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## STUDY ON THE RETENTION OF AMINES IN REVERSED-PHASE ION-PAIR CHROMATOGRAPHY ON BONDED PHASES

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### SUMMARY

The retention behaviour of a series of amines was investigated in phase systems consisting of an alkyl-modified silica as column packing material and an aqueous buffer or buffer-propanol mixtures containing low concentrations of alkylsulphonates as the mobile phase. The adsorption of the alkylsulphonates on the surface of the column packing material was studied by measuring adsorption isotherms. The amphiphilic ions form monomolecular films at the support-eluent interface. Charged electrical double layers are formed, with the sulphonate ions constituting the surface charge and the counter ions forming a diffuse layer in the eluent phase. The adsorption can be described by a Langmuirian equilibrium in which allowance is made for the electrical contributions to the adsorption energy. The retention of amines can be described by an ion-exchange process, *i.e.*, the protonated amines exchange with the counter ions concentrated near the charged surface. The molar ion-exchange selectivity constants were found to depend on the density of the ionized monolayer.

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### INTRODUCTION

It is common knowledge that the retention of ionized compounds in reversed-phase liquid chromatography is strongly enhanced by the addition of a suitable amphiphilic ion such as a long chain quaternary ammonium compound, an alkylsulphate or alkylsulphonate to the aqueous mobile phase. Johansson *et al.*<sup>1</sup> have investigated the influence of the addition of 1-octanesulphate to the mobile phase on the retention of protonated amines in a reversed-phase liquid-liquid partition system.

Increased retention due to the presence of amphiphilic ions in the eluent is also observed for alkyl-modified silica without any liquid bulk coating. Haney and co-workers<sup>2-4</sup> and Knox and co-workers<sup>5,6</sup> have pioneered this technique, which is commonly referred to as paired-ion chromatography<sup>4</sup>, soap chromatography<sup>6</sup>, dynamic solvent generated ion-exchange chromatography<sup>7</sup> or hetaeric chromatography<sup>8</sup>. As for this technique, Kissinger<sup>9</sup> and Kraak and co-workers<sup>7,10</sup> demonstrated the strong adsorption of amphiphilic ions on the hydrophobic column packing material, and recent results are indicative of a relation between the adsorption of the amphiphilic ion and the capacity factors of ionized solutes as predicted by simple ion exchange models<sup>10-12</sup>.

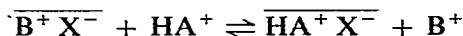
The adsorption of amphiphilic ions at the interface between water and non-aqueous phases has been the subject of a great many studies (*e.g.*, refs. 13 and 14). The interaction between the adsorbed amphiphilic ions and the aqueous phase is strongly influenced by the charge at the interface resulting from the adsorption. The main objective of the present study was further to elucidate the retention mechanism of ionized solutes on alkyl-modified silica in the presence of amphiphilic ions. To that purpose, we have investigated the formation of charged films of these ions at the surface of reversed-phase packing materials, and examined the relation between the adsorption and selectivity. Particular attention was paid to the reliability of the retention data.

## THEORETICAL

### *The ion-exchange model*

Detailed discussions of the ion-exchange model for "paired-ion" chromatography can be found elsewhere<sup>10-12,15</sup>. We confine ourselves to recalling some simplified basic equations.

Amines which are present in the eluent as cations  $HA^+$  are considered to exchange with the counter ions  $B^+$  at the ion-exchange sites formed by the alkylsulfonate  $X^-$ , which is adsorbed on the hydrophobic surface:



The bar denotes the "complex" site-solute at the surface. This equilibrium can be described by the molecular selectivity constant for ion exchange

$$K_e = \frac{[\overline{HA^+ X^-}][B^+]}{[\overline{B^+ X^-}][HA^+]} \quad (1)$$

where  $[B^+]$  and  $[HA^+]$  are the concentrations of the species  $B^+$  and  $HA^+$  in the aqueous bulk solutions, and  $[\overline{HA^+ X^-}]$  and  $[\overline{B^+ X^-}]$  denote the surface concentrations of the respective complexes (mol/g).

For a partition process based on ion exchange the partition coefficient,  $K$ , of a protonated amine may be written as:

$$K = \frac{[\overline{HA^+ X^-}]}{[HA^+]} = K_e \frac{[\overline{B^+ X^-}]}{[B^+]}$$

Now we find for the capacity factor,  $k'$ ,

$$k' = q K_e \frac{[\overline{B^+ X^-}]}{[B^+]} \quad (2)$$

where  $q$  is the phase ratio, which can be calculated from the amount of packing material in the column and the liquid hold up.

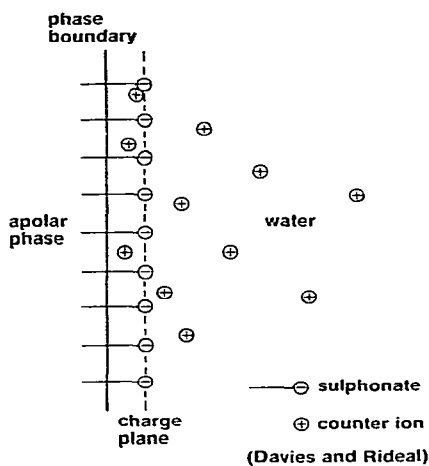


Fig. 1. Hydrocarbon chain ions at a liquid interface.

### Model of the double layer

Amphiphilic ions such as long-chain alkylsulphonates are known to be readily adsorbed at the interface between two immiscible liquids of greatly different polarity, *e.g.*, octane and water. A model of the ionized monolayer formed is shown in Fig. 1. It is analogous to that proposed by Haydon and Taylor<sup>16,17</sup> and Davies and Rideal<sup>14</sup>. The adsorbed amphiphilic ions are oriented such that the ionic headgroups are situated in the aqueous phase and the apolar alkyl chains in the hydrocarbon phase. The ionic headgroups will project some distance into the aqueous phase. The adsorbed ions are referred to as potential-determining ions, since they are responsible for a potential difference,  $\psi_0$ , between the plane of the ionic headgroups (charge plane) and the bulk solution. The concentration of electrical charge near the phase boundary brings about a non-random distribution of other ions in the aqueous solution. Ions of opposite charge (counter ions) are attracted towards the fixed charges at the charge plane. It is generally accepted that the counter ions may penetrate into the zone between the charge plane and the phase boundary<sup>16,17</sup>. On the other hand, ions of like charge (co-ions) are repelled from the surface region.

The methods for estimating the potential  $\psi_0$  as a function of the amount of detergent adsorbed have been reviewed (*e.g.*, ref. 13, 14, 18). In the present study we used a simplified method due to Van den Tempel<sup>19</sup>. In this model it is assumed that, for the counter ions, two zones may be distinguished. A proportion of the counter ions is contained, together with the ionic headgroups, in a layer situated in the immediate neighbourhood of the interface. This layer, which is commonly referred to as the Stern layer, has a depth of only several times  $10^{-8}$  cm. It is assumed to have a uniform potential  $\psi_0$  with respect to the homogeneous bulk solution. The remaining counter ions are located in the diffuse Gouy layer and neutralize the net charge of the Stern layer.

The charge,  $\sigma_1$ , of the counter ions located in the Stern layer is calculated from a simplified Langmuir–Stern equation

$$\sigma_1 = N_1 zF [1 + (1/x_s) \exp(zF\psi_0/RT)]^{-1} \quad (3)$$

where  $N_1$  is the number of available sites in  $1 \text{ cm}^2$  of the Stern layer,  $x$  is the mole fraction of the counter ions of valence  $z$  in the homogeneous bulk solution,  $F$  is Faraday's number,  $R$  the gas constant and  $T$  the temperature. The number of sites in the Stern layer,  $N_1$ , may be estimated as  $10^{15}$  if the depth of this layer is taken as  $3 \cdot 10^{-8} \text{ cm}$ . The charge  $\sigma_2$  of the diffuse Gouy layer is given by

$$\sigma_2 = \left( \frac{\epsilon \epsilon_0 R T C}{125} \right)^{\frac{1}{2}} \sinh \left( \frac{z F \psi_0}{R T} \right) \quad (4)$$

where  $\epsilon$  is the dielectric constant of the medium,  $\epsilon_0$  is the permittivity constant and  $C$  is the counter ion concentration in the bulk solution. The condition for electric neutrality of the whole double layer systems is:

$$\sigma_1 + \sigma_2 = \sigma \quad (5)$$

where  $\sigma$  is the charge associated with the adsorbed amphiphilic ions. Thus, the potential  $\psi_0$  can be calculated as a function of the adsorbed amount of the detergent,  $\sigma$ , and the counter ion concentration ( $C$  and  $x_s$ ).

This model comprises some drastic simplifications compared with more recent and more elaborate models. Moreover, it is essentially derived for flat surfaces and neglects geometrical complications such as curved interfaces. Recently, Cantwell and Puon<sup>20</sup> used a model derived from the Stern–Gouy–Chapman theory for describing the adsorption of aromatic ammonium compounds on Amberlite XAD-2. In this model it is assumed that counter ions are completely excluded from the region between the ionic headgroups of the detergent and the phase boundary. It is not realistic for ionized layers of adsorbed detergents<sup>14,16,17</sup>.

## EXPERIMENTAL

### Apparatus

Separations were carried out on a Spectra-Physics Type 3500 liquid chromatograph equipped with a Model 770 variable-wavelength UV photometer; catecholamines were detected at 220 nm. All columns ( $15 \text{ cm} \times 4.6 \text{ mm I.D.} \times 6.35 \text{ mm O.D.}$ ) were of precision-bore stainless-steel tubing, thermostatted to within  $0.1^\circ\text{C}$  by water-jackets connected to a water-bath. The eluent was thermostatted before the injection valve by means of a heat-exchanger consisting of 1 m of stainless-steel tubing ( $0.051 \text{ cm I.D.}$ ). High-pressure sampling valves (Rheodyne Type 70-10) equipped with  $20\text{-}\mu\text{l}$  sample loops were used for sample injection. A Waters Type R401 refractive index detector was used for monitoring breakthrough curves.

### Chemicals

Quartz-distilled water and analytical-grade solvents were used for all experiments. Catecholamines were obtained from Aldrich and Serva: NADR = noradrenaline; ADR = adrenaline; DOP = dopamine; OCT = octopamine and TYR = tyramine. The sodium salts of 1-octanesulphonic acid and 1-dodecanesulphonic acid (zur Tensid-analyse) were purchased from E. Merck (Darmstadt, G.F.R.). The purity of the surfactants was verified by surface tension measurements: the curve of surface

tension against surfactant concentration showed no minimum<sup>21,22</sup>. Buffers were prepared from Titrisol solutions of sodium hydroxide and orthophosphoric acid (E. Merck). The sodium concentration in the aqueous phosphate buffers was 0.01 or 0.05 *M*. Mixed organic aqueous eluents were prepared from known volumes of 1-propanol and aqueous phosphate buffers.

The reversed-phase packing material was prepared from *n*-octadecyldimethylmonochlorosilane and 10- $\mu$ m SI-100 silica (E. Merck)<sup>23</sup>; the carbon content was 17.6%. The specific surface area was determined by the BET method as 180 m<sup>2</sup> g<sup>-1</sup>. This packing material is coded as C<sub>18</sub>.

### Procedures

The columns were packed by a balanced-density slurry technique with 1,1,2,2-tetrabromoethane-tetrachloromethane-dioxane (36:32:32) as the suspension medium and at pressures of about 50 MPa. The columns were washed successively with 100 cm<sup>3</sup> each of 2,2,4-trimethylpentane, dichloromethane, 1-propanol and water before the mobile phase was applied.

The capacity factor,  $k'_i$ , for a component *i* was determined from its retention volume,  $V_{Ri}$ , and the hold-up of the column,  $V_{RO}$ . The hold-up of the column and the amount of adsorbed 1-propanol,  $V_s$ , were determined as follows. The column, which had previously been filled with the eluent, was rinsed with about 45 cm<sup>3</sup> dimethylformamide. The eluate was collected in a 50-cm<sup>3</sup> calibrated flask and diluted to 50 cm<sup>3</sup>. The water content of the collected eluate was determined by Karl Fischer titration, and the amount of 1-propanol by gas chromatography. The composition of the eluent was determined in the same way. From these data  $V_{RO}$  as well as  $V_s$  can be calculated. The repeatability of this procedure was found to be better than 1% (rel.) for both  $V_{RO}$  and  $V_s$ .

Adsorption isotherms were calculated from breakthrough curves<sup>24</sup>. At the beginning of the experiment the column was equilibrated with the eluent but without the sulphonate. Then the eluent containing a known concentration of the detergent was fed to the column and the breakthrough volume was measured with the refractive index detector. By using a series of eluents with increasing sulphonate concentrations the adsorption isotherm could be constructed. Generally, the increase of the surface excess concentration of the sulphonate,  $\Delta\Gamma_2^y(n)$ , resulting from a stepwise change from concentration  $C_2(n-1)$  to  $C_2(n)$  with  $C_2(n) > C_2(n-1)$  can be calculated from<sup>25</sup>

$$\Delta\Gamma_2^y = \frac{[V_B(n) - V_1][C_2(n) - C_2(n-1)]}{mS} \quad (6)$$

where  $V_B(n)$  represents the corresponding breakthrough volume.  $V_1$  is the difference between the volume of the empty column and the volume of the packing material,  $m$  the mass of the adsorbent and  $S$  its specific surface area. Its value was determined by filling the column with the aqueous buffer, rinsing it with dimethylformamide and determining the water content of the collected eluate. The surface excess  $\Gamma_2^y(n)$  corresponding to the bulk concentration of the sulphonate,  $C_2(n)$ , is obtained by adding up the successive  $\Delta\Gamma_2^y(n)$  values. In the present study we identify the surface excess  $\Gamma_2^y$  with the amount of detergent ion,  $n_s$ , adsorbed on unit surface area<sup>19</sup>. If no excess

of inert electrolyte is present,  $\Gamma_2^v$  will not correspond exactly with  $n_s$ , because of the deficiency of soap anions in the diffuse part of the double layer. This deficiency amounts to only a few percent of  $n_s$ , however<sup>18-20</sup>.

## RESULTS AND DISCUSSION

### Adsorption of 1-propanol

Adsorption of non-electrolytes from binary mixtures at a homogeneous surface can often be described by the Langmuir equation

$$A_0/(A - A_0) = xe^{-\Delta G/RT} \quad (7)$$

where  $A$  is the area ( $\text{\AA}^2$ ) occupied by the adsorbed molecule at the interface,  $A_0$  the limiting value of  $A$  at monolayer coverage,  $x$  the mole fraction of the solute in the bulk solution and  $\Delta G$  the free energy of adsorption. This equation can easily be transformed into the more familiar form:

$$\frac{1}{n_s} = \frac{1}{Kx} + \frac{1}{n_{s,0}} \quad (8)$$

Here  $n_s$  is the number of molecules of solute adsorbed at the interface per unit of surface area ( $\text{cm}^{-2}$ ),  $n_{s,0}$  is the limiting value of  $n$  at monolayer coverage and  $K$  is a constant.

We measured the adsorption of 1-propanol from an aqueous phosphate buffer (pH 3.00, 0.01 M  $\text{Na}^+$ ) on the reversed-phase packing material. A plot of the data according to eqn. 8 yielded  $1/n_{s,0} = 22 \text{ \AA}^2$  for the limiting area per molecule,  $A_0$ , which corresponds very well with the value of  $20 \text{ \AA}^2$  found by surface tension measurements for alcohols at the water-decane interface<sup>16</sup>. In the latter case, the low limiting area is adduced as proof that the molecules are oriented perpendicularly to the inter-

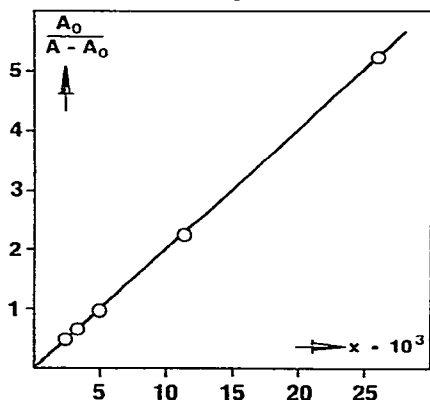


Fig. 2. Adsorption isotherm (eqn. 7) for the adsorption of 1-propanol from an aqueous phosphate buffer (0.01 M  $\text{Na}^+$ , pH = 3.00) at 40°C on  $\text{C}_{18}$  silica.

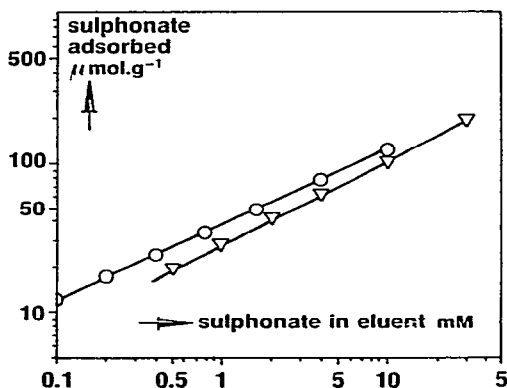


Fig. 3. Adsorption isotherms (Freundlich plots) of sodium 1-octanesulphonate on  $\text{C}_{18}$  silica at 40°C. Eluents: ○, phosphate buffer (0.05 M  $\text{Na}^+$ , pH 3.00); ∇, phosphate buffer (0.01 M  $\text{Na}^+$ , pH 3.00) + 2% (v/v) 1-propanol.

face. Fig. 2 shows the plot of the adsorption data according to eqn. 7 for  $A_0 = 22 \text{ \AA}^2$ . From the slope we find  $-\Delta G = 12.9 \text{ kJ mol}^{-1}$ , which is in good agreement with the value of  $13.4 \text{ kJ mol}^{-1}$  reported for the adsorption of 1-propanol at the water-decane interface<sup>16</sup>.

#### Adsorption of alkylsulphonates

Fig. 3 shows the adsorption isotherms for sodium 1-octanesulphonate from an aqueous phosphate buffer and a phosphate buffer containing a low concentration of 1-propanol, respectively. In accordance with earlier findings<sup>11,12</sup>, these isotherms are well fitted by a Freundlich equation

$$n_s = aC^b \quad (9)$$

where  $C$  is the detergent concentration in the bulk solution. The error made by assuming  $n_s = \Gamma_2^v$  for the adsorption of the sulphonates may be estimated as follows. From the experimental data on the exclusion of inorganic anions from reversed-phase columns "loaded" with anionic detergents<sup>26</sup> it may be concluded that the external void volume of the columns is almost completely accessible to anions. If the detergent is completely excluded from the internal void volume, *i.e.*, the pore system of the column packing material,  $V_1$  in eqn. 6 should be replaced by  $V_e$ , the external void volume of the column. For the columns used we found  $V_1 = 1.6\text{--}1.7 \text{ cm}^3$ , depending on the mobile phase composition, and  $V_e = 1.1\text{--}1.2 \text{ cm}^3$ . Since the breakthrough volumes,  $V_B$ , usually exceeded  $10 \text{ cm}^3$ , the error in  $n_s$  will be 5% at most.

The use of the Freundlich equation for describing the adsorption of ionic detergents on reversed-phase packing materials is merely empirical and has no theoretical background<sup>11,12</sup>. The adsorption of amphiphilic ions at the interface between water and an apolar hydrocarbon can also be described by a Langmuirian form of the adsorption isotherm, *e.g.*, eqn. 7 (refs. 14, 16, 27). The free energy of adsorption,  $\Delta G$ , represents the work done by one mole of the surfactant ion on adsorption. This work may be divided into two parts: the work of transfer of the molecules from the aqueous bulk phase to the surface,  $\Delta G_0$ ; and the work done against the electrical potential at the surface,  $\Delta G_{el}$ . Therefore we may write:

$$\Delta G = \Delta G_0 + \Delta G_{el} \quad (10)$$

For the present study  $\Delta G_0$  is assumed to be constant. This simplification is justified by experimental data<sup>27</sup>. Further, the electrical work,  $\Delta G_{el}$ , done by a univalent ion is given by

$$\Delta G_{el} = N \int_0^{\psi_0} zed\psi = zF\psi_0 \quad (11)$$

where  $e$  is the elementary charge and  $N$  is Avogadro's number.

The validity of the modified Langmuir isotherm for describing the adsorption of ionic detergents on reversed-phase packing materials was checked in two ways. First, we consider the case that  $A \gg A_0$ . Now eqn. 7 can be written as follows:

$$A_0/A = xe^{-\Delta G/RT} \quad (12)$$

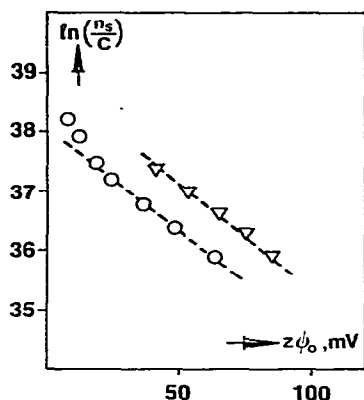


Fig. 4. Test of eqn. 13 for the adsorption of sodium 1-octanesulphonate on  $C_{18}$  silica at  $40^\circ\text{C}$ . Eluents as in Fig. 3.

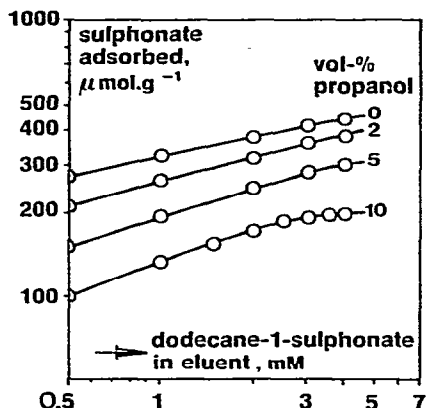


Fig. 5. Adsorption isotherms (Freundlich plots) of sodium 1-dodecanesulphonate on  $C_{18}$  silica from phosphate buffer ( $0.01\text{ M Na}^+$ , pH 3.00) containing various amounts of added 1-propanol. Temperature:  $40^\circ\text{C}$ .

For low concentrations of the detergent ion in water the mole fraction  $x$  can be replaced by  $C/55.5$ . With  $A = 10^{16}/n_s$ , we find by combining eqns. 10–12

$$\ln \frac{n_s}{C} = \alpha - \frac{ZF\psi_0}{RT} \quad (13)$$

where  $\alpha = \ln(1.8 \times 10^{14} RT/A_0 \Delta G_0)$ . In Fig. 4  $\ln(n_s/C)$  is plotted as a function of  $\psi_0$  for the adsorption data from Fig. 3. The lines have the theoretical slope  $-F/RT$ , and  $\psi_0$  is calculated by eqns. 3–5. At low values of  $\psi_0$ , deviations from the straight line are observed, which may result from the very low surface coverage,  $n \approx 5 \cdot 10^{12} \text{ cm}^{-2}$ .

As a second test for the validity of eqns. 7, 9 and 11 we used the adsorption data for a strongly adsorbed detergent. Fig. 5 shows the adsorption isotherms for sodium 1-dodecanesulphonate from an aqueous phosphate buffer and mixtures of phosphate buffer and increasing amounts of 1-propanol. For the neat aqueous buffer and for mixtures containing low propanol concentrations the isotherms approximately obey the Freundlich equation. As the surface coverage is rather high, the approximation of the adsorption by eqn. 12 cannot be applied. The general equation for adsorption of amphiphilic ions is

$$\frac{A_0}{A - A_0} \exp\left(\frac{zF\psi_0}{RT}\right) = x \exp\left(-\frac{\Delta G_0}{RT}\right) \quad (14)$$

A plot of the left-hand side of this expression vs.  $x$  should yield a straight line from the slope of which  $\Delta G_0$  can be calculated. This expression, however, can be verified only when a value for  $A_0$  is available. It has been deduced from surface-tension measurements that a constant area per molecule adsorbed at the air–water or hydrocarbon–water interface is obtained when the bulk surfactant concentration is at the critical micelle concentration,  $\text{CMC}^{28,29}$ . For linear alkylsulphonates, values of  $50\text{--}55 \text{ \AA}^2$



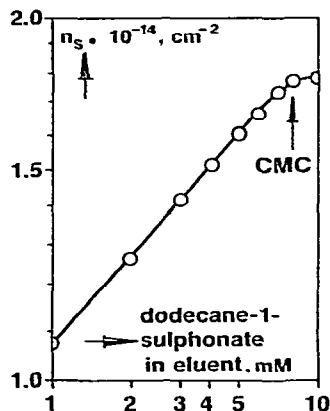


Fig. 6. Saturation adsorption of sodium 1-dodecanesulphonate from phosphate buffer (0.01 M Na<sup>+</sup>, pH 3.00) on C<sub>18</sub> silica at 40°C.

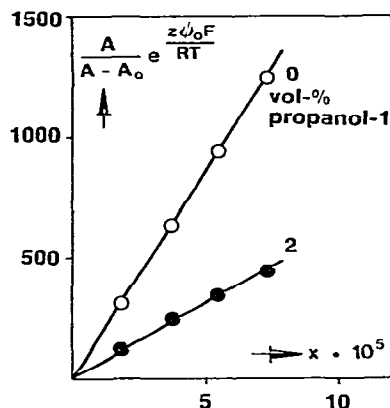


Fig. 7. Test of eqn. 14 for the adsorption of sodium 1-dodecanesulphonate on C<sub>18</sub> silica from phosphate buffer (0.01 M Na<sup>+</sup>, pH 3.00) at 40°C.

have been reported for  $A_0$ . Fig. 6 shows the adsorption isotherm for sodium 1-dodecanesulphonate from an aqueous phosphate buffer. At low concentrations the adsorption isotherm obeys a Freundlich equation. When the surfactant concentration approaches the CMC, the adsorption isotherm flattens and tends to a limiting value for  $n$ , which corresponds to a limiting area,  $A_0$ , of approximately 55 Å<sup>2</sup> per ion adsorbed. Flattening of adsorption isotherms near the CMC has also been observed for the adsorption of alkylsulphonates on Graphon<sup>30</sup>.

Now, we may estimate  $\Delta G_0$  by means of eqn. 14 from the adsorption data in Fig. 5 and the calculated  $\psi_0$  values for the eluents containing 0 and 2% 1-propanol assuming  $A_0 = 55$  Å<sup>2</sup>. Fig. 7 shows plots according to eqn. 14 for these eluents.

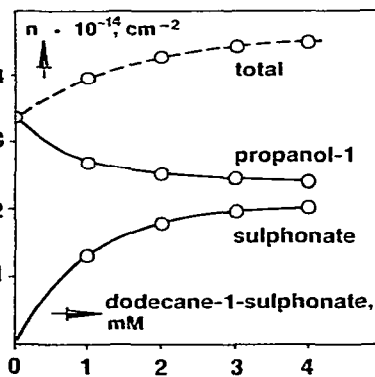
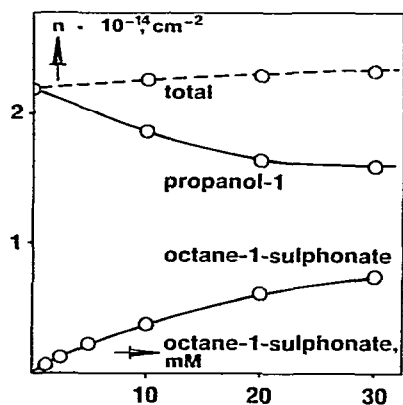


Fig. 8. Simultaneous adsorption of 1-propanol and sodium 1-octanesulphonate on C<sub>18</sub> silica from phosphate buffer (0.01 M Na<sup>+</sup>, pH 3.00) + 2% (v/v) 1-propanol. Temperature: 40°C.

Fig. 9. Simultaneous adsorption of 1-propanol and sodium 1-dodecanesulphonate on C<sub>18</sub> silica from phosphate buffer (0.01 M Na<sup>+</sup>, pH 3.00) + 10% (v/v) 1-propanol. Temperature: 40°C.

Straight lines are obtained for both eluents and from the slopes we calculated  $\Delta G_o$ . For the adsorption of sodium 1-dodecanesulphonate from an aqueous phosphate buffer we find  $-\Delta G_o = 43 \text{ kJ mol}^{-1}$ . A value of  $46 \text{ kJ mol}^{-1}$  has been reported for the adsorption of the corresponding alkylsulphate at the water-petroleum ether interface<sup>16</sup>. The value of  $-\Delta G_o$  decreases upon addition of propanol. For the eluent with 2% propanol we find  $-\Delta G_o = 41 \text{ kJ mol}^{-1}$ . Apparently, the detergent displaces propanol from the surface. The influence of the adsorption of alkylsulphonates on the amount of propanol adsorbed is illustrated in Figs. 8 and 9. The coverage of the surface increases upon adsorption of the detergent, the amount of propanol displaced being only a fraction of the detergent adsorbed.

Since we had no value for  $A_o$  in the eluents containing high propanol concentrations we could not check the validity of eqn. 14 for these cases. At first sight it is surprising that the adsorption of the sulphonates can be described by the modified Langmuir isotherm (see eqn. 8) as well as by a Freundlich isotherm (see eqn. 9). However, in a number of cases<sup>14</sup>, the values for  $\psi_o$  obtained by solving eqns. 3-5 are well fitted by the following empirical relation

$$\psi_o = \beta + \gamma \ln n_s \quad (15)$$

where  $\beta$  and  $\gamma$  are constants. Combining eqns. 13 and 15 we find, after some rearrangements

$$n_s = a C^b$$

which is equivalent to the empirical Freundlich equation.

#### Retention behaviour of amines

Fig. 10 shows the  $k'$  values for some catecholamines on  $C_{18}$  reversed-phase packing material as a function of the 1-octanesulphonate concentration in an

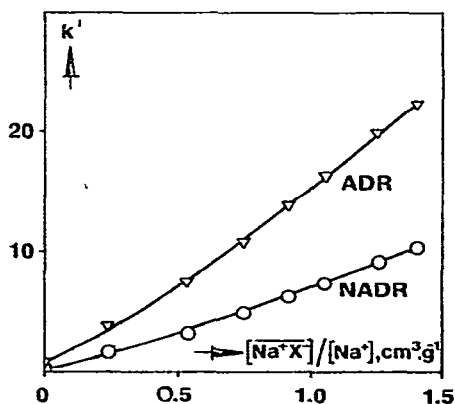
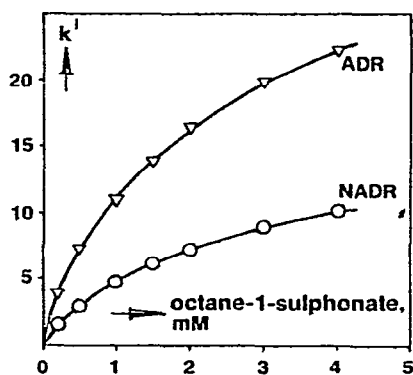


Fig. 10. Capacity factors of catecholamines as a function of sodium 1-octanesulphonate concentration. Column packing:  $C_{18}$  silica. Eluent: phosphate buffer,  $0.05 \text{ M Na}^+$ , pH 3.00. Temperature:  $40^\circ\text{C}$ .

Fig. 11. Capacity factors from Fig. 10 plotted according to eqn. 2.

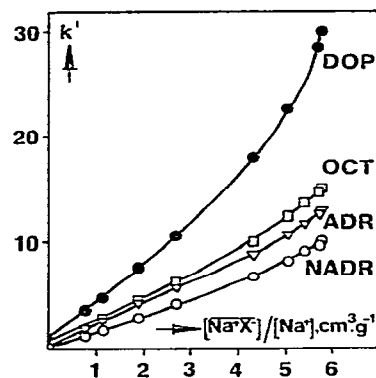
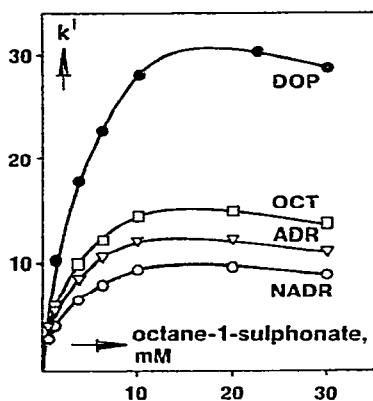


Fig. 12. Capacity factors of catecholamines as a function of sodium 1-octanesulphonate concentration. Column packing:  $C_{18}$  silica. Eluent: phosphate buffer,  $0.01 M Na^+$ , pH 3.00, 2% (v/v) 1-propanol. Temperature:  $40^\circ C$ .

Fig. 13. Capacity factors from Fig. 12 plotted according to eqn. 2.

aqueous phosphate buffer. Fig. 11 shows the dependence of the capacity factors on  $[Na^+ X^-]/[Na^+]$ . Although at first sight a fairly good linear dependence is observed according to eqn. 2, the plots show a slight but significant curvature. Close examination of earlier data also indicates a non-linear dependence<sup>11,31</sup>. It turns out that  $K_e$ , as calculated from eqn. 2, increases with increasing coverage of the surface by the amphiphilic ion,  $[Na^+ X^-]$ . Plots of  $k'$  against sulphonate concentration for eluents containing propanol are given in Fig. 12. These plots show the characteristic maxima for  $k'$ <sup>8,11,12</sup>. It seems most unlikely that these maxima arise from micelle formation, since the CMCs in the eluents are about  $0.1 M$  and  $0.012 M$  for 1-octanesulphonate and 1-dodecanesulphonate, respectively. A striking feature is the reversal of the elution order of ADR and NADR shown in Fig. 14, which is incompatible with the

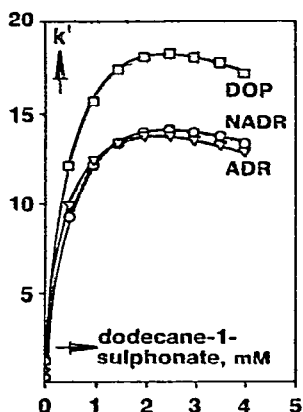


Fig. 14. Capacity factors of catecholamines as a function of sodium 1-dodecanesulphonate concentration. Column packing:  $C_{18}$  silica. Eluent: phosphate buffer,  $0.01 M Na^+$ , pH 3.0, 10% (v/v) 1-propanol. Temperature:  $40^\circ C$ .

simple linear relationship expressed by eqn. 2. Deviations from the linear behaviour are also observed for octylsulphonate as the amphiphilic ion, see Fig. 13. These results confirm earlier findings for eluents containing propanol<sup>11</sup>.

In the simple model of the double layer used in this study we assumed that the counter ions neutralize the ionized groups of the adsorbed detergent in two ways. A fraction of the counter ions is found in the Stern layer, the remainder being located in the diffuse Gouy layer. The latter ions are retained by non-specific, electrostatic forces and there is no selectivity. Therefore, we may write for the species  $\text{HA}^+$  and  $\text{B}^+$  (ref. 32)

$$\frac{n_{\text{HA}^+}}{n_{\text{B}^+}} = \frac{[\text{HA}^+]}{[\text{B}^+]} \quad (16)$$

where  $n_i$  is the number of counter ions of species  $i$  in the diffuse layer. Selectivity will result from specific interactions in the Stern layer between the ionic species and the primary surface charge. The surface densities of the ions concerned in both the Stern and Gouy layers are denoted by  $[\overline{\text{HAX}}]$  and  $[\overline{\text{BX}}]$ , respectively, and the fractions retained in the Stern layer by the combination of electrostatic and specific interactions by  $\alpha_{\text{HAX}}$  and  $\alpha_{\text{BX}}$ . Now we may write:

$$\frac{n_{\text{HA}^+}}{n_{\text{B}^+}} = \frac{1 - \alpha_{\text{HAX}}}{1 - \alpha_{\text{BX}}} \cdot \frac{[\overline{\text{HA}^+ \text{X}^-}]}{[\overline{\text{B}^+ \text{X}^-}]} \quad (17)$$

Combination of eqns. 16 and 17 gives:

$$K_c = \frac{[\overline{\text{HAX}}][\text{B}^+]}{[\overline{\text{BX}}][\text{HA}^+]} = \frac{1 - \alpha_{\text{BX}}}{1 - \alpha_{\text{HAX}}} \quad (18)$$

This equation relates the selectivity constant for ion exchange and the specific interactions between, on the one hand, the ions  $\text{B}^+$  and  $\text{HA}^+$  and, on the other, the charged surface.

Actually, the Stern–Langmuir equation (eqn. 3) as used by Van den Tempel for calculating the number of counter ions in the Stern layer accounts for electrostatic interactions only, neglecting any “specific” or “chemical” interaction. These interactions may be expressed through an additional energy term in the exponent of the Stern–Langmuir equation<sup>18</sup>

$$\sigma_1 = N_1 zF \{1 + (1/x_s) \exp [(zF\psi_o + \phi)/RT]\}^{-1}$$

where  $\phi$  is the specific adsorption energy of the ions.

The results of the present study indicate that the simplified eqn. 3 holds for the adsorption of alkylsulphonates in the presence of sodium as the counter ion. This suggests that for sodium the specific interactions are relatively minor compared with the purely electrostatic interactions, *i.e.*,  $\phi \ll zF\psi_o$ . On the other hand, the results of the study on the retention of amines indicate a strong specific interaction between the sample ions  $\text{HA}^+$  and the charged interface. As for the counter ions, the value of  $\alpha_{\text{BX}}$

can be calculated from eqns. 3–5 since  $\alpha_{\text{BX}} = \sigma_1/(\sigma_1 + \sigma_2)$ . For the diluted buffers and the detergent concentrations used in this study a typical value for  $\alpha_{\text{BX}}$  is about 0.5. As indicated earlier, the value for  $K_e$  is 10. Then, we find from eqn. 18 that  $\alpha_{\text{HAX}} = 0.95$ . This result indicates a strong specific interaction in the Stern layer.

At present, however, no theoretical or experimental method allows for the estimation of the specific adsorption energy,  $\phi$ , for the sample ions. Levine *et al.*<sup>33</sup> have predicted that for simple ions the specific adsorption energy will increase with the charge density of the monolayer. This theoretical result seems to be confirmed by experimental data<sup>34</sup>. The increase of the specific adsorption energy with increasing surface concentration of the amphiphilic ion may account for the dependence of  $K_e$  on the surface concentration of the sulphonate shown in Fig. 11. However, more quantitative information about the specific adsorption energy,  $\phi$ , is required for a better understanding of the retention of ionic compounds on surfaces covered by ionic detergents.

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