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Comparison between the adsorption behaviors of an organic cation and an organic anion on several reversed-phase liquid chromatography adsorbents

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Abstract

Adsorption data of an organic cation (propranololium chloride) and an organic anion (sodium 1-naphthalene sulfonate) were measured by frontal analysis on two RPLC adsorbents, Symmetry-C_{18} and XTerra-C_{18}, with aqueous solutions of methanol as the mobile phases. The influence of supporting neutral salts on the adsorption behavior of these two ions are compared. The Henry constants are close ($H \simeq 5$). The four sets of isotherm data are all well accounted for using the bi-Moreau model. However, the isotherms of the two ions behave differently at high concentrations. The initial behaviors of all the isotherms are antilangmuirian but remain so in a much wider concentration range for the cation than for the anion, due to its stronger adsorbate–adsorbate interactions on the low-energy adsorption sites. The retention times of both ions increase with increasing concentration of neutral salt in the mobile phase, suggesting the formation of ion-pair complexes, with Cl^- for the cation and with Na^+ for the anion. The adsorbate–adsorbate interactions vanish in the presence of salt and the bi-Moreau isotherm model tends toward a bi-Langmuir model. Differences in adsorption behavior are also observed between the cation and the anion when bivalent inorganic anions and cations, respectively, are dissolved in the mobile phase. High concentration band profiles of 1-naphthalene sulfonic acid are langmuirian, except in the presence of a trivalent cation, while those of propranolol are antilangmuirian under certain conditions even with uni- or divalent cations.

Keywords: Adsorption equilibria; Adsorption isotherms; Moreau isotherm model; Overloaded band profiles; Inverse method; Ion-pair complexes; Propranolol; Sodium 1-naphthalene sulfonate

1. Introduction

The adsorption equilibrium behavior of ionic species attracts attention because this behavior is critical in a wide spectrum of applications in the analysis and the purification of these compounds. An important body of literature is devoted to looking for a better understanding of the adsorption mechanism(s) of these compounds at the analytical level, investigating the effects of varying the mobile phase pH, the buffer nature and its concentration, and the possible addition of neutral compounds or of completely ionized supporting salts. A long list of recent publications was given in a previous report [1]. In contrast, relatively few reports have discussed the whole equilibrium isotherm.

Horvath [2], Schill [3] and Sokolowski [4,5] have elaborated similar theories to account for the adsorption behavior of ionic species. These theories are based on the formation of ion-pairs between ions of opposite charges. More recently Kazakevich named this approach chaotropicity [6,7] and applied it to study the retention behavior of several β-blockers and the influence of different mobile phase additives. Sokolowski derived adsorption models that are equivalent to the Langmuir isotherm model (or to the bi-Langmuir model

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in the case of heterogeneous adsorbents) and which describe successfully the adsorption behavior of series of alkylsulfonates. This model assumes that the adsorbate is an ion-pair, hence is electrically neutral. Accordingly, it does not include any electrostatic repulsion between adsorbate molecules. By contrast, other authors assume that, for fundamental reasons, the adsorption mechanism of ionic species must take into account the surface potential due to the adsorption of ions from the solution and that an electrical double layer forms (Stern–Gouy–Chapman model) [8]. This second approach was used by Ståhlberg to explain the adsorption of *p*-toluenesulfonate on RPLC adsorbents [9–11].

Whichever one of these assumptions is made regarding the fundamentals of the adsorption of ions onto RPLC stationary phases, the isotherm model that is derived from it is strictly convex upward, i.e., langmuirian. Unfortunately, this result is inconsistent with previous adsorption data measured for the organic cation propranololium on various commercial RPLC adsorbents [1,12–17]. S-shaped isotherms were found at low ionic strengths of the mobile phase [12–15] or with bivalent counter-anions (sulphate, phthalate, succinate, phosphate and citrate II) [16,17]. Strictly antilangmuirian isotherms were even observed with the trivalent anion citrate [17]. This observation, the results given by the perturbation method and reported earlier [18], and the fact that the saturation capacities estimated for these compounds are close to those of neutral compounds [12–17] support the idea that ionic species adsorb onto the surface as neutral forms and that there are no adsorbate–adsorbate repulsion of electrostatic origin. However, these observations and results, hence the demonstration apply only to the organic cation propranololium. Additional experiments made with other ions and particularly with organic anions are needed to generalize these first conclusions.

In this work, we compare the adsorption behavior of an organic cation (propranololium, as propranololium chloride) and an organic anion (1-naphthalene sulfonate as sodium 1-naphthalene sulfonate) on two commercial stationary phases, C_{18}-Symmetry and C_{18}-XTerra. The measurements of the isotherm data were first carried out by frontal analysis, with a mobile phase containing no supporting salt. This first series of data is used to select the best general isotherm model which must be in agreement with the shape of the experimental band profiles recorded. The inverse method of isotherm determination [13] was then used to derive the best values of the parameters of this model for different experimental conditions. This method minimizes the differences between the experimental band profiles recorded under a given set of experimental conditions (e.g., with a given concentration of a certain supporting salt in the mobile phase, at a given temperature) and the corresponding profiles calculated with the equilibrium-dispersive model of chromatography. The similarity and the differences between the adsorption behavior of the positively and the negatively charged compounds are now presented and discussed in the general context of the adsorption of ionic compounds.

2. Theory

2.1. Models of isotherm used

Previous reports [12–15] showed that the isotherm model that best accounts for the adsorption data of an organic cation on various commercial columns is the bi-Moreau model. This model is the simplest extension of the Langmuir model to the case of an heterogeneous adsorbent when significant adsorbate–adsorbate interactions take place in the adsorbed phase. It corresponds to a surface covered with two types of sites, each of which follows Moreau isotherm model behavior [19]. It is written:

$$q^* = q_{s,1}\frac{b_1C + I_1b_1^2C^2}{1 + 2b_1C + I_1b_1^2C^2} + q_{s,2}\frac{b_2C + I_2b_2^2C^2}{1 + 2b_2C + I_2b_2^2C^2} \quad (1)$$

where q^* and C are the equilibrium concentrations of the compound considered in the adsorbed and the liquid phase, respectively, while $q_{s,1}$, $q_{s,2}$, b_1, b_2, I_1 and I_2 are the monolayer saturation capacities, the low-concentration equilibrium constants, and the adsorbate–adsorbate interaction parameters on the sites of types 1 and 2, respectively. Note that the bi-Moreau model morphs into the bi-Langmuir model when $I_1 = I_2 = 0$.

The equilibrium constants b_1 and b_2 are associated with the adsorption energies $\epsilon_{a,1}$ and $\epsilon_{a,2}$, respectively, through the following classical equation [20]:

$$b_i = b_0\, e^{\epsilon_{a,i}/RT} \quad (2)$$

where $\epsilon_{a,i}$ is the adsorption energy, R is the universal ideal gas constant, T is the absolute temperature and b_0 is a pre-exponential factor that could be derived from the molecular partition functions in the bulk and the adsorbed phases. b_0 is often considered to be independent of the adsorption energy [20]. The adsorbate–adsorbate interaction parameter, I, can be written as [19]:

$$I = \exp\left(\frac{\epsilon_{AA}}{RT}\right) \quad (3)$$

where ϵ_{AA} is the interaction energy (by convention, $\epsilon_{AA} \geq 0$) between two molecules of A adsorbed on close sites.

Note that the bi-Langmuir model is the limit case of the bi-Moreau model when the adsorbate–adsorbate interaction parameter, I, tends toward 0. Thus, in the work reported here, we adopted the bi-Moreau isotherm model as the initial model in the application of the IM method.

2.2. The inverse method of isotherm determination

This method consists in the numerical adjustment of the coefficients of an isotherm model in order to minimize the differences between a recorded experimental band profile and the profile calculated for the same sample, under the same experimental conditions, using the equilibrium-dispersive

model of chromatography (see next section) and the isotherm model selected. The main advantage of the inverse method of isotherm determination is that it requires the measurement of only one or a few experimental overloaded band profiles [21–24]. Accordingly, the method is fast and requires small amounts of solvent and sample. This method was described previously [13]. It gives results that are in excellent agreement with those of FA [24].

2.3. Modeling of band profiles in HPLC

The overloaded band profiles of propranolol and 1-naphthalene sulfonate were calculated using the equilibrium-dispersive model (ED) of chromatography [25–27]. The ED model assumes instantaneous equilibrium between the mobile and the stationary phases and a finite column efficiency originating from an apparent axial dispersion coefficient that accounts for the dispersive phenomena (molecular and eddy diffusion) and for the non-equilibrium effects (mass transfer kinetics) that take place in the chromatographic column. The axial dispersion coefficient is directly related to the column efficiency under linear conditions.

At $t = 0$, the stationary phase is in equilibrium with the pure mobile phase and the solute concentrations in both phases in the column are uniformly equal to zero. The boundary conditions used are the classical Danckwerts-type boundary conditions [25,28] at the inlet and outlet of the column.

The ED model was solved using the Rouchon program, based on a finite difference method [25,29–31].

3. Experimental

3.1. Chemicals

The mobile phases used in this work were aqueous solutions of methanol (25:75 and 10:90 (v/v) for the measurements of the adsorption data of propranololium and 1-naphthalene sufonate, respectively). Both water and methanol were of HPLC grade. They were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The supporting salt solutions were first prepared in pure water and methanol was added thereafter to the salt solution to prepare the final mobile phase. The salt concentrations given in the text are reported to the mobile phase mixture. Prior to their use, the solvents were filtered on an SFCA filter membrane, 0.2 μm pore size (Suwannee, GA, USA). Thiourea was chosen as the unretained tracer, to measure the column hold-up volume. The solutes studied were propranolol, an aminoalcohol of structure $C_{10}H_7OCHOHCH_2NHCH(CH_3)_2$, and 1-naphtahlene sulfonic acid of structure $C_{10}H_7SO_3H$. Propranolol and 1-naphthalene sulfonic acid were injected under the acidic protonated form (as the hydrochloride, $M =$ 295.8 g/mol) and the basic anionic form (as the sodium salt, $M = 230.2$ g/mol), respectively. Thiourea, propranolol chloride, sodium 1-naphthalene sulfonate, ammonium chloride, sodium chloride, calcium chloride, barium chloride, disodium sulphate, diammonium sulphate, aluminium chloride and tetramethyl-, ethyl-, propyl-, and butylammonium chloride were all obtained from Aldrich. (Milwaukee, WI, USA).

Table 1
Characteristics of the C_{18}-bonded Symmetry and Xterra columns

	Symmetry	XTerra
Particle size (mm)	5	5
pore size (Å)	86	120
Pore volume[a] (mL/g)	0.90	0.64
Surface area[a] (m^2/g)	346	176
Particule shape	Spherical	Spherical
Total carbon (%)	19.6	15.2
Surface coverage (μmol/m^2)	3.18	2.40
Total porosity[b]	0.5804[b]; 0.6334[c]	0.6178[b]; 0.6719[c]
Endcapping	Yes	Yes

[a] Data for the packing before derivatization.
[b] Data from injection of the non-retained thiourea compound in a methanol:water mobile phase (25/75, v/v).
[c] Data from injection of the non-retained thiourea compound in a methanol:water mobile phase (10/90, v/v).

3.2. Columns

The two 150 mm × 3.9 mm commercial columns used in this study were packed, one with Symmetry-C_{18}, the other with XTerra-C_{18}. They were gifts from the manufacturer (Waters, Milford, MA, USA). The main characteristics of these packing materials are summarized in Table 1. The Symmetry column was one of the lot of ten columns previously used to test the column-to-column and batch-to-batch reproducibility under linear conditions [32]. The void volumes at 25/75 and 10/90 (v/v), of the Symmetry and the XTerra columns, respectively, were derived from the average of the retention times of two consecutive thiourea injections. They are 1.040 and 1.107 mL for a 25/75 (v/v) solution on the one hand, and 1.135 and 1.204 mL for a 10/90 (v/v) solution, on the other, respectively. The column porosities remained constant, whatever the nature of the salt used and its concentration in the mobile phase. They were found to depend only on the methanol concentration of the mobile phase (25% or 10%, v/v).

3.3. Apparatus

The overloaded band profiles were acquired using a Hewlett-Packard (now Agilent Technologies, Palo Alto, CA, USA) HP 1090 liquid chromatograph. This instrument includes a multi-solvent delivery system (volume of each tank, 1 L), an auto-sampler with a 250 μL sample loop, a diode-array UV-detector, a column thermostat and a data station. Compressed nitrogen and helium bottles (National Welders, Charlotte, NC, USA) are connected to the instrument in order to allow the continuous operations of the pump, the auto-sampler, and the solvent sparging. The extra-column volumes are 0.058 and 0.93 mL as measured from the auto-sampler and from the pump system, respectively, to the column inlet. All

the retention data were corrected for these contributions. The flow-rate accuracy was controlled by pumping the pure mobile phase at 23°C and with a flow rate of 1 mL/min, during 50 min, successively from each pump head, into a volumetric glass of 50 mL. The relative error was less than 0.4%, so that we estimate the long-term accuracy of the flow-rate at 4 μL/min at flow rates around 1 mL/min. All measurements were carried out at a constant temperature of 23°C, fixed by the laboratory air-conditioner. The daily variation of the ambient temperature never exceeded ±1°C.

3.4. Measurements of the adsorption isotherm of propranolol and 1-naphthalene sulfonate by FA

The adsorption isotherms of propranolol and 1-naphthalene sulfonate were measured in two different aqueous solutions of methanol, selected so that the two compounds had comparable retention. Due to the difference between the hydrophobicities of these two compounds, methanol concentrations of 25% and 10% were chosen for the mobile phases with which to measure the adsorption data of propranolol and 1-naphthalene sulfonate, respectively. Under these conditions, the retention factors of both compounds are of the order of 3, a value large enough to acquire accurate adsorption data. The maximum concentration of each analyte applied in FA was fixed at 40 g/L in their respective mobile phases to avoid any precipitation inside the instrument. Two master solutions were prepared, at 10% and 100% of the maximum concentration selected. The samples were always dissolved in the same salt solution that was used as the mobile phase.

Two consecutive FA runs and a total of 34 data points were then measured, starting from the lowest (first run, 0.2 to 4 g/L, 9 points) to the highest concentrations (second run, 2 to 40 g/L, 25 points). One pump of the HPLC instrument was used to deliver a stream of the pure mobile phase (methanol:water, 25:75 or 10:90, v/v), the second pump for the 100% master solution, the third for the 10% master solution. The concentration of the studied compound in the FA stream is determined by the concentration of the sample solution and the flow rate fractions delivered by the two pumps. The breakthrough curves were recorded at a flow rate of 1 mL/min, with a sufficiently long time delay between breakthrough curves (20 min) to allow for the complete reequilibration of the column with the pure mobile phase. The injection time of the sample was fixed at 5 min for all FA steps, in order to reach a stable plateau at the column outlet whatever feed concentration was used. To avoid recording any UV-absorbance signal larger than 2000 mAU and the corresponding signal noise at high concentrations while keeping a large enough signal at the lowest concentrations, the detector signal was recorded at 325 and 323 nm (10% solution) and 331 and 360 nm (100% solution) for propranolol and 1-naphthalene sulfonate, respectively. In each case, the detector response was calibrated accordingly by using the UV absorbance at the plateau observed on the breakthrough curves.

The adsorbed amount at equilibrium q^* is given by:

$$q^* = \frac{C(V_{eq} - V_0)}{V_a} \quad (4)$$

where V_{eq} and V_0 are the elution volume of the equivalent area and the column hold-up volume, respectively, and V_a is the volume of stationary phase.

3.5. Measurements of the overloaded band profiles of propranolol

Injection of propranolol chloride and sodium 1-naphthalene sulfonate were made with the auto-sampler (maximum volume 250 μL) in set of experimental conditions. 250 μL of a 1.5 and 4 g/l solution of propranolol and 1-naphthalene sulfonate, respectively, were injected to record a moderately overloaded band profile for each salt. The samples were always dissolved in the same salt solution as was used for the mobile phase. These profiles were recorded at 325 and 323 nm for propranolol and 1-naphthalene-sulfonate, respectively. Segments of these elution profiles having between 500 and 1000 points were used to perform the IM calculations.

4. Results and discussion

4.1. Adsorption properties of anions and cations derived from frontal analysis data

Fig. 1 shows the plots of the adsorption data points derived from the treatment of each of the four series of 34 breakthrough curves recorded during the FA runs for the two compounds, on the two columns studied, using mobile phases that contained no salts. Two presentations of these data are given, plots of the isotherm curves (q^* versus C, top) and plots of the isotherm slopes (q^*/C versus C, bottom) versus the concentration plateau in the mobile phase. This second plot illustrates better the variation of the curvature of the isotherm with increasing concentration. Because the mobile phase compositions were selected for this purpose, the Henry constants of the two compounds are comparable, between 4 and 6 on both Symmetry and XTerra. At high concentrations in the mobile phase, the amount of naphthalene sulfonate adsorbed at equilibrium is always smaller than that of propranolol.

In order to derive accurate frontal analysis data, k' must be sufficiently large (in practice, $k' \geq 3$). In order to acquire a sufficiently larger number of data points, k' must not be too large (in practice, $k' < 10$). Accordingly, the mobile phase composition must be different for the two compounds (10% and 25% methanol content for 1-naphtahlene sulfonate and for propranololium, respectively). For a mobile phase containing 25% methanol (v/v), 1-naphthalene sulfonate is almost unretained while with only 10% methanol in the mobile phase, propranololium is retained too strongly. Thus, a rigorous comparison cannot be made between the two sets

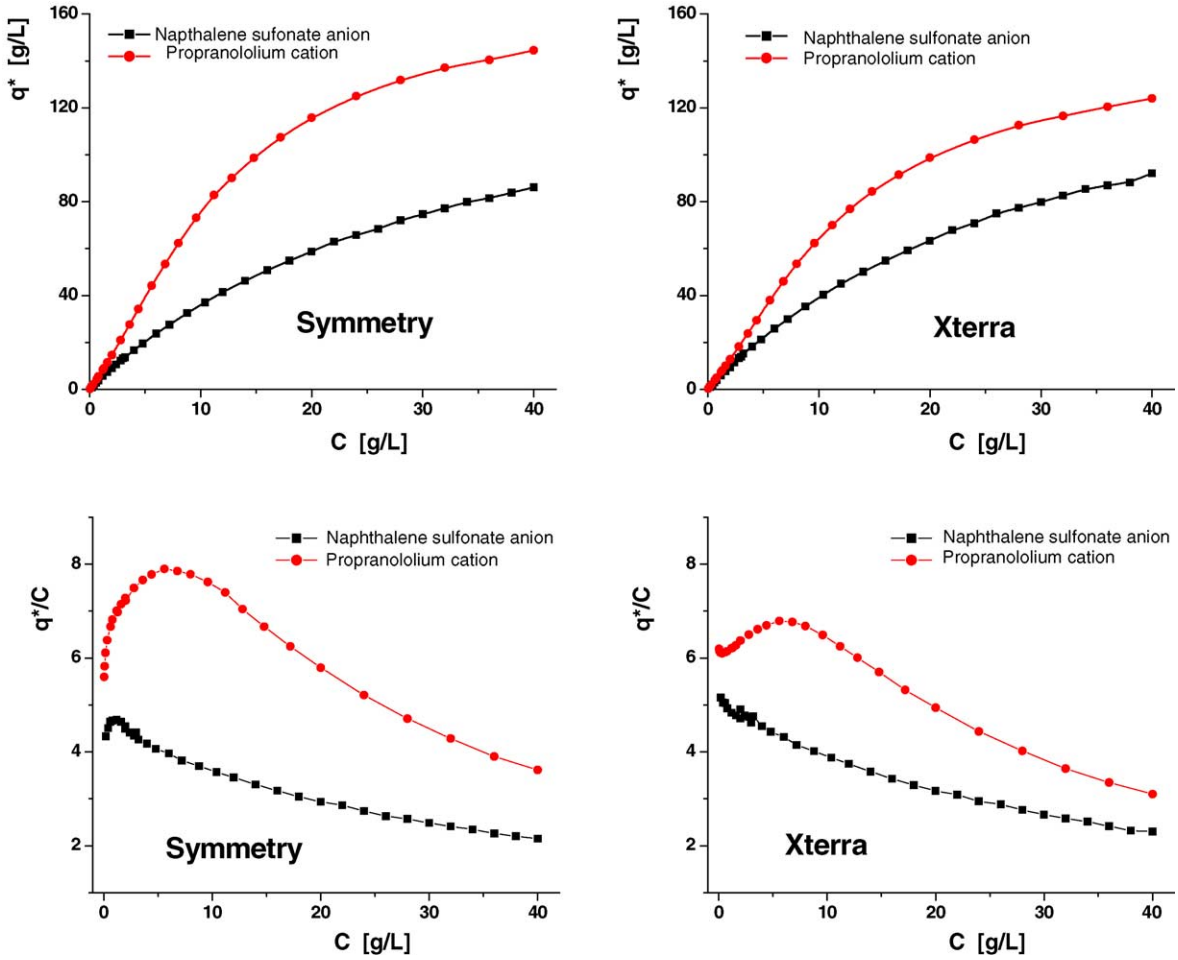

Fig. 1. Comparison between the adsorption data of an organic anion and an organic cation measured by FA on two different columns, Symmetry-C_{18} and XTerra-C_{18}. $T = 296$ K, methanol:water mixtures, 10:90 and 25:75 (v/v) for naphtahlene sulfonate and propranololium, respectively. (Top) Isotherm data. (Bottom) Scatchard representation.

of isotherm data. However, the influence of the change in mobile composition is rather small and it should not affect either the nature of the best model of adsorption isotherm or the value of the saturation capacities of the adsorbent [33]. The only significant effect of the mobile phase composition is only on the saturation capacity of the high-energy sites, which increases with increasing water concentration of the mobile phase [33]. When the density of the high-energy sites is low (i.e., less than 5% of the total column saturation capacity), the comparison between the total saturation capacities measured at different mobile phase compositions is straightforward.

At first glance, the isotherm of naphthalene sulfonate appears to be quasi-langmuirian while that of propranolol is clearly S-shaped. However, a more careful look at the breakthrough curves of the anion at low concentrations ($C_{plateau} = 0.2$ g/L, for instance, Fig. 2) on either Symmetry and XTerra shows that the adsorption front exhibits a diffuse boundary while the desorption rear has a clear shock layer, much like the corresponding parts of the breakthhrough curves of propranolol. This result is in agreement with the plot of q^*/C versus C for Symmetry (Fig. 1, bottom left) but not with the same plot for XTerra (Fig. 1, bottom right) which shows a monotonous decrease of the isotherm slope. This apparent contradiction arises from the combination of a very low concentration for the inflection point of the corresponding isotherm and from errors made in the calculation of the adsorbed mass by the equivalent area method [25], due to the unstability of the equilibrium plateau recorded at low concentrations and the poor definition of the front and rear of the breakthrough curves (see Fig. 2). This instability of the outlet concentration was not due to any fluctuations or variations of the column temperature or of the mobile phase composition nor to any dysfunction of the mixing system of the solvent delivery system during the frontal analysis measurements. This was demonstrated by the injection of the same concentration plateaus into the instrument fitted without column generating the correct, flat plateaus expected. A slow, oscillating equilibrium between the solution and the adsorbent at low concentrations could explain this unexpected phenomenon.

These results demonstrate the important fact that the shape of the equilibrium isotherm is the same for both the cation and the anion. The only differences between them are quantitative

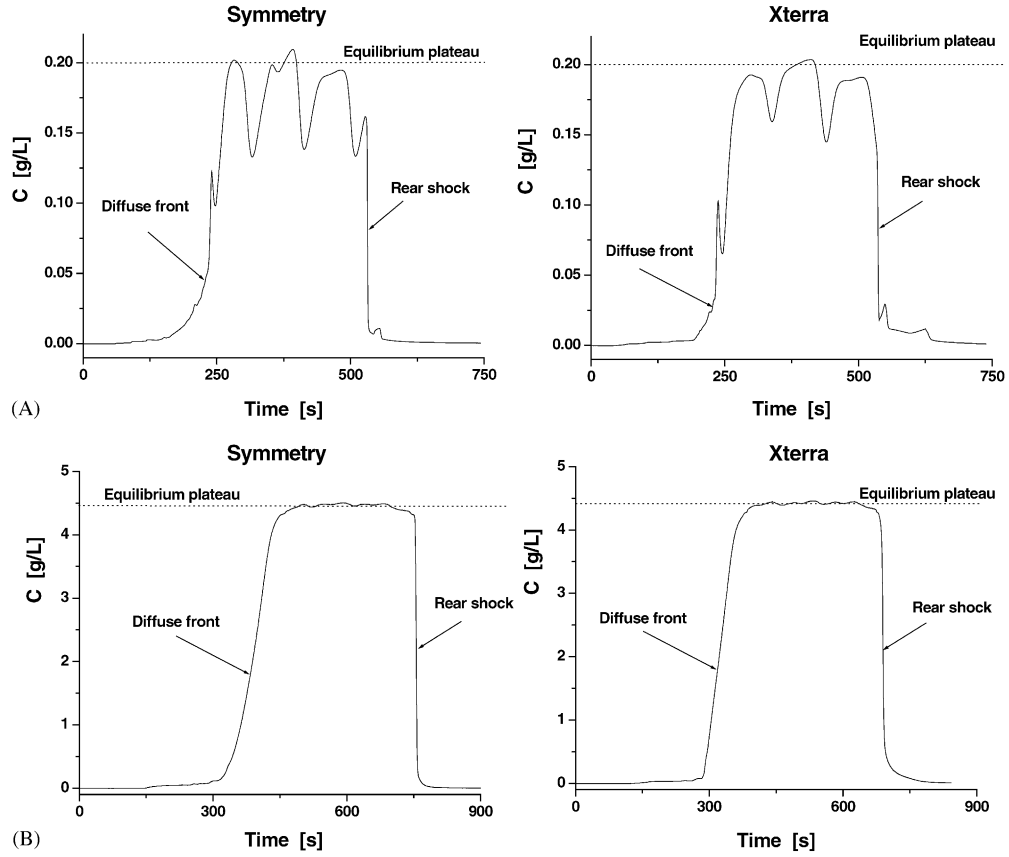

Fig. 2. Breakthrough curves recorded in the low concentration range making evidence of the initial anti-langmuirian behavior of the adsorption isotherm (detection of a diffuse front and a rear shock) for both ionizable compounds on the Symmetry (left) and XTerra (right). $T = 296$ K, Flow rate 1 mL/min. (A) Naphthalene sulfonate. Methanol:water, 10:90 (v/v). The strict anti-langmuiriran behavior is limited for concentration inferior to 0.2 g/L. Note the difficulty to derive with accuracy the mass adsorbed because of the oscillations on the plateau. (B) Propranololium. Methanol:water, 25:75, (v/v). Note the persistence of the anti-langmuiriran behavior at concentrations around 4–5 g/L.

not qualitative, they deal with the concentration at which the inflection point is observed and with the concentration range within which the isotherm is convex downward (i.e., anti-Langmuirian). This range is much smaller with the anionic sulfonate ($0 \leq 0.3$ g/L) than with the cationic amine ($0 \leq 5$ g/L). These differences explain the difference in the shape of the overloaded band profiles of the two ions recorded on Symmetry and XTerra for a maximum peak concentration of 2 g/L (see Fig. 3). The profile of the sulfonate anion peak exhibits a front shock layer followed by a diffuse boundary that ends with a short rear shock layer. In contrast, the cation peak has the classical anti-langmuirian profile, with a diffuse front boundary and a rear shock layer.

The fitting of the isotherm data of the naphthalene sulfonate anion to the bi-Moreau model (six parameters) was unsuccessful because these data are inaccurate at low concentrations. This lack of accuracy prevents from estimating properly the parameters of the first term of the model, the one that corresponds to the high-energy adsorption sites, those that begin to be populated at low concentrations. Instead, we estimated the isotherm parameters by applying the inverse method of isotherm determination. Large samples (250 μL) were injected with the auto-sampler to achieve wide elution peaks and limit as much as possible the consequences of extra-column dispersion and of sample dilution [24]. A rectangular injection profile was assumed in the calculations. The calculated profiles (solid lines) that show the best agreement with the corresponding experimental profiles and these band profiles (dotted lines) are overlaid in Fig. 3. The best values of the parameters are listed in Table 2 ([NaCl] = 0).

In a second step, the FA adsorption data were fitted to a bi-Moreau isotherm equation in which the parameters $q_{s,2}$ and I_2 were set equal to the values derived with the IM method while the other four parameters were allowed to float. This procedure gave slightly different values for these four parameters, 0.634 mol/L, 6.68 L/mol, 52.9 L/mol and 1.30 for $q_{s,1}$, b_1, b_2 and I_1 on Symmetry, respectively, instead of 0.578 mol/L, 7.60 L/mol, 75.0 L/mol and 0.20 obtained by the IM method. For XTerra, the IM method gave for these same parameters 0.513 mol/l, 8.748 L/mol, 125.7 L/mol and 0.13, while the fitting of the FA data gives 0.643 mol/L, 7.366 L/mol, 90.9 L/mol and 1.42, respectively. This good agreement confirms the validity of the results afforded by the IM method. The main differences observed concern the saturation capac-

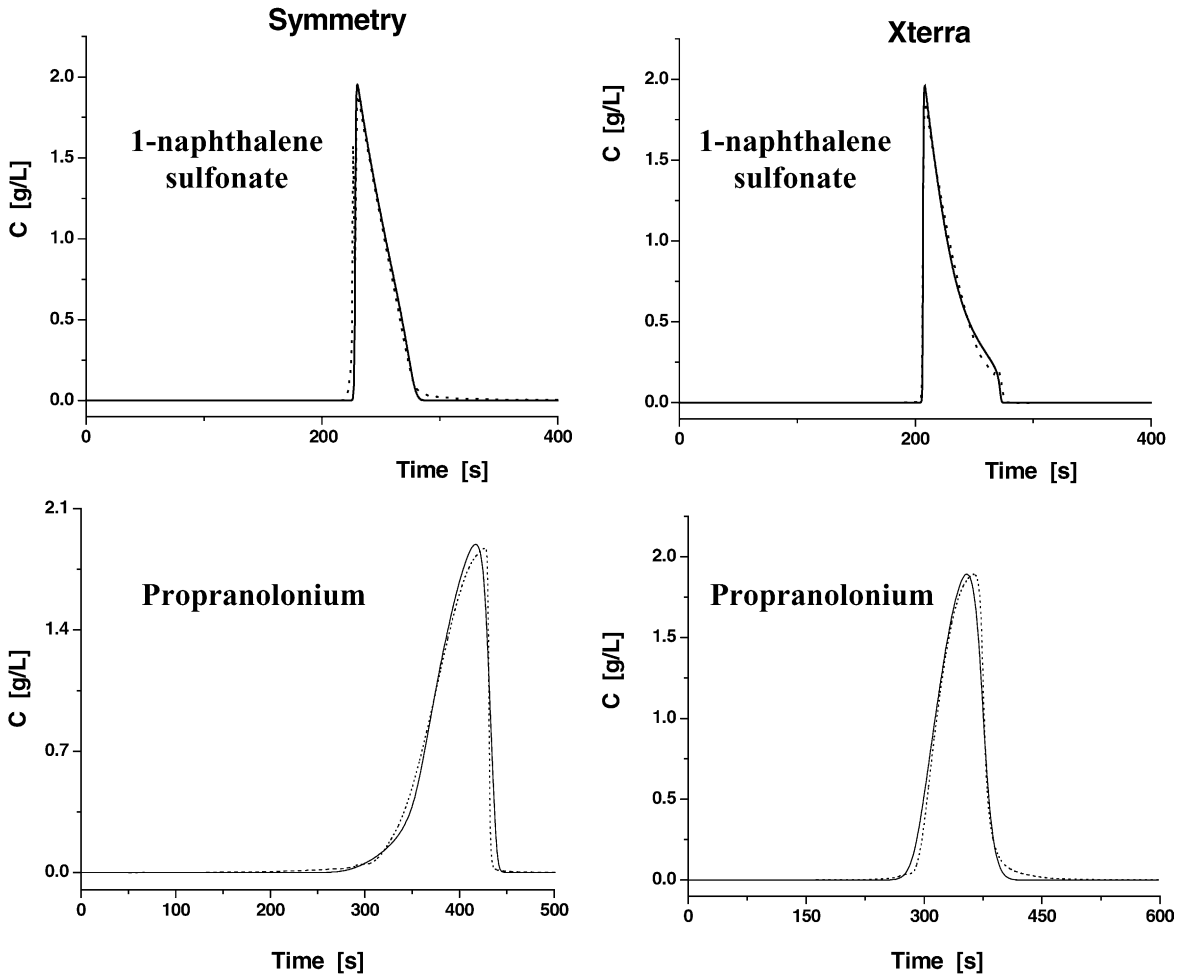

Fig. 3. Experimental (dotted lines) and best calculated (from IM or FA best parameters, solid lines) band profiles of 1-naphthalene sulfonate and propranolol on the Symmetry and XTerra columns. $T = 296$ K, flow rate 1 mL/min. (Top) Injection of 250 μL (from the autosampler to limit the extra-column dispersion) of a 4 g/L solution of 1-naphthalene sulfonate (methanol:water, 10/90, v/v). Note the signature of an anti-langmuirian behavior, according to the change in the shape of the rear of the band profile ($C \leq 0.25$ g/L). The best isotherm parameters derived by the IM are listed in Table 2. (Bottom) Injection (from the pump delivery system) during 60 s of a 2 g/L solution of propranolol chloride (methanol:water, 25/75, v/v). Despite the smoothing of the band along the extra column volume, the band shape is clearly related to anti-langmuirian isotherm.

Table 2
Best isotherm parameters estimated by the inverse method (IM) for isotherm determination

SALT (cation valence)	C_{Salt} (mM)	$q_{s,1}$ (g/L)		b_1 (L/g)		I_1		$q_{s,2}$ (g/L)		b_2 (L/g)		I_2	
		Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra
NaCl (I)	100	151	143	0.140	0.129	0	0	8.3	8.6	5.2	4.9	0	0
	20	165	118	0.068	0.086	0	0	4.4	4.7	10.2	8.9	0	0
	2	122	120	0.040	0.037	0.23	0.43	1.9	2.0	10.5	9.9	0	0
	0	133	118	0.033	0.038	0.20	0.13	1.3	0.4	0.3	0.5	4.6	32.1
NH_4Cl (I)	100	142	133	0.158	0.160	0	0	8.5	8.3	4.9	4.8	0	0
$N(CH_3)_4Cl$ (I)	100	143	133	0.177	0.179	0	0	8.5	8.1	4.3	4.7	0	0
Na_2SO_4 (I)	33	143	135	0.132	0.120	0	0	6.3	7.1	8.2	7.4	0	0
$(NH_4)_2SO_4$ (I)	33	138	112	0.145	0.16	0	0	7.0	7.0	7.4	7.0	0	0
$CaCl_2$ (II)	33	155	134	0.222	0.251	0	0	5.3	4.5	4.1	4.7	0	0
$BaCl_2$ (II)	33	155	132	0.252	0.274	0	0	5.1	4.9	3.4	4.1	0	0
$AlCl_3$ (III)	20	139	132	0.262	0.273	19.1	16.0	1.7	1.5	11.1	11.0	0	0

Optimization made on a band profile recorded after the injection of a 4 g/L solution of sodium 1-naphthalene sulfonate during 15 s. Same ionic strength of 0.1 M for all salts. Methanol:water, 10:90 (v/v).

ity, $q_{s,1}$, and the adsorbate–adsorbate interaction parameter, I_1, on the low-energy adsorption sites. The main reason for these discrepancies is that the IM method determines the values of the parameters that lead to the best agreement between the calculated profile and an experimental band profile whose maximum concentration is much lower than the largest concentration used in FA (2 g/L against 40 g/L). This effect arises as a consequence of the relatively low concentration of the injected band and of its dilution along the column.

The total saturation capacities of the columns ($q_{s,1}$ accounts for more than 97% of the total saturation capacity) derived from the FA data are quite similar on the two columns for propranolol (169 and 146 g/L for Symmetry and XTerra, respectively, or 0.57 and 0.49 mol/L, respectively) and for naphthalene sulfonate (147 and 149 g/L or 0.64 and 0.65 mol/L for Symmetry and XTerra, respectively). The results of a comparison depend on whether the saturation capacity is reported to the mass or to the number of moles adsorbed. This is reasonable since the molecule of propranolol is only slightly larger than that of naphthalene sulfonic acid. The saturation capacities reported in g/L are close to those previously reported for the adsorption of neutral, low molecular mass compounds (e.g., phenol, caffeine, alkylbenzene, alkylbenzoate). These results suggest that both the anion and the cation studied are probably adsorbed as neutral complexes or ion pairs formed with the available co-ions (sodium or chloride). Otherwise, repulsive electrostatic interactions between two adsorbate ions of the same charge would markedly reduce the saturation capacity of the adsorbents. We will discuss further this assumption in the next section in which the influence of different counter-ions and their concentrations on the isotherms of the two ions studied are investigated.

The values of the low-energy adsorption constants of the two compounds are similar ($b_1 \simeq 0.033$ L/g). This result was expected since the mobile phase compositions (10% and 25% methanol) were adjusted in order to give comparable retention factors (around 3). It is noteworthy that the adsorbate–adsorbate interactions on the low-energy sites are much weaker with the sulfonate anion ($I_1 \simeq 1.4$) than with the propranolonium cation ($I_1 \simeq 7$). This small value of the interaction coefficient explains why the isotherm of the sulfonate anion is antilangmuirian in a much narrower concentration range than that of propranolol.

To summarize, the adsorption properties of sodium 1-naphthalene sulfonate and of propranolol chloride are qualitatively very similar on Symmetry-C_{18} and on XTerra-C_{18} in the absence of supporting salt in aqueous solutions of close composition. All sets of FA isotherm data and all band profiles are well accounted for by the bi-Moreau model of isotherm. The numerical values of the saturation capacities, the adsorption energies and the adsorbate–adsorbate interactions, although different for the two compounds, are typical of those derived for neutral compounds. These results suggest that it is unlikely that these ions adsorb as free solvated ions. Although the ions exist in solution, the apolar C_{18} environment favors the formation and adsorption of neutral ion pair complexes between the charged compound studied and the available counter-ions present in the mobile phase. When no supporting salt is added to the mobile phase, the only available counter-ion comes from the salt initially dissolved, e.g., sodium and chloride for naphthalene sulfonate and propranolonium, respectively. The presence of important concentrations of supporting salts must affect the formation of these ion pairs and the equilibrium isotherms of the two compounds.

4.2. Effect of the supporting salt concentration on the overloading behavior of naphthalene sulfonate

Fig. 4 (top) shows the experimental overloaded band profiles of naphthalene sulfonate on XTerra and Symmetry eluted with four different mobile phases having increasing concentrations of sodium chloride (0, 2, 20, and 100 mM). The higher the counter-ion concentration, the higher the band retention. This result could be explained by the parallel increase in concentration of the neutral, highly retained, ion-pair sodium-naphthalene sulfonate. This explanation is supported by the results of the IM applied to these experimental band profiles. The best band profiles calculated with this method, on the basis of a bi-Moreau isotherm model, are shown as the solid lines in Fig. 4 (bottom), to be compared with the experimental band profiles (dotted lines). There is a very good agreement between these calculated profiles and the experimental ones. The best numerical values of the coefficients of the bi-Moreau isotherm model are reported in Table 2. Both the saturation capacity and the equilibrium constant of the low-energy sites (sites 1) increase with increasing concentration of the supporting salt.

A similar behavior was observed in a previous study of the behavior of the organic cation propranolonium (see Fig. 5) [13,14], with potassium chloride as the supporting salt. This shows that, whether the analyte is positively or negatively charged, the equilibrium constant always increases with increasing concentration of the supporting salt. In both cases, the displacement of the equilibrium towards the formation of the ion-pair complex explains this general result.

4.3. Effect of the nature and valence of the supporting salt on the overloading behavior of naphthalene sulfonate

In addition to the monovalent sodium chloride salt, two monovalent salts (NH_4Cl and $N(CH_3)_3Cl$), four bivalent salts (Na_2SO_4, $(NH_4)_2SO_4$, $BaCl_2$ and $CaCl_2$), and one trivalent salt ($AlCl_3$) were used as supporting salts, dissolved in a mobile phase containing 10% methanol. The ionic strength of the mobile phase was kept constant at 100 mM for every salt. Their respective concentrations are given in Table 2. The corresponding overloading band profiles obtained upon injection of 250 μL of a 4 g/L solution of naphthalene sulfonate were recorded. Figs. 6–9 show these chromatograms. Table 2 gives the best values of the parameters of the bi-Moreau isotherm

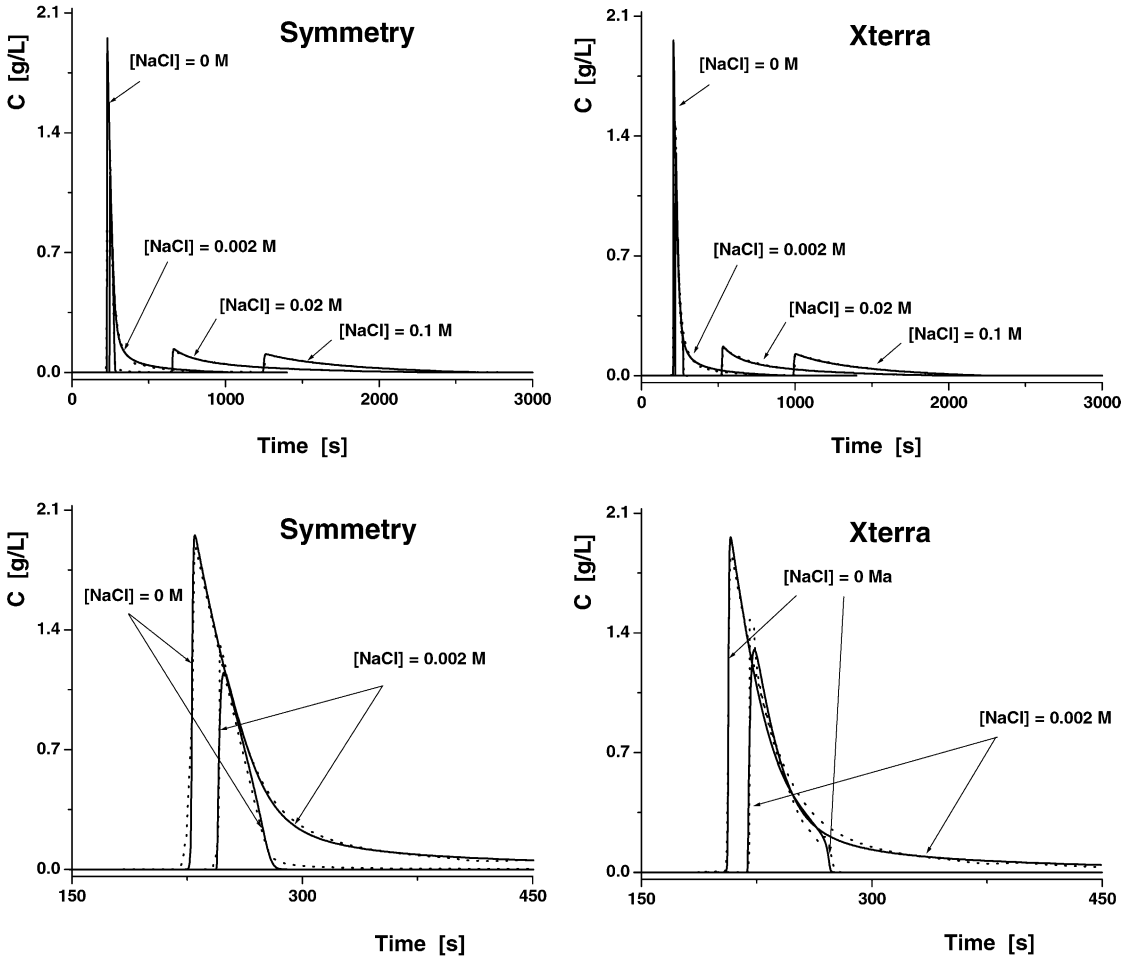

Fig. 4. Evolution of the position and shape of the overloaded band profiles of 1-naphthalene sulfonate (injection of a 4 g/L solution during 15 s) on Symmetry and XTerra as a function of the salt concentration or ionic strength of sodium chloride in the mobile phase (methanol/water, 40/60, v/v). $T = 296$ K, flow rate 1 mL/min. Note that the displacement of the band toward high retention times when the concentration of the salt increases.

model derived from the IM method of isotherm determination.

The shape of all the band profiles is obviously langmuirian within the whole range of concentrations investigated for the monovalent and the bivalent salts (Figs. 6–8). There is an important difference in the behavior of naphthalene sulfonate and of propranolol. Fig. 7 shows a langmuirian behavior for the adsorption of the organic anion in the presence of the bivalent salt disodium sulphate while the parameters in Table 2 confirm a bi-Langmuir isotherm ($I_1 = I_2 = 0$). By contrast, in the presence of the same salt, the cation propranolol exhibits an anti-langmuirian behavior on Kromasil-C_{18}, Symmetry-C_{18}, and XTerra-C_{18} [13,14]. This is confirmed by the value of the isotherm parameter I_1 reported in Table 3, value that is very different from 0. This difference is easily explained. It was shown in this earlier work that the antilangmuirian isotherm behavior of propranolol is explained by the formation of a neutral complex between a sulphate anion and two propranolonium cations. This cannot happen with the negatively charge sulfonic anion and the band profile like the isotherm behavior remain langmuirian.

However, the formation of a 1:2 complex between a bivalent cation and the monovalent sulfonate anion is possible. If this mechanism is correct, we should expect that naphthalene sulfonate exhibits antilangmuirian behavior in the presence of a salt of a bivalent cation, e.g., calcium chloride or barium chloride. This is not so. The band profiles are langmuirian (Fig. 8) and the adsorbate–adsorbate interaction coefficients are equal to 0 (Table 2). However, we note that the equilibrium constant b_1 is larger in the presence of the bivalent cations of $CaCl_2$ and $BaCl_2$ than in that of any of the monovalent cations in NaCl, NH_4Cl, $N(CH3)_4Cl$, Na_2SO_4, or $(NH4)_2SO_4$ (b_1 = 0.25 L/g instead of 0.15 L/g). It might be that only one ion naphthalene sulfonate binds to the cations Ca^{2+} or Ba^{2+} and the complex is neutral because it includes one chloride ion.

Finally, in the presence of a trivalent cation ($AlCl_3$), the adsorption behavior becomes antilangmuirian as expected. This is illustrated by the band profiles in Fig. 9 and by the values of the parameters of the isotherm in Table 3. The behavior of naphthalene sulfonate in this case is most similar to that of propranolol in the presence of salts with a bivalent anion [13,14]. The adsorbate–adsorbate interaction parame-

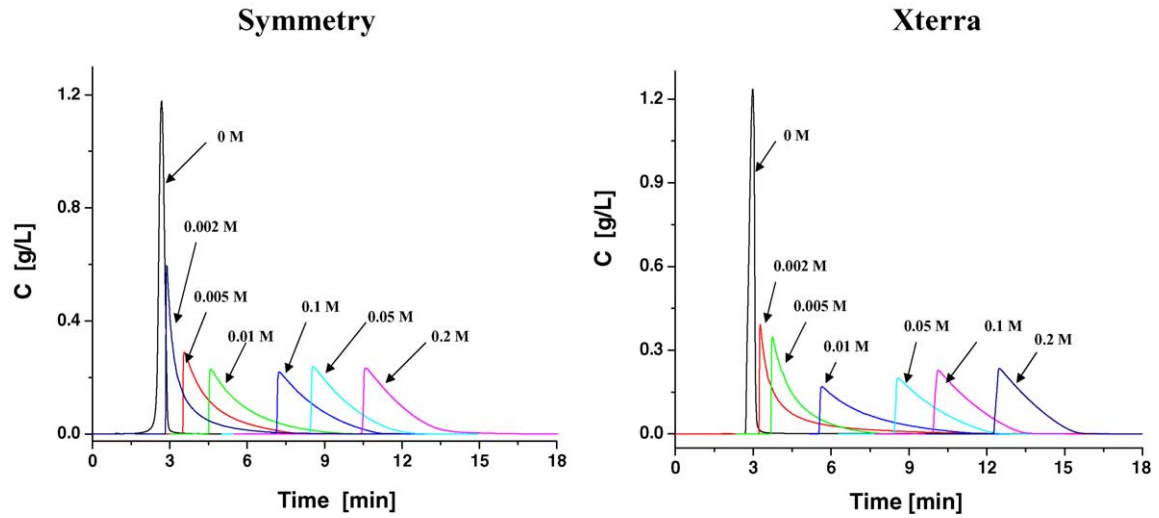

Fig. 5. Same as in Fig. 4, except analyte (propranololium), mobile phase composition (methanol/water, 10/90, v/v) and salt (potassium chloride). Note the same trend as in Fig. 4 when the concentration of the salt is increasing.

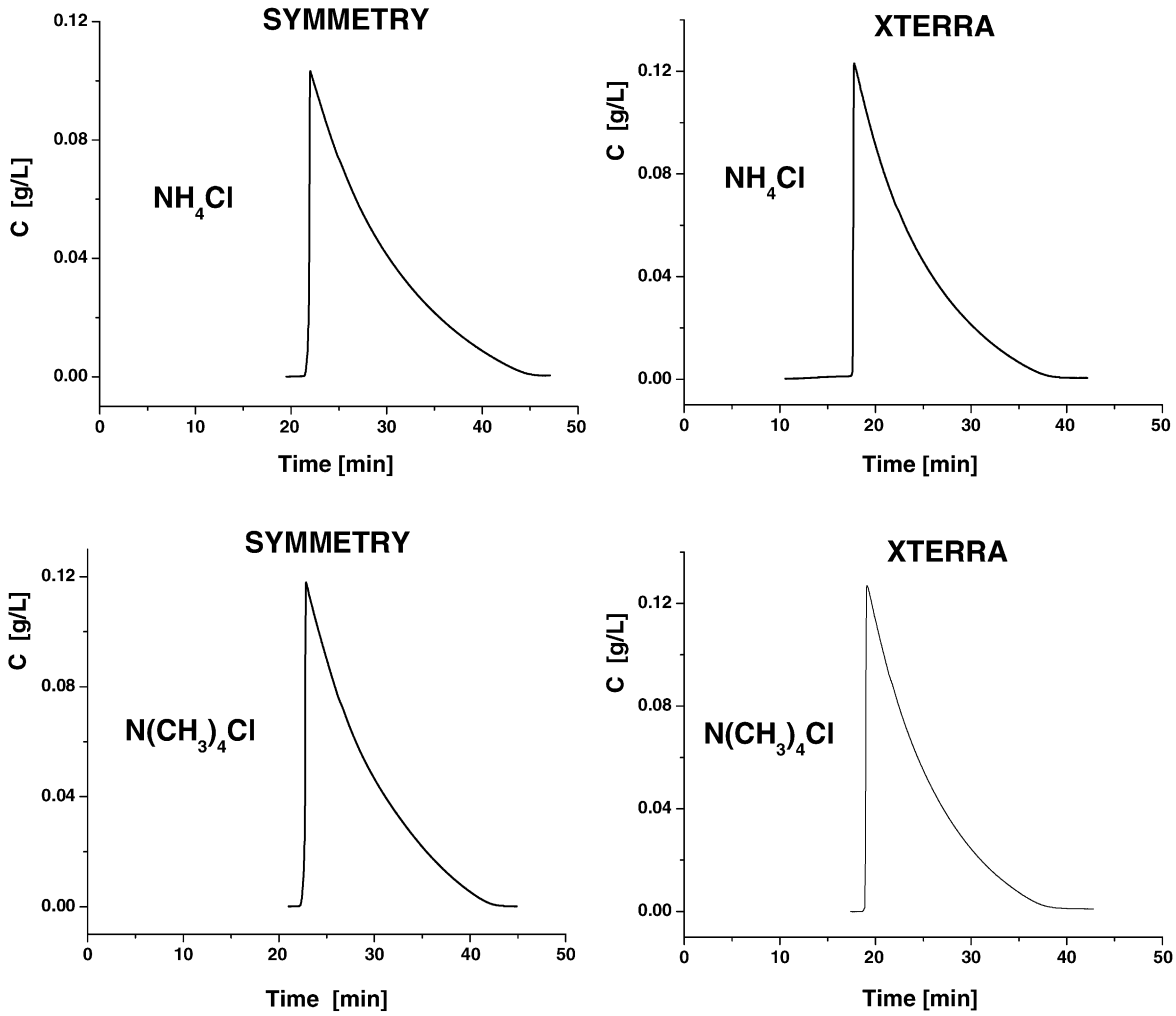

Fig. 6. Experimental band profiles of 1-naphthalene sufonate (injection of 250 μL of a 4 g/L solution) with monovalent cations and anions in the salt (NH_4Cl and $N(CH_3)_4Cl$, 100 mM) on Symmetry and XTerra. $T = 296$ K, flow rate 1 mL/min. Note the classical langmuirian shape and the higher band retention with the more hydrophobic cation in the salt, tetramethylammonium.

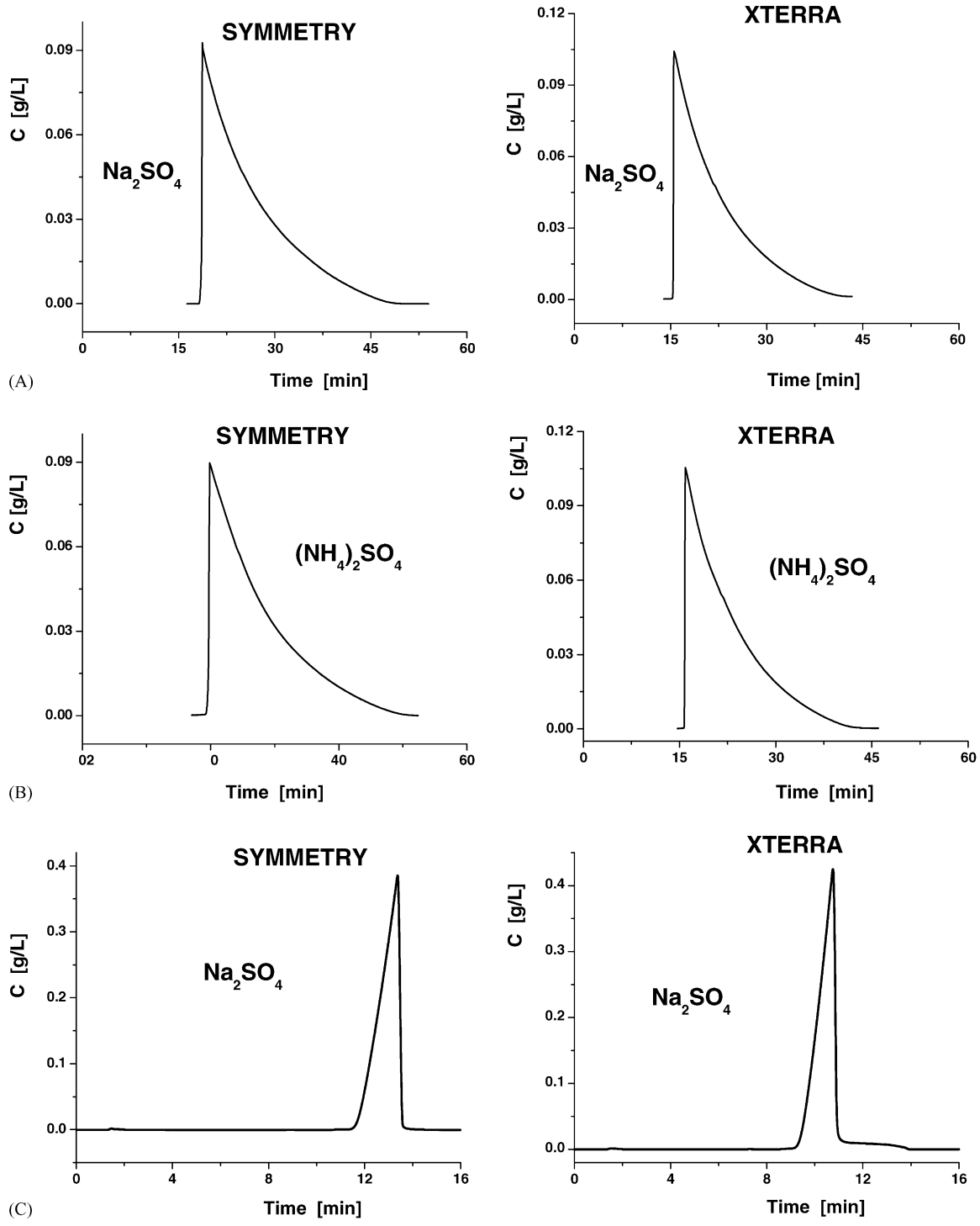

Fig. 7. (A, B) Experimental band profiles of 1-naphthalene sufonate (injection of 250 μL of a 4 g/L solution) with monovalent cations and the same bivalent anion in the salt (Na_2SO_4 and $(NH_4)_2SO_4$, 33 mM). Note, still, the classical langmuirian shape for the band profiles. (C) Experimental band profiles of the positively charged propranololium ion (injection of 250 μL of a 1.5 g/L solution) with Na_2SO_4 (66 mM) as the supporting salt. Note, by contrast to the negatively charged analyte, the antilangmuirian shape of the band profile.

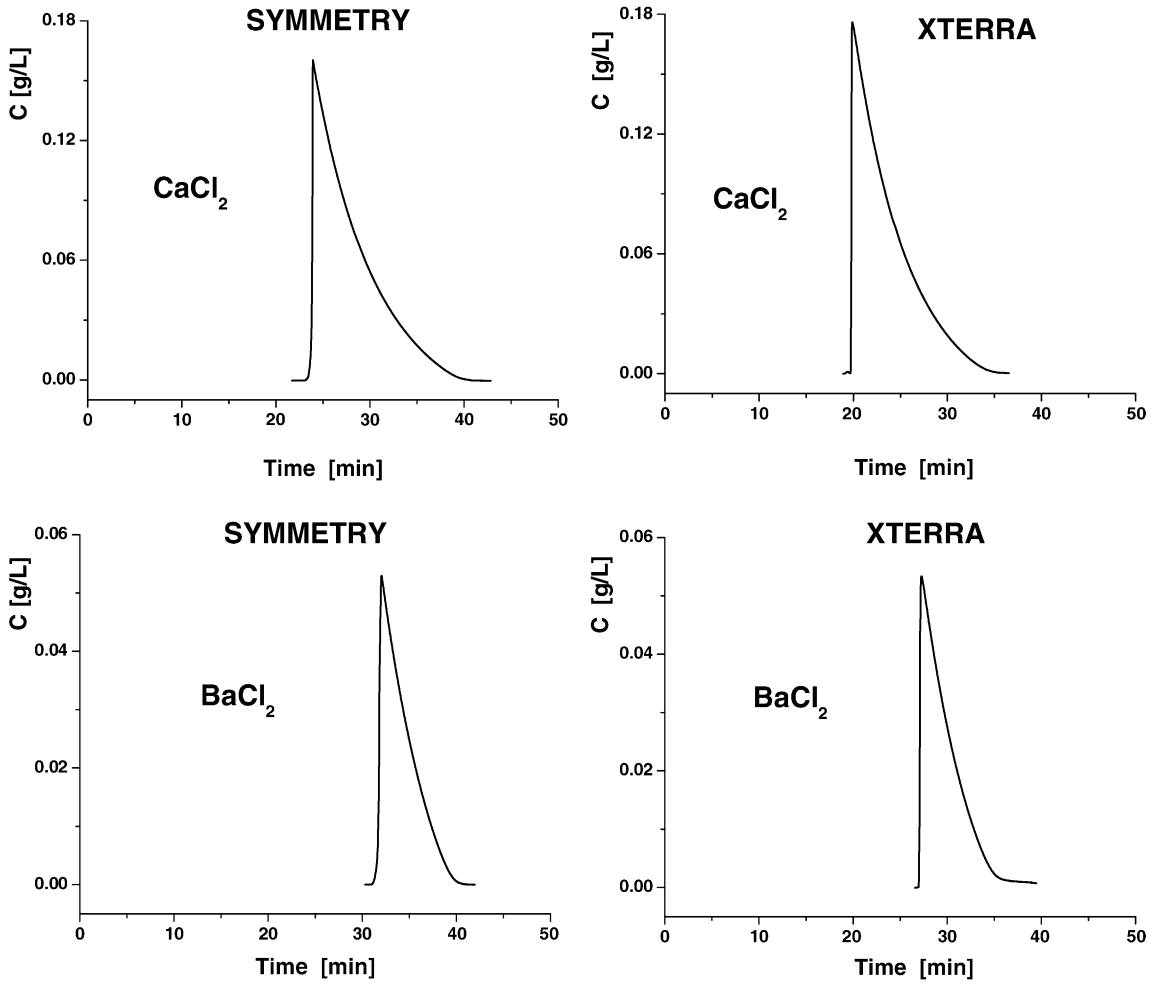

Fig. 8. Same as in Fig. 6, except bivalent cations, e.g. $BaCl_2$ and $CaCl_2$ (injection of a 1 and 4 g/L solution of naphthalene sulfonate, respectively). No change is observed in the shape of the band profile which remain langmuirian.

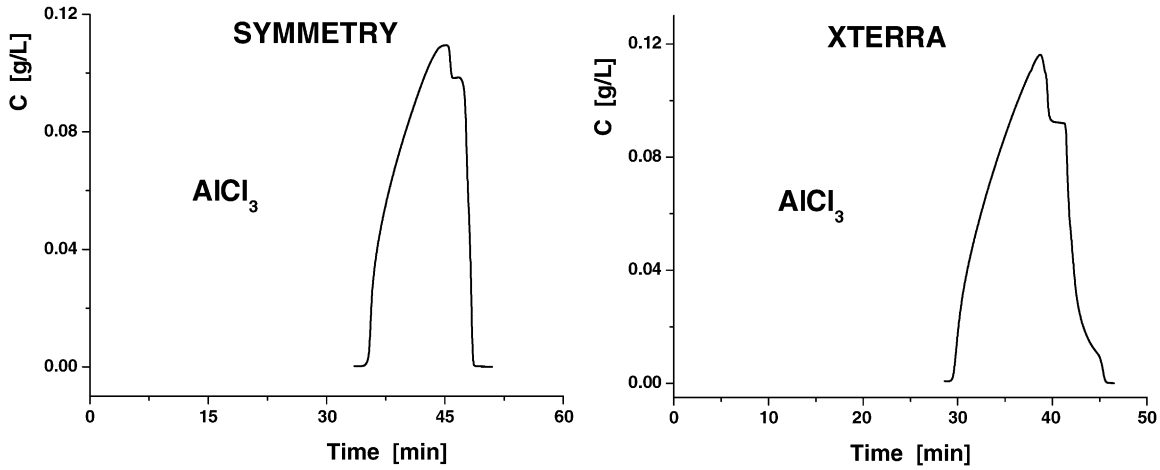

Fig. 9. Same as in Fig. 6, except trivalent cation ($AlCl_3$). Note this time, by comparison to Figs. 7 and 8, the appearance of a complex anti-langmuirian band profiles.

Table 3
Best isotherm parameters estimated by the inverse method (IM) for isotherm determination

SALT (anion valence)	C_{Salt} (mM)	$q_{s,1}$ (g/L)		b_1 (L/g)		I_1		$q_{s,2}$ (g/L)		b_2 (L/g)		I_2	
		Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra	Sym	Xtra
KCl (I)	200	212	192	0.042	0.043	0.1	0.2	16.6	7.4	0.6	1.3	0.09	0.97
	50	158	135	0.025	0.030	1.0	1.6	13.3	4.9	0.8	1.9	0.13	0.52
	2	144	114	0.013	0.014	10.9	11.1	0.9	0.9	14.9	7.9	0.20	0.33
	0	133	113	0.011	0.012	15.2	15.2	0.9	0.7	0.8	0.7	0.66	4.25
NaCl (I)	200	217	208	0.040	0.042	2.0	0.1	15.7	5.7	0.7	1.3	0.07	0.97
CsCl (I)	200	185	167	0.040	0.043	2.0	0.5	15.0	7.7	0.6	1.0	0.09	0.80
$CaCl_2$ (I)	66	195	196	0.038	0.035	$\cong 0$	0.5	14.0	6.4	1.0	1.3	0.34	1.13
Na_2SO_4 (II)	66	177	145	0.085	0.075	5.3	6.2	0.5	0.5	1.7	1.5	$\cong 0$	$\cong 0$

Optimization made on a band profile recorded after the injection of a 1.5 g/L solution of propranololium chloride during 15 s. Same ionic strength of 0.2 M for all salts. Methanol:water, 40:60 (v/v).

ter I_1 reaches the large value of 20 while it was practically to zero with salts of monovalent and bivalent anions. This difference between the behaviors of an organic anion and an organic cation could well be explained by a lower affinity of the sulfonate anion toward common bivalent cations compared to that of propranolol for common bivalent anions. Noteworthy is the decrease of the saturation capacity of naphthalene sulfonate, $q_{s,2}$, from about 8 g/L (monovalent cations) to 5 g/L (bivalent cations) and down to less than 2 g/L for the trivalent cation. The progressively larger size of the ion-pair complexes may restrict more and more the accessibility of the neutral complex to the high-energy sites.

4.4. Effect of the hydrophobicity of the organic salt on the overloading behavior of naphthalene sulfonate

In order to confirm our conclusion regarding the formation of ion-pair complexes for anionic compounds as well as for cationic ones, overloaded band profiles of 1-naphthalene sulfonate were recorded on Symmetry-C_{18} in mobile phases containing organic cations of increasing hydrophobicities. Tetramethylammonium bromide, tetraethylammonium bromide, tetrapropylammonium bromide, and tetrabutylammonium bromide were successively dissolved in a (30/70, v/v) methanol:water solution, for a constant ionic strength of 100 mM (i.e., at the same concentration of 100 mM). It was necessary to increase the methanol concentration of the mobile phase to 30% instead of 10% for the other salts tested, in order to keep the retention time of the anion within reasonable limits and be able to record the four chromatograms with the same methanol concentration. The retention times increased from a few minutes to about 50 minutes when one cation is replaced by the next.

The injection of 250 μL of a 5.75 g/L solution of 1-naphthalene sulfonate was performed and the four corresponding overloaded band profiles were used for isotherm determination using IM. Fig. 10 shows the very good agreement obtained between the best calculated and the experimental band profiles. Since the salt concentration is rather high (100 mM), no adsorbate–adsorbate interactions are expected and the simple bi-Langmuir isotherm model was used to model the adsorption. The band profiles were calculated with the equilibrium-dispersive model. The validity of these choices was confirmed by the shape of the bands, all typical of a convex upward isotherm. The best values obtained for the isotherm parameters are given in Table 4. The saturation capacity $q_{s,1}$ and the equilibrium constant b_1 on the low-energy sites increase with increasing size of the tetraalkyl group, hence with its hydrophobicity. The large increase observed in the retention, hence the adsorption energy of the cation demonstrates that the anion does not adsorb alone but as a complex or ion-pair formed with the counter-cation tetraalkylammonium. Surprisingly, the saturation capacity of the adsorbent increases with increasing size of the ion-pair complex.

It is also remarkable that the high-energy sites disappear progressively when the size of the organic cation increases.

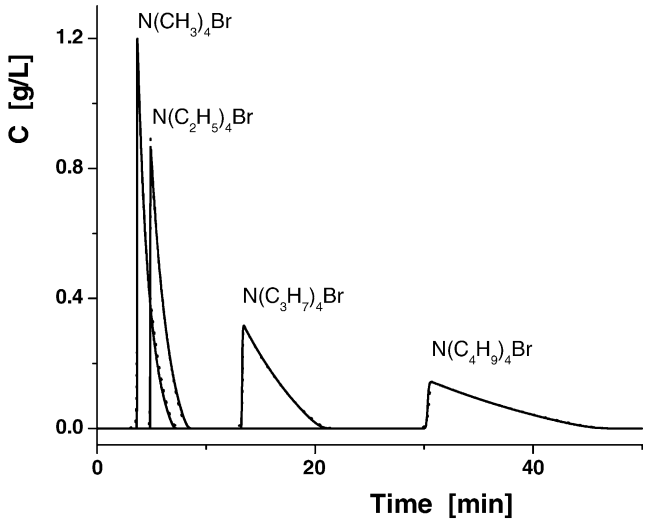

Fig. 10. Comparison between the best calculated (IM, solid lines) and the experimental (dotted lines) overloaded band profiles of 1-naphthalene sulfonate eluted with four different tetraalkylammonium salts (NR_4Br, R=-CH_3, -C_2H_5, -C_3H_7, -C_4H_9) on Symmetry-C_{18}. $T = 296$°K, flow rate 1 mL/min. Methanol:water mobile phase (30/70, v/v). Note the shift of the band profiles towards higher retention time with larger R alkyl groups.

Table 4
Best isotherm parameters estimated by the inverse method (IM) for isotherm determination

SALT	C_{Salt} (mM)	$q_{s,1}$ (g/L)	b_1 (L/g)	$q_{s,2}$ (g/L)	b_2 (L/g)
$N(CH_3)_4Br$	100	54.9	0.08533	3.7	1.06
$N(C_2H_5)_4Br$	100	59.0	0.1316	2.3	1.21
$N(C_3H_7)_4Br$	100	72.7	0.3905	0.4	1.05
$N(C_4H_9)_4Br$	100	86.3	0.7681	0	/

Optimization made on a band profile recorded after the injection of a 5.75 g/L solution of sodium 1-naphthalene sulfonate during 15 s. Same ionic strength of 0.1 M for all salts. Methanol:water, 30:70, (v/v).

The surface of the adsorbent becomes more and more homogeneous toward the ion-pair and a simple Langmuir isotherm model accounts well for the adsorption behavior of the sulfonate anion with tetrabutylammonium as the counter-ion. As shown for neutral molecules, progressive exclusion from the high-energy sites on the adsorbent might be the consequence of the increasing molecular size of the ion-pair complex. Noteworthy are also the low values of the saturation capacities in the presence of tetraalkylammonium salts in the mobile phase (between 55 and 87 g/L, Table 4) compared to those measured in the presence of inorganic salts (around 130 g/L, Table 2). The competition for adsorption between the tetraalkylammonium salt in a large excess and 1-naphthalene sulfonate may explain this difference between the saturation capacities. Tetraalkylammonium salts have been known for a long time to adsorb on their own on hydrophobic surfaces.

5. Conclusion

Our results confirm and extend some of our previous results regarding the adsorption behavior of organic cations [13,14] by showing the great similarities between this behavior and that of an organic anion, sodium naphthalene sulfonate. This suggests that the thermodynamics of adsorption is very similar for organic anions and cations.

In a mobile phase without salt, the best isotherm model is the bi-Moreau model, as shown by the FA and IM methods. The addition of increasing concentrations of salt into the mobile phase causes a progressive decrease of the adsorbate–adsorbate interactions and the evolution of the isotherm from a bi-Moreau to a bi-Langmuir model (with no adsorbate–adsorbate interactions). The increase of the salt concentration in the mobile phase affects similarly the equilibrium isotherm behavior and the overloaded elution band profiles of the organic cation and that of the anion. The saturation capacities of the two isotherm terms increase, the adsorbate–adsorbate interactions decrease, the equilibrium constant on the low-energy sites increase and that on the high-energy sites decrease (Tables 2 and 3).

A retention mechanism based on the formation of a neutral ionic complex in the adsorbed phase is consistent with all the observations made, the evolution of all the parameters measured, and the progressive changes in the overloaded band profiles reported for either the anionic or the cationic compound, in the whole range of concentrations and nature of the various salts dissolved in the mobile phase. This is also confirmed by the close values obtained for the saturation capacities of the anion and the cation on the two commercial columns used in this work (XTerra-C_{18} and Symmetry-C_{18}) and for several neutral compounds. The higher the valence of the counter-ion in the complex, the higher the likelyhood of the binding of more than one organic ion in the adsorbed complex, resulting in an anti-langmuirian behavior of the analyte. Bivalent anions with propranolol, trivalent cations with naphthalene sulfonate cause a strong anti-langmuirian behavior. This suggest that different compounds, having different affinities for the co-ions, will differ quantitatively in their adsorption behavior. The systematic acquisition of numerical results is needed to clarify this situation.

These results are not consistent with reports that the column loadability is much lower for ionizable compounds than for neutral ones. Work is in progress attempting to clarify the reasons for this apparent contradiction. For preparative purposes, it is clear that the mobile phases used for the purification of ionic compounds should contain sufficiently concentrated buffers or supporting salts and preferably use co-ions with a high valence. These buffers or supporting salts should preferentially derive from co-ions having a high affinity for the stationary phase (strong hydrophobicity and high polarizability) to keep a high loading capacity and, in the same time, avoid the high buffer concentration that could be inconvenient for further desalting process or even detection.

Acknowledgments

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