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## EXTENSION OF THE ELECTROSTATIC THEORY OF REVERSED-PHASE ION-PAIR CHROMATOGRAPHY FOR HIGH SURFACE CONCENTRATIONS OF THE ADSORBING AMPHIPHILIC ION

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### SUMMARY

To understand the mechanism of ion-pair chromatography, a correct description of the adsorption isotherm of the amphiphilic modifier is important. The adsorption isotherms of butyl-, hexyl- and octylsulphonate were investigated according to the concepts of the electrostatic theory of ion-pair chromatography. This theory was also extended to include the simultaneous effect of surface potential and competition between the amphiphile and the analyte for the available surface area. It was found that there is good agreement between the theory and experimental results.

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### INTRODUCTION

Liquid chromatographic analysis of organic molecular ions is usually performed with a reversed stationary phase (RP) and a polar mobile phase containing an amphiphilic ion as modifier. The capacity factor of the ionic analytes is regulated by varying the concentration of the amphiphile in the mobile phase. A number of different names have been proposed for this chromatographic technique<sup>1</sup>, and this reflects the uncertainty that exists about the physical mechanism that regulates the capacity factor of the analytes. The name ion-pair chromatography seems to be most widely used and will therefore be used in this paper.

In recent years a number of papers have been published by Bartha, Vigh and co-workers that contain experimental data<sup>2–4</sup> which can be used to test the existing theories of ion-pair chromatography. An important aspect of these studies was to test if the most frequently proposed isotherms, *i.e.*, the Langmuir and Freundlich isotherms, agree with the isotherm experimentally obtained. It is generally found that

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the experimental isotherm does not fit either of these two theoretical isotherms when the mobile phase concentration of the amphiphilic ion is varied over wide, but chromatographically meaningful, concentrations. As the isotherm of the amphiphile is fundamental to all theories of ion-pair chromatography, a correct description is needed in order to understand its mechanism.

It is not surprising, from a theoretical point of view, that isotherms that do not consider an electrostatic surface potential disagree with what is found experimentally. A surface potential exists whenever there is an excess of charged species of one type of sign over species of the opposite sign on the surface. In ion-pair chromatography, the affinity of the amphiphile for the surface is higher than that of the electrolytic counter ions. This creates a surface potential, *i.e.*, there is a higher concentration of amphiphilic ions than of electrolytic counter ions in the hydrophobic surface layer. It can therefore be concluded that the theoretical expression for the isotherm must include the effect of the surface potential. This conclusion also holds for the mechanism of ion-pair chromatography, *i.e.*, a physically realistic theory must consider the effect of the surface potential. A theory has been developed which assumes that the surface potential is responsible for the changes in capacity factor when an amphiphile is added to the mobile phase<sup>5</sup>. It has been found that this theory of ion-pair chromatography agrees well with experimental results<sup>5-8</sup>.

In a recent paper a quantitative evaluation of the adsorption isotherm of tetrabutylammonium ion on an RP-18 surface was reported<sup>8</sup>. It was found that the isotherm, when expressed in terms of the electrostatic theory, is independent of ionic strength and type of counter ion. It was also found that the experimental isotherm agrees with a Langmuir type of isotherm modified with a term for the surface potential. A similar approach was used in this work and it was found that a number of different alkylsulphonates also follow this isotherm.

The electrostatic theory of ion-pair chromatography assumes that the relative changes in capacity factors are due to changes in the surface potential of the stationary phase. When the surface concentration of amphiphilic modifier is high, the amphiphilic modifier competes with the analyte ions for the limited surface area available. In this paper the electrostatic theory is extended to include this effect on the relationship between the capacity factor and the concentration of amphiphile in the mobile phase. A comparison of the theory with experimental results indicates that this extension of the theory is correct and necessary at high surface coverage of amphiphile.

## THEORY

In the electrostatic theory of ion-pair chromatography, it is assumed that the relative change in the capacity factor of an ionic analyte is determined only by changes in the electrostatic surface potential of the stationary phase. This assumption gives the following relationship<sup>6</sup> between the capacity factor for an analyte B,  $k'_{cB}$ , its charge,  $z_B$ , and the electrostatic surface potential,  $\psi_0$ :

$$k'_{cB} = k'_{0B} \exp(-z_B F \psi_0 / RT) \quad (1)$$

where  $k'_{0B}$  is the capacity factor for B at a reference composition of the mobile phase for which the surface potential is set to zero, *e.g.*, when no amphiphilic modifier is added to the mobile phase.

The theory is extended here to include the effect of competition between the amphiphilic modifier and the analyte for the limited surface area available in the column. This is done by equating the electrochemical potential of the different species  $i$ ,  $\mu_i$ , in the mobile phase, m, and stationary phase, s. The electrochemical potentials for an amphiphilic modifier, A, of charge  $z_A$  and an analyte, B, of charge  $z_B$  are expressed by the following equations:

$$\mu_{Am} = \mu_{Am}^0 + RT \ln c_A \quad (2)$$

$$\mu_{As} = \mu_{As}^0 + RT \ln X_{As} + z_A F \psi_0 \quad (3)$$

$$\mu_{Bm} = \mu_{Bm}^0 + RT \ln c_B \quad (4)$$

$$\mu_{Bs} = \mu_{Bs}^0 + RT \ln X_{Bs} + z_B F \psi_0 \quad (5)$$

The electrochemical potential of a surface site is expressed by the following equation:

$$\mu_s = \mu_s^0 + RT \ln X_s \quad (6)$$

In eqns. 3 and 5,  $X_{is}$  ( $i = A$  or  $B$ ) is the fraction of the total surface area occupied by A or B molecular ions and  $X_s$  in eqn. 6 is the fraction that is unoccupied. Assuming that the analyte ion and the amphiphilic ion require the same surface area, the following relationship holds:

$$X_{As} + X_{Bs} + X_s = 1 \quad (7)$$

The conditions of equilibrium are

$$\mu_{As} = \mu_{Am} + \mu_s \quad (8)$$

and

$$\mu_{Bs} = \mu_{Bm} + \mu_s \quad (9)$$

Combination of eqns. 2, 3 and 8 gives

$$\frac{X_{As}}{c_A X_s} = K_{As} \exp(-z_A F \psi_0 / RT) \quad (10)$$

where  $K_{As} = \exp[-(\mu_{As}^0 - \mu_s^0 - \mu_{Am}^0)]$ . From eqns. 4, 5 and 9 we obtain

$$\frac{X_{Bs}}{c_B X_s} = K_{Bs} \exp(-z_B F \psi_0 / RT) \quad (11)$$

where  $K_{Bs} = \exp[-(\mu_{Bs}^0 - \mu_s^0 - \mu_{Bm}^0)]$

Solving eqn. 10 for  $X_s$  and inserting in eqn. 11 gives

$$\frac{X_{Bs}c_A}{c_B X_{As}} = \frac{K_{Bs} \exp(-z_B F\psi_0/RT)}{K_{As} \exp(-z_A F\psi_0/RT)} \quad (12)$$

where  $X_{is} = n_i/n_{oi}$ ,  $n_{oi}$  is the monolayer capacity of the surface and  $n_i$  is the surface concentration of species  $i$  on the surface. Eqn. 12 can therefore be reformulated as

$$\frac{n_B}{c_B} = \frac{n_A}{c_A} \cdot \frac{K_{Bs} \exp(-z_B F\psi_0/RT)}{K_{As} \exp(-z_A F\psi_0/RT)} \cdot \frac{n_{oB}}{n_{oA}} \quad (13)$$

Assuming that the surface concentration of analyte ions is negligible in relation to the surface concentration of amphiphilic modifier, *i.e.*,  $X_{Bs} \rightarrow 0$  in eqn. 7, the adsorption isotherm of the amphiphile is then found to be eqn. 14 (see ref. 8). This means that the adsorption isotherm for A is independent of the presence of B.

$$n_A = \frac{n_{oA} K_{As} c_A \exp(-z_A F\psi_0/RT)}{1 + K_{As} c_A \exp(-z_A F\psi_0/RT)} \quad (14)$$

Inserting eqn. 14 in eqn. 13 and introducing the capacity factor gives

$$k'_{cB} = \varphi \cdot \frac{n_{oB} K_{Bs} \exp(-z_B F\psi_0/RT)}{1 + K_{As} c_A \exp(-z_A F\psi_0/RT)} \quad (15)$$

where  $\varphi$  is the phase ratio.

In the absence of an amphiphilic modifier the capacity factor of the analyte is

$$k'_{oB} = \varphi n_{oB} K_{Bs} \quad (16)$$

which gives

$$k'_{cB} = k'_{oB} \exp(-z_B F\psi_0/RT) \cdot \frac{1}{1 + K_{As} c_A \exp(-z_A F\psi_0/RT)} \quad (17)$$

In order to test this equation experimentally it is combined with eqn. 14 to give

$$n_A = \left( \frac{k'_{cB}}{k'_{oB}} \right) \exp(z_B F\psi_0/RT) K_{As} c_A \exp(-z_A F\psi_0/RT) \quad (18)$$

When  $z_B = z_A$  this equation is reduced to a form that is easily tested, *i.e.*,

$$n_A = \left( \frac{k'_{cB}}{k'_{oB}} \right) \cdot K_{As} c_A \quad (19)$$

Another way to test this equation will also be used in this paper. Consider two analytes,

$B_1$  and  $B_2$ , with charge of different sign but with the same magnitude. Using eqn. 17 for the capacity factor of the two analytes it is found that the ratio is

$$\frac{k'_{cB_1}}{k'_{cB_2}} = \frac{k'_{OB_1} \exp(-z_{B_1}F\psi_0/RT)}{k'_{OB_2} \exp(-z_{B_2}F\psi_0/RT)} \quad (20)$$

By considering that  $z_{B_1} = -z_{B_2}$ , the equation can be rewritten as

$$\psi_0 = -\frac{RT}{2z_{B_2}F} \ln \left[ \left( \frac{k'_{OB_1}}{k'_{cB_1}} \right) \left( \frac{k'_{cB_2}}{k'_{OB_2}} \right) \right] \quad (21)$$

The value of the electrostatic potential calculated from this equation can be compared with that obtained from the Gouy–Chapman equation. It can also be used in eqn. 14 to calculate the adsorption isotherm of the amphiphilic modifier.

## EXPERIMENTAL

The solutes were purchased from Janssen Chimica (Beerse, Belgium). The ion-pairing reagents [sodium butylsulphonate ( $BuSO_3^-$ ), sodium hexylsulphonate ( $HexSO_3^-$ ) and sodium octylsulphonate ( $OctSO_3^-$ )] and the buffer components were obtained from Merck (Darmstadt, F.R.G.). Mobile phases were prepared from deionized water and contained 25 mM phosphoric acid, 25 mM sodium dihydrogenphosphate (pH 2.1), varying amounts of sodium bromide and/or alkylsulphonate pairing ion. In some series of experiments the eluents also contained 10% (v/v) of methanol. ODS-Hypersil (5  $\mu$ m) with a BET surface area of 173 m<sup>2</sup>/g and a nominal carbon content of 8.8% (w/w) (according to the manufacturer) was used as the stationary phase (Shandon Southern Products, London, U.K.).

The equipment and the experimental technique used were as described previously<sup>2,3</sup> and allowed for the simultaneous determination of both the adsorption isotherm (by using the breakthrough method) and retention data for the solutes<sup>2</sup>. All measurements were performed at 25  $\pm$  0.1°C.

## RESULTS AND DISCUSSION

In Fig. 1 two different adsorption isotherms of  $BuSO_3^-$  on RP-18 stationary phase are shown. The experimental difference between the two curves is due to the difference in ionic strength. One curve represents the adsorption isotherm with a constant ionic strength ( $\times$ ), where the pairing ion variation is compensated by sodium bromide, whereas the other adsorption isotherm is obtained with a varying ionic strength ( $\circ$ ). The variation in ionic strength is accomplished by starting with 25 mM sodium dihydrogen phosphate and then adding  $NaBuSO_3$  to the mobile phase. As the concentration of  $BuSO_3^-$  varies between each experiment, each point represents different ionic strengths. The adsorption isotherm for  $HexSO_3^-$  on RP-18 from a buffer–methanol mixture (90:10, v/v) at constant ionic strength is also shown in Fig. 1. According to the electrostatic theory of ion-pair chromatography, the adsorption isotherm should follow eqn. 14. To use this equation the surface potential must be

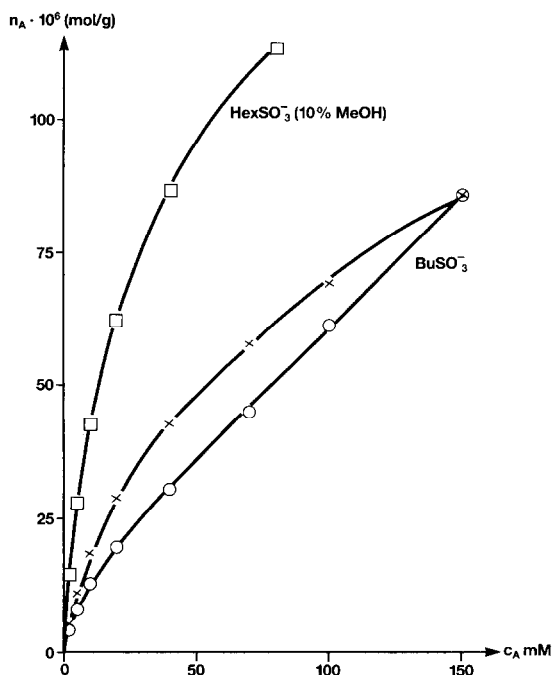


Fig. 1. Adsorption isotherm of  $\text{BuSO}_3^-$  from a phosphate buffer (pH 2.1) on to an RP-18 stationary phase at constant ( $\times$ ) ( $175 \text{ mM Na}^+$ ) and varying ( $\circ$ ) ionic strength ( $25\text{--}175 \text{ mM Na}^+$ ). Also shown is the adsorption isotherm of  $\text{HexSO}_3^-$  ( $\square$ ) from phosphate buffer-methanol (90:10, v/v) (pH 2.1;  $[\text{Na}^+] = 175 \text{ mM}$ ).

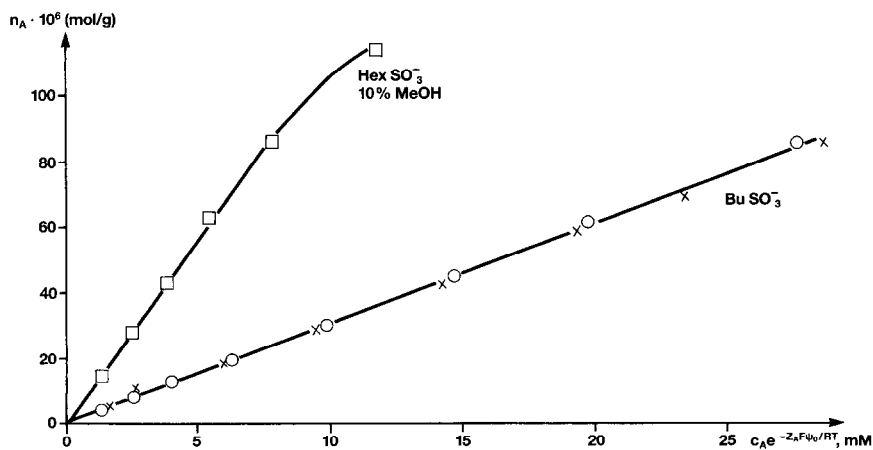


Fig. 2. Adsorption isotherms shown in Fig. 1 after correction for the surface potential. Symbols as in Fig. 1.

known. For all isotherms in this paper the surface potential was calculated using eqn. 21. Solute  $B_1$  is *p*-toluenesulphonate in the buffer systems and naphthalene-sulphonate in the buffer-methanol eluents, and solute  $B_2$  is adrenaline in all instances. All the experimental data for the  $BuSO_3^-$  system can be found in ref. 3. Capacity factors below 0.4 are neglected because of the uncertainties in the determination of the column dead volume.

In Fig. 2 are shown the adsorption isotherms from Fig. 1 after appropriate correction for the surface potential. It can be seen that the two different adsorption isotherms for  $BuSO_3^-$  now coincide. This is in agreement with the electrostatic theory and illustrates how isotherms can be rationalized by including the surface potential. It can also be seen that the surface potential-modified isotherm is linear, *i.e.*, the value of the denominator in eqn. 1 is close to unity in this low concentration range. The corresponding isotherm for  $HexSO_3^-$  is also linear up to  $100 \cdot 10^{-6}$  mol/g surface concentrations, where non-linearity begins.

It can be concluded that the properties of these three systems are entirely in agreement with the electrostatic theory as formulated in refs. 5 and 8. However, when the surface concentration of the amphiphile increases, systematic deviations from this simple theory occur. This is seen in the disappearance of the symmetrical behaviour of the capacity factor for analytes of opposite charge as a function of amphiphile concentration in the mobile phase. This is illustrated in Fig. 3, where the relative changes in capacity factors for *p*-toluenesulphonate and adrenaline are plotted as

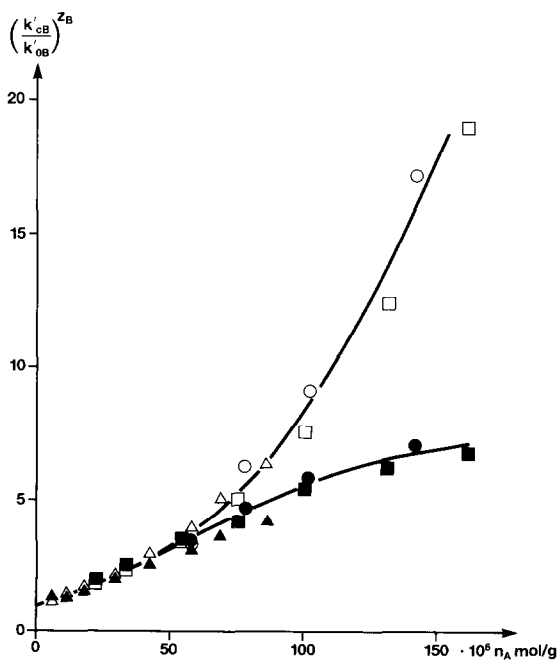


Fig. 3.  $(k'_{cB}/k'_{oB})^{z_B}$  for *p*-toluenesulphonate (open symbols) and adrenaline (closed symbols) as a function of surface concentration of  $BuSO_3^-$  ( $\Delta$ ,  $\blacktriangle$ ),  $HexSO_3^-$  ( $\square$ ,  $\blacksquare$ ) and  $OctSO_3^-$  ( $\circ$ ,  $\bullet$ ). Mobile phase, phosphate buffer (pH 2.1;  $[Na^+] = 175$  mM) for all points.

a function of surface concentration of various alkylsulphonates in a phosphate buffer eluent. A corresponding plot for naphthalenesulphonate and adrenaline in a buffer-methanol (90:10, v/v) eluent is shown in Fig. 4.

From Fig. 3 it can be seen that large discrepancies in the retention behaviour of the two ions start at about  $100 \cdot 10^{-6}$  mol/g. The plots in Fig. 4 show the same behaviour but shifted to higher surface concentrations. The hypothesis made in this paper is that this deviation from the simple theory is due to the decrease in available surface area for the analytes, *i.e.*, it is connected with the Langmuir behaviour of the adsorption isotherm of the amphiphile (see eqn. 14). This hypothesis was tested in two ways: (i) by testing eqn. 19 and (ii) by examining the isotherms according to eqn. 14.

In Figs. 5 and 6 the experimentally obtained data are presented according to eqn. 19. The data in Fig. 5 are for the amphiphile  $\text{HexSO}_3^-$  with phosphate buffer as mobile phase and for  $\text{OctSO}_3^-$  with buffer-methanol (90:10, v/v) as mobile phase. The corresponding values for the capacity factors were obtained with the analytes *p*-toluenesulphonate and naphthalenesulphonate, respectively. In Fig. 6 the experimental findings are shown for  $\text{OctSO}_3^-$  as amphiphile in buffer solution and with *p*-toluenesulphonate as analyte.

The results are in good agreement with the extended theory as presented in this paper, *i.e.*, the relationships are linear and pass through the origin. However, in Fig. 5 and at the highest surface concentrations there is a slight tendency for the analyte ion to overcompensate the non-linearity of the isotherms. More experimental data and a refined theory are needed in order to understand the origin of this behaviour.

The agreement between the presented theory and experimental results indicates that it is possible to calculate the surface potential from eqn. 21, even when analytes of opposite charge show asymmetric behaviour. According to the presented theory it is

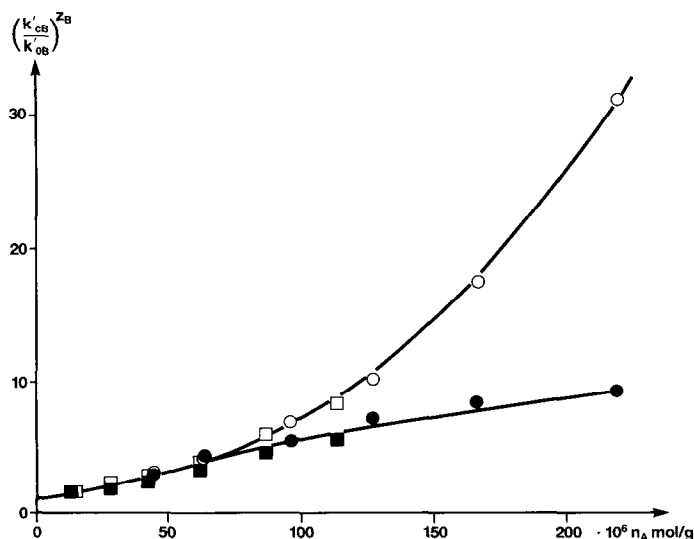


Fig. 4.  $(k'_{cb}/k'_{ob})^{z_a}$  for naphthalenesulphonate (open symbols) and adrenaline (closed symbols) as a function of surface concentration of  $\text{HexSO}_3^-$  ( $\square$ ,  $\blacksquare$ ) and  $\text{OctSO}_3^-$  ( $\circ$ ,  $\bullet$ ). Mobile phase, phosphate buffer-methanol (90:10, v/v) (pH 2.1;  $[\text{Na}^+] = 175 \text{ mM}$ ) for all points.



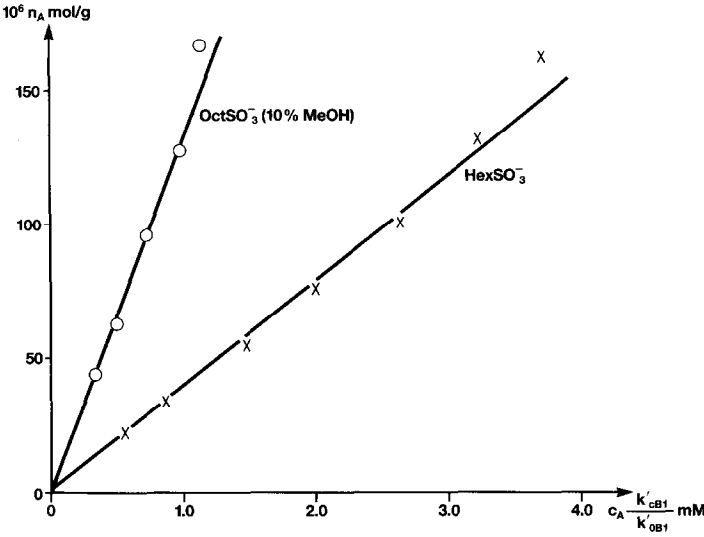


Fig. 5. Surface concentration of HexSO<sub>3</sub><sup>-</sup> (×) and OctSO<sub>3</sub><sup>-</sup> (○) as a function of  $c_A(k'_{CB}/k'_{OB})$  (see eqn. 19). B is *p*-toluenesulphonate when HexSO<sub>3</sub><sup>-</sup> is used and naphthalenesulphonate when OctSO<sub>3</sub><sup>-</sup> is used. Mobile phase: HexSO<sub>3</sub><sup>-</sup>, phosphate buffer (pH 2.1; [Na<sup>+</sup>] = 175 mM); OctSO<sub>3</sub><sup>-</sup>, phosphate buffer-methanol (90:10, v/v) (pH 2.1; [Na<sup>+</sup>] = 175 mM).

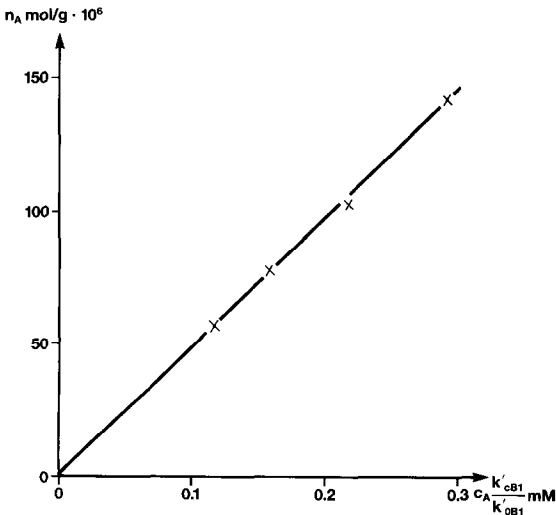


Fig. 6. Surface concentration of OctSO<sub>3</sub><sup>-</sup> as a function of  $c_A(k'_{CB}/k'_{OB})$  (see eqn. 19). B is *p*-toluenesulphonate; Mobile phase, phosphate buffer (pH 2.1; [Na<sup>+</sup>] 175 mM).

therefore possible to calculate the surface potential by using eqn. 21. This conclusion can be tested by inserting the value obtained for the surface potential in the equation for the isotherm (eqn. 14) and evaluating the result. To simplify the evaluation, eqn. 14 is rewritten in a reciprocal form:

$$\frac{c_A \exp(-z_A F \psi_0 / RT)}{n_A} = \frac{1}{n_{0A} K_{As}} + \frac{c_A \exp(-z_A F \psi_0 / RT)}{n_{0A}} \quad (22)$$

If the obtained potential is correct, the left-hand side of eqn. 22 will be a linear function of  $c_A \exp(-z_A F \psi_0 / RT)$  and from the slope  $n_0$  can be calculated. The experimental results are plotted in Figs. 7–9, from which it is seen that in all instances, and over the entire concentration range, the adsorption isotherms follow eqn. 22. It can therefore be concluded that the obtained surface potential is correctly estimated over the whole concentration range.

It is also of interest to compare the experimentally obtained relationship between the surface potential and surface charge concentration with the corresponding relationship obtained by solving the Poisson–Boltzmann equation. The solution of the Poisson–Boltzmann equation is, however, dependent of the geometry of the system. As the Debye length (7.3 Å) is small, compared with the pore radius of the particles (60–100 Å), it is possible to use the Gouy–Chapman equation for a plane surface in these instances. This equation expresses the relationship between the surface potential and the concentration of the charges expressed in mol/m<sup>2</sup>. The difficulty is then how to relate the amount of adsorbed amphiphile per gram of stationary phase to the concentration in mol/m<sup>2</sup>. This is formally done by using the surface area as a conversion factor. The surface area reported by the manufacturer is 173 m<sup>2</sup>/g. Using

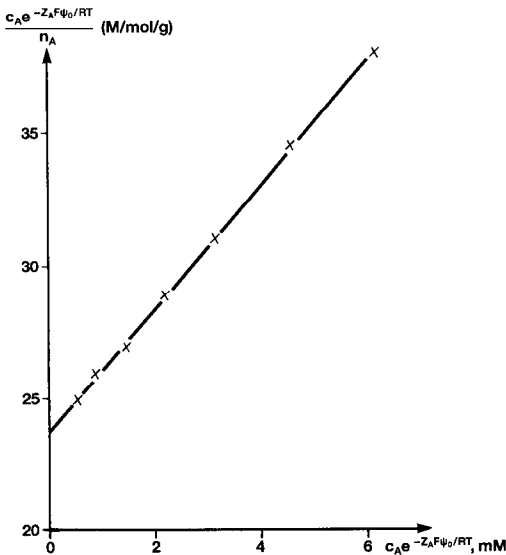


Fig. 7. Surface potential-modified Langmuir isotherm for HexSO<sub>3</sub><sup>-</sup> (see eqn. 22). Mobile phase, phosphate buffer (pH 2.1; [Na<sup>+</sup>] = 175 mM).

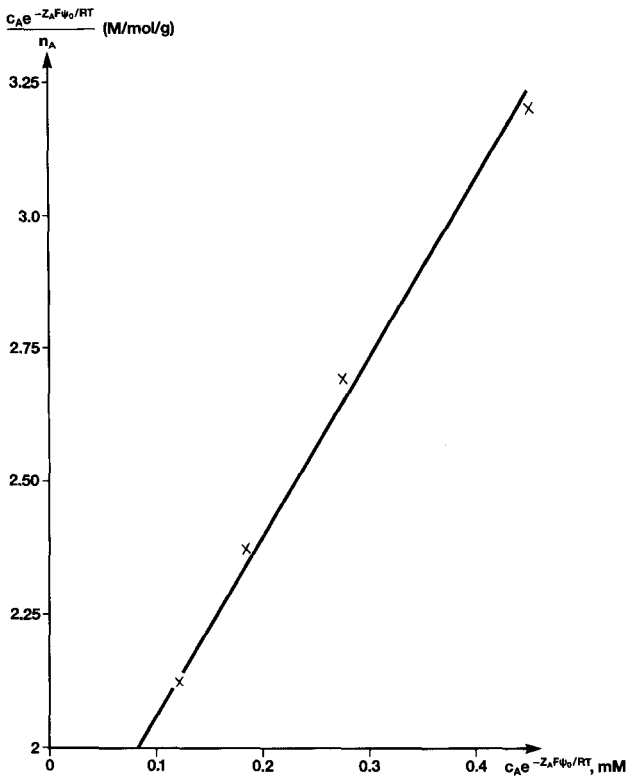


Fig. 8. Surface potential-modified Langmuir isotherm for OctSO<sub>3</sub><sup>-</sup> (see eqn. 22). Mobile phase, phosphate buffer (pH 2.1; [Na<sup>+</sup>] = 175 mM).

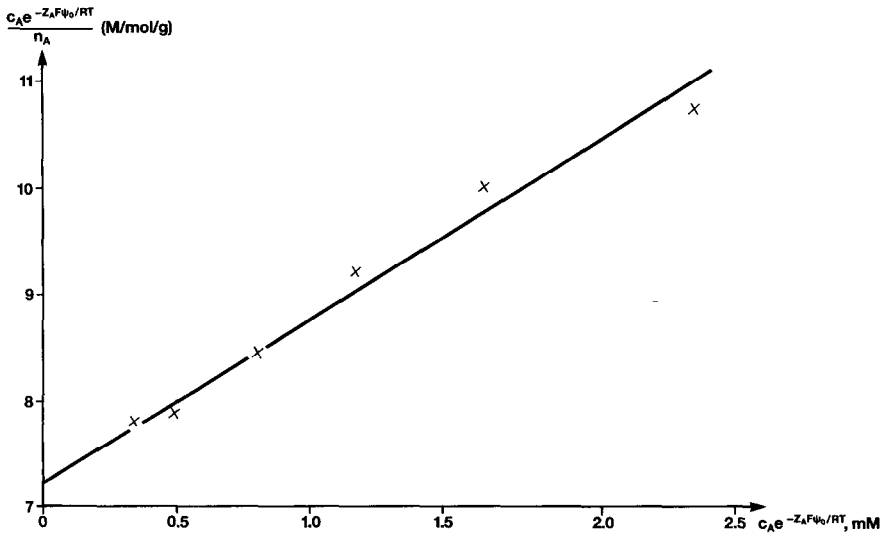


Fig. 9. Surface potential-modified Langmuir isotherm for OctSO<sub>3</sub><sup>-</sup> (see eqn. 22). Mobile phase, phosphate buffer-methanol (90:10, v/v) (pH 2.1; [Na<sup>+</sup>] = 175 mM).

this value for the surface area in combination with the Gouy–Chapman theory, the full line in Fig. 10 is obtained. Fig. 10 also shows the experimental values of the surface potential for all the studied amphiphiles in the buffer and in the buffer–methanol mixture. It is seen that the relationship between surface potential and surface concentration is independent of the chain length of the alkylsulphonate and that the same relationship holds when the mobile phase contains 10% of methanol. Both of these observations are in agreement with the concept of the electrostatic theory. Bartha and Vigh<sup>9</sup> have shown that retentions of ionic solutes form a common retention surface when plotted against the surface concentration of adsorbed alkylsulphonates, irrespective of the length of the alkyl chain, at constant inorganic counter ion concentration. As shown above, surface concentration and ionic strength are two of the parameters that determine the surface potential and consequently the solute retention, providing a theoretical explanation of the empirically found behaviour.

From the slope of the plots in Figs. 7–9 in combination with the surface area, it is possible to calculate the area that the ions occupy at the surface. The results are  $44 \text{ \AA}^2$  for  $\text{OctSO}_3^-$  (10% methanol),  $68 \text{ \AA}^2$  for  $\text{HexSO}_3^-$  and  $92 \text{ \AA}^2$  for  $\text{OctSO}_3^-$ . The results can be compared with the cross-sectional areas for straight-chain acids at a water–oil interface ( $45\text{--}60 \text{ \AA}^2$ ). It is concluded that the values found on this stationary phase are of the correct order of magnitude except for that of  $\text{OctSO}_3^-$  in buffer, which is higher than expected. It is interesting that the results indicate that the cross-sectional area for octylsulphonate is smaller at the methanol–buffer/RP-18 interface than at the buffer/RP-18 interface. The same trend is found when Figs. 3 and 4 are compared, *i.e.*, the asymmetric behaviour is shifted to higher surface concentration for the buffer–methanol mixture.

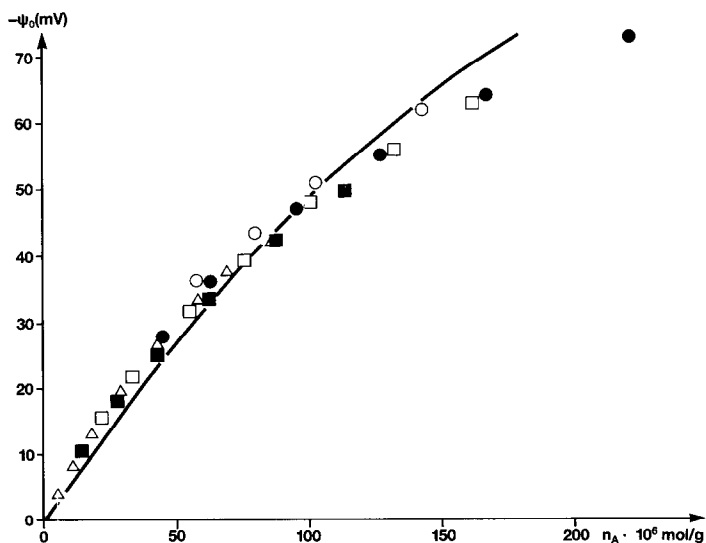


Fig. 10. Surface potential as a function of surface concentration of  $\text{BuSO}_3^-$  ( $\Delta$ ),  $\text{HexSO}_3^-$  ( $\square$ ,  $\blacksquare$ ) and  $\text{OctSO}_3^-$  ( $\circ$ ,  $\bullet$ ). The full line is the theoretical function according to the Gouy–Chapman theory with surface area  $173 \text{ m}^2/\text{g}$ . Mobile phase for open symbols, phosphate buffer (pH 2.1;  $[\text{Na}^+] = 175 \text{ mM}$ ). Mobile phase for closed symbols, phosphate buffer–methanol (90:10, v/v) (pH 2.1;  $[\text{Na}^+] = 175 \text{ mM}$ ).

It is appropriate in this context to comment on the determination of surface area for irregular surfaces. The surface area is usually measured with the BET method using nitrogen as a probe molecule. For irregular materials the surface accessibility may depend on the size of the probe molecule, which is due to the inability of a large adsorbate molecule to follow the irregularity of the surface<sup>10</sup>. The value obtained from BET measurements can therefore *a priori* not be used. In this particular instance there is, however, relatively good agreement between the values from the BET method and the Gouy–Chapman theory. The use of this value for the surface area in the determination of the cross-sectional areas above is therefore justified. The relationship between the geometric structure of the surface, the adsorption conformation of the molecules and the electrostatic laws is a complicated topic on which further studies are needed.

It is important to note that a number of secondary effects are neglected in this theory, *e.g.*, specific interactions between the ions, monopole–dipole interactions, changes in the properties of the surface layer and mobile phase when varying the concentration of amphiphile, image forces, etc.

## CONCLUSIONS

Several important conclusions regarding the mechanism of ion-pair chromatography can be drawn from this work. Differences in the isotherms of  $\text{BuSO}_3^-$  can be rationalized by the different surface potential at different inorganic counter ion concentrations. The isotherms coincide and become linear when the effect of the surface potential is taken into account. The variation of the surface potential with the ionic strength is also in agreement with the electrostatic theory. Differences in adsorption isotherms have previously been shown to be caused by pure electrostatic effects also for tetrabutylammonium ion as amphiphile<sup>8</sup>. When the surface concentration of the amphiphile is high, the simultaneous effect of competition for surface area and the effect of surface potential must be considered. This simultaneous effect can be treated quantitatively by the extended electrostatic theory presented in this paper. Good agreement is found between the theoretically expected and experimentally obtained adsorption isotherms of alkylsulphonate amphiphilic ions in both aqueous and methanol (10%, v/v) containing mobile phases. The consistency of the theory used is also illustrated in the agreement between the theoretical and experimental surface potential–surface charge density relationship (*cf.*, Fig. 10).

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