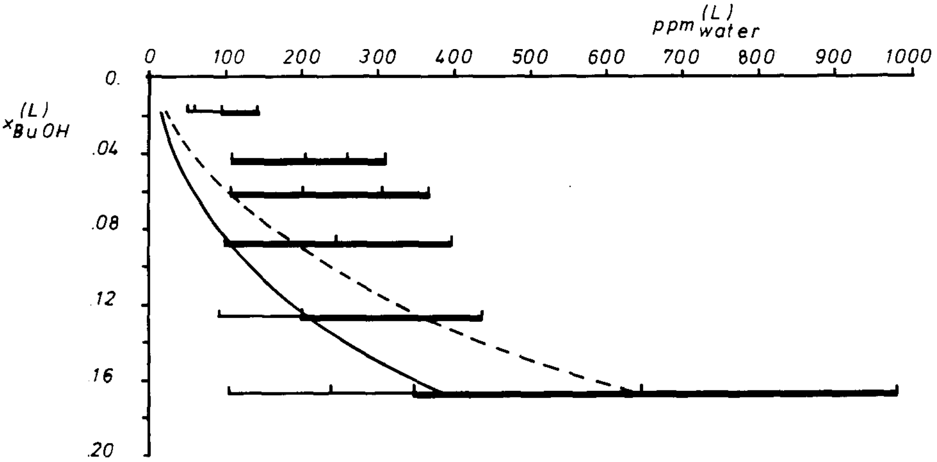

Fig. 3. Water concentration in the mobile phase, $x_{\mathrm{water}}^{(\mathrm{L})*}$, at which a second layer of water starts to build up at the surface, calculated by use of eqn. 6. (———, $K_{23} = 0$; – – –, $K_{23} = 0.045$) (*cf.*, Table IV). The upper horizontal lines represent the region of water content (in vol. ppm) investigated by experiment[1], where the distinct points of measurement are indicated. The lower lines show the region where the measured capacity factors give a series of increasing values. (Note that in those instances where the first member of an increasing series is the first experimental point, one cannot exclude that the series would start at lower water concentrations, if capacity factors had been measured there).

the water content in the mobile phase. However, as the multilayer formation is still accompanied by the completion of the first layer, the possible role of heterogeneity effects must still be investigated. The results of this investigation will be given in a subsequent publication. Secondly, beyond this concentration, a significant contribution may come from solvation effects by water molecules affecting the adsorbed solutes. Water molecules in the second layer are adsorbed on the first water layer. They can be assumed to be less fixed and oriented and to have a stronger potential for motion. Therefore, they might be able to contribute to a better solvation of polar groups of the adsorbed solutes adjacent to them and consequently to a decrease in the activity coefficients of the solute in the adsorbed phase. This interpretation is supported by the data in Fig. 3, which compares the *a priori* calculated water concentration at which a water double layer is expected to be built up, $x_{\mathrm{water}}^{(\mathrm{L})*}$, with the water concentration where the experiments[1] show the beginning of an increase in retention with increasing water concentration. It can be seen that there is an

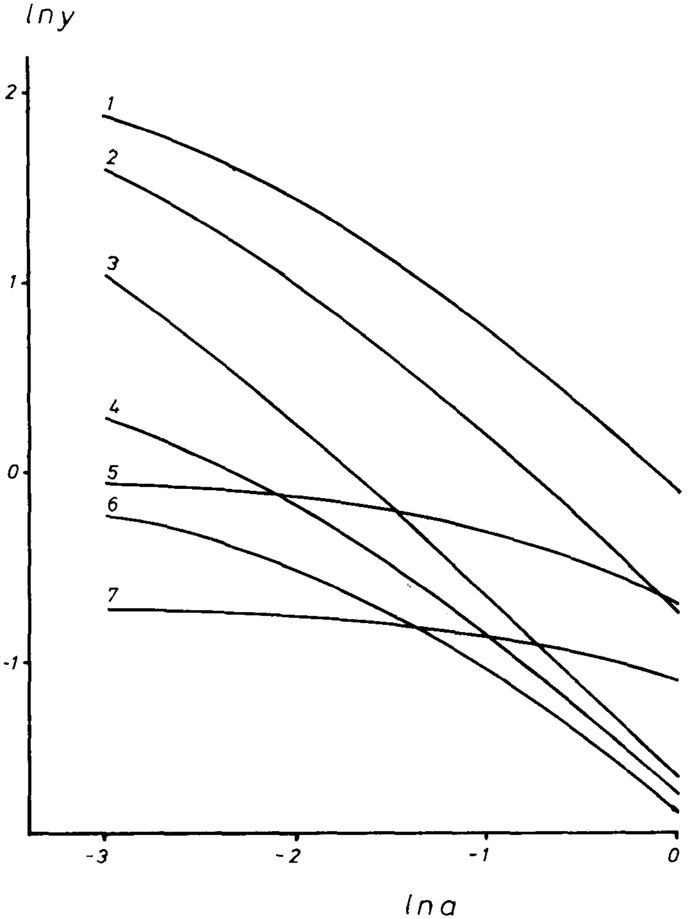

Fig. 4. Model calculation for the equation $\ln y = C_0 - \ln (A+Ba)$, presented in a $\ln y$ *vs.* $\ln a$ plot, for different values of the parameters A and B; $C_0 = 0$. (1) $A = 0.1$, $B = 1$; (2) A 0.1, $B = 2$; (3) $A = 0.1$, $B = 5$; (4) $A = 0.5$, $B = 5$; (5) $A = 1$, $B = 1$; (6) $A = 1$, $B = 5$; (7) $A = 2$, $B = 1$.

agreement between these two data sets (only the values near 1-butanol layer completion show some deviation). This supports considerations that attribute the phenomenon of enhanced retention by increased water concentration to the phenomenon of multilayer formation of water.

"Effective" constants for competitive adsorption

Having quantified the bulk phase activity coefficients of solutes, eqns. 9 and 10 enable one to discuss the phenomena of competitive adsorption of solute and solvents on the surface or on already adsorbed layers. For three of the solutes and the adsorption systems investigated by Paanakker *et al.*[1], Fig. 2 illustrates the dependence of the capacity factors, divided by the mobile phase activity coefficients, on the mobile phase composition by use of a ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ *vs.* ln $a_{BuOH}^{(L)}$ diagram.

Model calculations. In order to facilitate this discussion, two model calculations will illustrate the influence of the choice of the adsorption constant, K_{ni}', according to eqn. 10 in this type of diagram. Fig. 4 shows the behaviour of the equation ln y

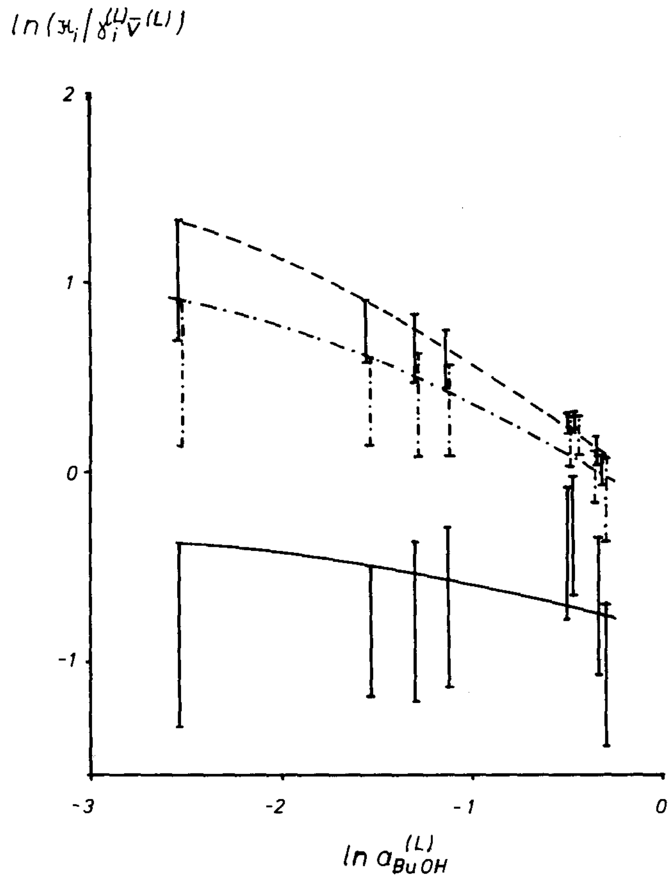

Fig. 5. Model calculation of ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ according to eqn. 10 at the mobile phase compositions shown in Table II. K_{1i} = 0.045, K_{2i} = 1.0 and K_{3i} = 5.0 (———), 1.0 (—·—·—) and 0.5 (— — —). The bars represent the variation of ln $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ with the water activities shown in Table II.

$= C_0 - \ln(A + Ba)$ in a $\ln y$ *vs.* $\ln a$ plot. This equation is analogous to eqn. 10, where $\ln y = \ln [\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$, $A = K_{1i}'\, a_1^{(L)} + K_{3i}'\, a_3^{(L)}$, $B = K_{2i}'$ and $a = a_2^{(L)}$. The plots in Fig. 4 can therefore be compared directly with those in Fig. 2. Fig. 4 shows the following: (i) the higher the ratio B/A, the more linear is the curve; (ii) the "slope" of the curve is determined by the ratio B/A; and (iii) regression analysis allows one to determine the ratio B/A, but not the absolute values of B and A, as long as C_0 is not fixed.

Fig. 5 illustrates the results of the second model calculation, where the same composition data are used as in Fig. 2. The lines in Fig. 5 show the model calculation results for phases with approximately equal water and isooctane activities, using eqn. 10 and applying different values for the ratio K_{2i}'/K_{3i}' (and a constant K_{1i} value of 0.05). (Additional data to Fig. 5 are collected in Table V). The bars illustrate the calculated variation due to the variable water content in the mobile phases (analogous to Fig. 2). It is obvious that the length of these bars differs with the value for the constant K_{3i}'. Conversely, it implies that the variation of $\ln [\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ with the water activity allows one to determine the constant K_{3i}'. One should not overlook a trivial but still important point illustrated in Fig. 5 and Table V, that according to eqn. 10 equal differences in $a_3^{(L)}$ produce much smaller variations in $\ln [\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ at high modifier activity, $a_2^{(L)}$, than at low modifier activity.

Regression data. Considering again the experimental data in Fig. 2 (and Table III), a regression analysis using eqn. 10 allows one to evaluate the ratio of the adsorption constants, K_{3i}'/K_{2i}' and K_{3i}'/K_{1i}'. This regression analysis is performed by minimizing the following least-square function:

$$F = (1/N) \sum_i \left(\frac{y_i - \hat{y}_i}{y_i}\right)^2$$

where $y_i = \ln [\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$. These values are taken from Table III and contain the *a priori* calculated mobile phase activity coefficients of the solutes, $\hat{y}_i = C_0 - \ln [K_{1i}'a_1^{(L)} + K_{2i}'a_2^{(L)} + K_{3i}'a_3^{(L)}]$ which contains the three regression parameters K_{1i}', K_{2i}' and K_{3i}'. The solvent component activities at various mixture compositions are taken from Table II. C_0 is fixed in this regression analysis to a certain arbitrarily choosen value (it cannot be determined *a priori*) in order to allow a unique solution. This implies that the absolute values of the regression parameters obtained cannot be used for interpreting adsorption constants, but only their ratios.

The results of the regression analysis are given in Table VI. The last two columns show the adsorption constant ratio, K_{3i}/K_{2i}, which is to be expected according to (i) a strict monolayer model and (ii) to a model where "additive" adsorption takes place on molecules adsorbed in a prior layer, respectively. A comparison of the regression results reveals that competitive adsorption within a monolayer model can be excluded. We suggest the following interpretation of the regression data:

(i) For polar compounds the ratio K_{3i}'/K_{2i}' obtained is significantly smaller than 1. This may be due to adsorption of the solutes on the water layer, whereas adsorption on 1-butanol molecules seems to be unlikely.

(ii) The value of K_{3i}'/K_{2i}' obtained for anthracene is still a surprisingly small value for a non-polar solute. It can be interpreted by adsorption of anthracene on

TABLE V

MODEL CALCULATION OF LN $[\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)}]$ AT DIFFERENT MOBILE PHASE COMPOSITIONS ACCORDING TO EQN. 10

The solvent activity coefficients have been taken from Table II. K_{1i} is set to 0.045, K_{2i} = 1.0 and the K_{3i} values are chosen as 5.0, 1.0 and 0.5.

$x_1^{(L)}$	$x_2^{(L)}$	$x_3^{(L)}$	$a_2^{(L)}$	$a_3^{(L)}$	$ln\ [\kappa^{(L)}/\gamma^{(L)}\bar{v}^{(L)}]$ *		
					K_{3i} = 5.0	K_{3i} = 1.0	K_{3i} = 0.5
0.9981	0.0018	0.000128	0.079	0.271	−0.40	0.92	1.33
0.9980	0.0018	0.000238	0.079	0.496	−0.96	0.47	0.98
0.9978	0.0018	0.000366	0.078	0.749	−1.35	0.13	0.69
0.9945	0.0053	0.000155	0.214	0.279	−0.50	0.61	0.91
0.9944	0.0053	0.000229	0.213	0.406	−0.83	0.40	0.76
0.9944	0.0053	0.000347	0.212	0.607	−1.19	0.14	0.57
0.9927	0.0072	0.000137	0.270	0.226	−0.37	0.60	0.84
0.9926	0.0072	0.000228	0.269	0.373	−0.78	0.37	0.68
0.9924	0.0072	0.000384	0.267	0.613	−1.22	0.07	0.47
0.9909	0.0090	0.000128	0.321	0.195	−0.30	0.57	0.76
0.9906	0.0090	0.000374	0.318	0.554	−1.14	0.08	0.44
0.9817	0.0179	0.000445	0.503	0.455	−1.04	−0.01	0.25
0.9816	0.0179	0.000545	0.501	0.551	−1.20	−0.10	0.19
0.9812	0.0179	0.000863	0.495	0.840	−1.56	−0.33	0.04
0.9808	0.0179	0.001290	0.487	1.196	−1.87	−0.55	−0.13
0.9548	0.0441	0.001059	0.699	0.426	−1.06	−0.16	0.04
0.9541	0.0441	0.001830	0.684	0.689	−1.43	−0.35	−0.08
0.9536	0.0441	0.002314	0.675	0.836	−1.59	−0.45	−0.13
0.9531	0.0441	0.002779	0.667	0.965	−1.71	−0.52	−0.18
0.9377	0.0613	0.000953	0.726	0.246	−0.70	−0.02	0.11
0.9369	0.0613	0.001789	0.712	0.434	−1.08	−0.18	0.02
0.9360	0.0613	0.002713	0.698	0.615	−1.34	−0.31	−0.05
0.9355	0.0613	0.003245	0.689	0.708	−1.45	−0.37	−0.09
0.9126	0.0865	0.000863	0.721	0.129	−0.35	0.11	0.18
0.9113	0.0865	0.002155	0.704	0.299	−0.81	−0.05	0.10
0.9100	0.0865	0.003462	0.688	0.445	−1.09	−0.17	0.04
0.8718	0.1274	0.000781	0.643	0.059	0.01	0.29	0.33
0.8709	0.1274	0.001733	0.635	0.127	−0.28	0.21	0.29
0.8688	0.1274	0.003763	0.618	0.252	−0.66	0.08	0.23
0.8321	0.1670	0.000899	0.657	0.042	0.09	0.29	0.32
0.8310	0.1670	0.002016	0.650	0.090	−0.14	0.24	0.29
0.8301	0.1670	0.002945	0.644	0.128	−0.29	0.20	0.28
0.8275	0.1670	0.005455	0.630	0.218	−0.57	0.11	0.24
0.8248	0.1670	0.008246	0.615	0.303	−0.78	0.03	0.20

* This value is obtained by model calculation using eqn. 10.

the 1-butanol molecules, which is not much influenced by the water adsorption owing to the "additive" adsorption of 1-butanol on the water layer.

(iii) Concerning the K_{1i}'/K_{3i}' ratios, only the value obtained for anthracene suggests a certain competitive effect of isooctane with respect to the adsorption of solutes. This could be understood by assuming adsorption of anthracene on the 1-butanol layer (which has already been concluded before).

Interpretation. We now consider Fig. 2 again. In Fig. 2, the circles indicate the

TABLE VI

RATIO OF THE ADSORPTION CONSTANTS K_{3i}'/K_{2i}' AND K_{3i}'/K_{1i}', OBTAINED BY REGRESSION ANALYSIS OF THE LN $(\kappa_i/\gamma_i^{(L)}\bar{v}^{(L)})$ DATA IN TABLE II BY USE OF EQN. 10

The regression data obtained are compared with the values corresponding to different adsorption models.

Solute	K_{3i}'/K_{2i}'	K_{3i}'/K_{1i}'	K_{3i}/K_{2i} *according to*	
			*CAML**	*Additive adsorption on a layer of solvent*
Anthracene	0.33–0.7	~1	>1	
Acetophenone	0.10–0.2	10–20	>1	<1 (water)
Benzyl alcohol	0.10–0.20	10–20	>1	<1 (water)

* CAML: competitive adsorption within a monolayer model.

experimental data at water concentrations near the corresponding calculated $x_{\text{water}}^{(L)*}$ values shown in Table IV. All these data points were therefore obtained at a beginning double layer of water.

First we consider the case where the surface phase is not saturated by 1-butanol, *i.e.*, $x_{\text{BuOH}}^{(L)}$ smaller than about 0.014–0.020, or ln $a_{\text{BuOH}}^{(L)}$ less than about -1.20 to -1.00 (we assume here that the mobile phase 1-butanol concentration at which one layer of 1-butanol is completed is not much influenced by the water content[1]. It can be seen from Table IVA that the $x_{\text{water}}^{(L)*}$ values for molar fractions of 1-butanol less than 0.014 are about 10. This implies that the water concentrations used in the investigations of Paanakker *et al.*[1] are greater than the corresponding $x_{\text{water}}^{(L)*}$ values. Therefore, we would expect in all these instances the first adsorbed layer to consist mainly of adsorbed water. The (more or less) straight descent of the curve in Fig. 2 in this region implies that 1-butanol is adsorbed competitively with the solutes on the layer of water. The constants K_{3i}' and K_{2i}' in Table VI therefore refer to this adsorption. It is evident from the numerical values obtained for these constants that a pure monolayer model will fail in explaining these data.

When discussing mobile phase molar fractions of 1-butanol higher than 0.014, we expect a nearly complete layer of adsorbed 1-butanol, depending on the water content, either on the silica surface or on the layers of water.

The coincidence between the $x_{\text{water}}^{(L)*}$ values and the beginning of the increase in retention with increasing water content in this region has already been discussed (Fig. 3). If one intends to explain this phenomenon by solvation effects on the surface, where the corresponding decrease in surface activity coefficients of the solutes overcompensates the competitive effect of water, one should note that such an overcompensation would be especially likely in a region where the competitive effect of water is small (*cf.*, the discussion of Fig. 5 and Table V).

Non-ideal mixing in the surface phase: orientation and solvation effects on the surface

In the previous sections we have mentioned the presumptive role of activity coefficients in the surface phase. Its possible influence and importance in our investigated system will now be discussed; again, we shall use some model calculations.

Accepting a random orientation of the molecules in the adsorbed layers, the model calculations presented in Table VII give activity coefficients in the surface layers that are obviously in disagreement with experimental results: for high water concentrations in the surface layer the model postulates high activity coefficients where the predominant contribution comes from the "hydrophobic" water–alkyl interaction. An enhanced water content in the first layer (C and D in Table VII) would be connected with a strong increase in the surface phase activity coefficients (especially for solutes with a large non-polar part) and consequently with a sharp decrease in capacity factors. This cannot be observed experimentally. Therefore, one has to conclude that the solute and the alcohol modifier are adsorbed in an oriented position perpendicular to the surface; in that case, the "hydrophobic" contribution between alkyl groups and water molecules is small. Accepting the mentioned orientation of the adsorbates, the contribution of the surface activity coefficients to the capacity factors can be expected to be relatively small compared with bulk phase activity coefficients, when considering dipolar solutes and solvents of the type used by Paanakker *et al.*[1] in adsorption on silica surfaces [this justifies ignoring the $\gamma_n^{(\sigma)}$ of the solvents in eqns. 3 and 8, and the choice of α_{in} values near unity]. However, this should not lead to the misleading interpretation that the contribution of surface activity coefficients can be concluded to be negligible generally, especially if significant variations in the composition of the adsorbed layers take place. This would ignore a possible role of water in interacting with the adsorbed functional groups of the solutes.

The quantitative calculation of solvation effects for oriented molecules near a surface is a problem for a statistical–thermodynamic approach. It needs a proper knowledge of the geometry of the adsorption sites and of interatomic distances between the molecules in the adsorbed state. These data are not available for the systems investigated. The following discussion on the possible influence of water on the solvation of adsorbates is therefore based on a qualitative argument only. Prior to this discussion we have to define which model we have accepted for the geometry of the adsorbed molecules in the first surface layers: (i) water molecules in the first layer, bonded to "strong" silanol groups[19], are fixed in a given geometric arrangement and are strongly hindered in motion; water adsorbed in a second layer is not so strongly fixed in a given geometry; (ii) 1-butanol molecules, adsorbed either on the silanol groups or on adsorbed water molecules, are oriented in such way that the polar hydroxy group is directed towards the surface and the alkyl chains behave more or less like the hairs of a brush, *i.e.*, they are oriented perpendicular to the surface. A similar geometry is to be expected for the solutes.

For this geometric arrangement the solvent–solute interaction in the adsorbed phase can be concluded to be not predominantly determined by the very high contributions of the alkyl–water interaction, which would be source of high $\gamma_i^{(\sigma)}$ values. On the contrary, it is likely that the hydration of a polar group that is adjacent to the surface may contribute to a decrease in surface phase activity coefficients. This assumption is supported by the results of Vilallonga *et al.*[28], who calculated the free energies of dehydration of the polar groups in *n*-alcohols, alkyl ketones and alkylamides. All these values obtained are greater than zero, reflecting the tendency of the polar groups to remain hydrated. Following this picture, one may conclude that the water molecules adsorbed in a second layer should be considered to contribute to better solvation of the polar group of the adsorbed solute.

As a second aspect, we consider the geometric constraints within the first sur-

TABLE VII

CALCULATED ACTIVITY COEFFICIENTS OF SOLUTES IN THE SURFACE PHASE. $\gamma_i^{(\sigma)\mathrm{RO}}$, ASSUMING A MODEL OF RANDOM ORIENTATION (RO)

Several assumptions (A–D) are made for the composition in the first two surface layers.

	Assumed solvent concentrations (%, v/v) in the first two layers		*Mean over-all composition (%, v/v) around a solute in the first layer*			$\gamma_i^{(\sigma)\mathrm{RO}}$***				
	*1st layer**	*2nd layer***	C_8H_{18}	*Butanol*	*Water*	*Benzene*	*Ethylbenzene*	*Anthracene*	*Acetophenone*	*Benzyl alcohol*
A	100% Butanol	100% isooctane	33.3	66.6	–	2.5	2.8	7.3	5.2	1.8
B	50% Butanol 50% Water	100% isooctane	33.3	33.3	33.3	13	19	109	4.3	2.6
C	50% Butanol 50% Water	100% Butanol	–	66.6	33.3	17	32	198	5.6	3.2
D	100% Water	100% Butanol	–	33.3	66.6	116	470	~10000	28	13

* Assumed to contribute with 66.6% of nearest neighbours.

** Assumed to contribute with 33.3% of nearest neighbours.

*** RO = random orientation.

face layer on a solid surface, where the distance between the functional groups of the adsorbed molecules is determined by the geometry of the solid surface. Assuming that the distance between the adsorption sites is not equal to, but larger than, the mean intermolecular distance in the bulk liquid, adsorption may be accompanied by a decrease in density in the first layer near the surface. This might have some importance considering chain-like molecules fixed in an oriented position. A decrease in density changes the chemical potential of the adsorbed species in a way that corresponds to an increase in the activity coefficient. Additional adsorption of small dipolar molecules of water that are not so strongly fixed in a given geometry when adsorbed in a second layer is expected to permit a better interaction with the polar functional groups of the adsorbed solutes, owing to an optimal geometry including an optimal distance of interaction (increased density).

Both of the aspects mentioned, (i) the better solvation of the polar groups of the adsorbed solutes by the formation of additional hydrogen bridges with additional water molecules and (ii) a better geometry of interaction by an increased density at the surface, result in a decrease in the surface phase activity coefficients, which means favoured adsorption by better solvation in the adsorbed state.

Although this picture is based on some physico-chemical considerations, the conclusions are somewhat speculative. However, adapting this concept for a moment, we expect the adsorbed solutes, *i.e.*, the functional groups of the adsorbed solutes, not to be influenced equally strongly by the solvation effects of water as postulated before; the effect is expected to be important for solutes that build strong hydrogen bridges in the liquid state (phenols and alcohols) and solutes carrying functional groups with electron-donor qualities such as CN and CO. Amines, however, must be expected to behave differently. The strong basicity of the nitrogen atom causes a favourable acid–base interaction of the amino group with the acidic silanol group, which is stronger than the interaction with a less basic oxygen atom of water. Amines and water are therefore expected to act predominantly competitively with each other, because adsorption of the amines on water molecules would be much less favoured. The experimental capacity factor data reported by Paanakker *et al.*[1] reveal that aniline is in fact the only exception from the described phenomenon of increasing retention with increasing water content.

CONCLUSION

Chromatographic capacity factor data obtained by liquid adsorption chromatography on silica surfaces and using ternary mobile phases[1] have been investigated by a theoretical treatment. Eqn. 2, based on the work of Rudziński and coworkers[10,18,20,21], was used as a starting point for these calculations.

The influence of bulk phase activity coefficients could be quantified for the solvent components and for some selected solutes by *a priori* calculations.

Experimental evidence[19] for multilayer adsorption of water on silica from nonpolar solvents and the assumption of "additive" adsorption of water with respect to the other modifier[1] has led to a picture of multilayer adsorption of water and alcohol on silica from a ternary bulk phase. Using reasonable values for the adsorption constants of the solvent components, and introducing the concept of "effective" adsorption constants for "additively" (in multilayer-type) adsorbed components, the water coverage at the surface has been calculated and the bulk phase concentration at which the formation of a second layer of water can be expected has been determined.

The relative "effective" competitive adsorption constants for solutes and solvent components have been determined by regression analysis. These results give strong support to a model of multilayer adsorption of the solvent components, moderator and water.

Finally, the influence of non-ideal mixing in the surface phase is discussed in a qualitative way. Assuming the adsorbed solutes to be oriented perpendicular to the surface, the influence of the water content in the surface layer on the surface phase activity coefficients is expected to be small compared with those in the bulk phase. However, in contrast to the situation in bulk phases, even a decrease in the surface phase activity coefficients of the discussed solutes with increasing water concentration can be assumed due to a better solvation of the adsorbed polar groups by a second water layer at the surface. Such a case has to be taken into consideration as an explanation for the phenomenon of increasing chromatographic retention of several solutes with increasing water content in a certain range of mobile phase composition. This assumption is supported by the agreement between the predicted mobile phase concentration of water at which the water double layer is expected to be formed and the beginning of the trend of increasing capacity factor with increasing water concentration, and secondly by the predicted exception of aniline.

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APPENDIX

Calculation of activity coefficients by the "solution of groups" model

The activity coefficients of solutes were calculated by the "solution of groups" model described by Derr and Deal[25] and Fredenslund *et al.*[26]. The solution of groups model offers a method for treating multi-component liquid mixtures not as mixtures of molecules but rather as mixtures of structural increments, by which the molecules can be built up and which we call "groups". Generally, the activity coefficient, γ_i, has to account for contributions due to the interactions between the components and for the non-ideal entropies of mixing. In the solution of groups model the two contributions are considered to be independent. The contribution due to non-ideal interaction effects is assumed to be built up by additive contributions of the single groups, the "group activity coefficients", Γ_k. The contribution due to the non-ideal entropy of mixing is described by equations appropriate for athermal mixtures. These basic assumptions have been discussed extensively in earlier papers[25,26]. An inherent limitation of this model is the restriction to systems with additive group contributions, which means independent group interaction.

According to Derr and Deal[25] and Fredenslund *et al.*[26], the ASOG equation and the UNIFAC equation, respectively. served as analytical expressions for calculating the activity coefficients of the structural groups, Γ_k. For the ASOG equation the group interaction parameters (which are needed for each equation applied) were optimized for the region of strong dilution as described by Rizzi and Huber[27]. For this reason, the results discussed here are derived mainly from calculations by the ASOG equation. The results from the UNIFAC equation are used to check the accuracy and comparability of the results. Within these calculations of activity coefficients there is no parameter fitting procedure.

The mean molar volumes, $\bar{v}^{(L)}$, are calculated from molecular volume increments of groups, using values from Fredenslund *et al.*[26], and neglecting excess volumes.

Accuracy of activity coefficient calculations

The activity coefficients of solvent components were calculated by means of the NRTL equation of Renon and Prausnitz[23], where the interaction parameters are determined on the entire binary systems. The non-random parameters were set to 0.47, and to 0.30 only for the pair isooctane–water. The calculation results for $\gamma_{\mathrm{BuOH}}^{(L)}$ can be directly compared with measurements of Paanakker *et al.*[1] on the same system; the agreement is acceptable. The accuracy of calculations for isooctane can be expected to be better because it is the main component. The accuracy of $\gamma_{\mathrm{H_2O}}^{(L)}$ calculations was proved by calculating the activity coefficients at the solubility limits, which can be compared with measurements in ref. 1 (Table VIII).

The activity coefficients of the infinitely dilute solutes anthracene, acetophenone and benzyl alcohol are calculated by the solution of groups model described above. As errors of *a priori* calculations are generally larger in the region of strong dilution, even with parameters adjusted for this region, it is especially important to check the accuracy of the data calculated for the solutes. However, in our case the prediction of the changes of $\gamma_i^{(L)\infty}$ with composition is important. They are, of course, influenced by the accuracy of the calculated absolute values of $\gamma_i^{(L)\infty}$, but can be expected to be much less erroneous than the absolute values themselves. The data are checked in the following ways.

(i) For non-polar or less polar compounds, absolute values of $\gamma_i^{(L)\infty}$ are not very high and there is no, or not much, association. The absolute error of calculated $\gamma_i^{(L)\infty}$ values can be expected to be not too serious. This is reflected by the fact that $\gamma_i^{(L)\infty}$ calculated by interaction parameters adjusted especially for the region of infinite dilution (ASOG) and by parameters taken from the literature, which come from

TABLE VIII

COMPARISON BETWEEN THE EXPERIMENTAL[1] AND CALCULATED MOBILE PHASE ACTIVITY COEFFICIENTS OF WATER AT THE SOLUBILITY LIMIT

The calculations were made by use of the NRTL equation.

$BuOH^{(L)}$ (%, v/v)	$x_{BuOH}^{(L)}$	γ^{exp}	γ^{calc}
0.1	0.0018	2222	2022
0.5	0.0090	1852	1449
1.0	0.0179	752	919
2.5	0.0441	196	285
5.0	0.0865	81.3	80
10.0	0.1670	29.4	19

finite concentration data and have not been specially adjusted, do not show much difference. This has been found for anthracene and acetophenone.

(ii) With benzyl alcohol, the absolute error is expected to be much higher. However, in this instance the accuracy of the calculated results can be tested in similar systems, *i.e.*, in 2-propanol–*n*-heptane mixtures, where headspace measurements have been made by Slaats *et al.*[8]. Here, the absolute values are calculated too high, whereas the relative error, the trend of changes, is not badly predicted.

SYMBOLS

${}^{x}K_i$	distribution coefficient of component *i* between the surface and the bulk phase in terms of molar fractions.
K_{nm}	equilibrium constant for a quasi-chemical bulk surface exchange reaction.
a_n	activity of component *n*.
x_n	molar fraction of component *n*.
$\bar{v}$	mean molar volume.

Greek letters

α_{nm}	surface area parameter associated with the adsorbed molecule *n* in relation to *m*.
Γ_k	group activity coefficient of the group *k* according to the "solution of groups" model.
γ_n	activity coefficient of component *n*.
κ_n	capacity factor of component *n*.
ρ_{nm}	binary surface heterogeneity parameter.

Superscripts

(L)	indicates the liquid bulk phase.
(σ)	indicates the surface phase.

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