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Extension of the electrostatic retention model of reversed-phase ion-pair chromatography to include the simultaneous effects of the organic modifier and the pairing ion

AKOS BARTHA[a] and GYULA VIGH*
Chemistry Department, Texas A&M University, College Station, TX 77843-3255 (U.S.A.)
and
JAN STÅHLBERG[b]
Astra Pharmaceutical Production AB, Sjödertälje (Sweden)

SUMMARY

The electrostatic retention model of reversed-phase ion-pair chromatography is extended to include the simultaneous effects of the organic modifier and the pairing ion on both the adsorption of the pairing ion and the retention of charged solutes. A linear relationship is obtained between solute retention and the concentration of both the organic modifier and the pairing ion. Both the intercept and the slope values of the extended retention equation increase for the oppositely charged and decrease for the similarly charged solutes when a pairing ion is added to the eluent. The slope reflects the reversed-phase chromatographic retention of the solute and the solvent dependence of the adsorption term of the pairing ion. The intercept depends on the type of the organic modifier and both the concentration and hydrophobicity of the pairing ion. Qualitative and quantitative predictions made by the extended model agree well with the experimental results obtained with binary mixtures of aqueous buffers and three common organic modifiers, methanol, acetonitrile and tetrahydrofuran.

INTRODUCTION

In reversed-phase chromatography (RPC), the logarithm of the capacity factor (k') of non-ionic solutes is often described as a linear function of the concentration (φ) of the organic modifier in the eluent[1,2]:

$$\ln k'(\varphi) = \ln k'_{wB} - S\varphi \quad (1)$$

where k'_{wB} is the capacity factor of solute B in water and S is a constant for a given

[a] On leave from the University of Chemical Engineering, Veszprem, Hungary.
[b] Affiliated to the Institute of Physical Chemistry, University of Uppsala, Uppsala, Sweden.

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solute–solvent combination. Extensive retention data sets are available and have been analysed to determine the effects of type and/or strength of the organic solvent. Differences in the slopes (S) of the ln k' *vs.* φ plots of closely related solutes have been utilized to optimize their separation.

In reversed-phase ion-pair chromatography (RP-IPC), mixtures of non-ionic, ionic and/or ionizable components are usually separated by varying the pH and/or the concentration of the pairing ion, while the concentration of the organic modifier is used only to control the solvent strength of the eluent. However, mixtures of ionic solutes with similar charge and structure often cannot be separated adequately without at least exploiting[3–6] or, better, optimizing[7–10] the selectivity-modifying effects of organic solvents.

In RP-IPC, the organic modifiers decrease the retention of ionic solutes through at least two effects, via the decreased hydrophobic adsorption of the solutes and the decreased surface concentration of the adsorbed ion-pairing reagent[1]. As a result, in the presence of a pairing ion, the retention of ionic solutes varies more rapidly with φ than that of the uncharged solutes[3,12]. Owing to the paucity of relevant data, the effects of the type and concentration of the organic modifier on the retention and selectivity changes of charged solutes have not yet been evaluated systematically in RP-IPC, and the current retention models of RP-IPC could not include the simultaneous effects of the pairing ion and the organic modifier.

Stahlberg and co-workers, using the Gouy–Chapman theory, developed an electrostatic model[13–18] to describe both the adsorption isotherms of the pairing ions and the retention of ionic solutes as functions of the mobile phase concentration of the pairing ion. This model is extended in this paper to incorporate the effects of the type and concentration of the organic modifier into the adsorption isotherm equations of the pairing ions and the retention equations of charged solutes. Predictions made by the model are compared with experimental data obtained using methanol, acetonitrile and tetrahydrofuran as organic modifiers and sodium octylsulfonate and decylsulfonate as ion-pairing reagents.

THEORY

According to the electrostatic model of RP-IPC[13–15], the adsorbed hydrophobic pairing ions and their counter ions form an electrical double layer at the surface of the stationary phase and create a surface potential (ψ_0) between the surface of the stationary phase and the bulk of the mobile phase. The retention of ionic solutes depends both on their hydrophobicity and ψ_0. The capacity factor (k'_{cB}) of ionic solute B of charge z_B is

$$k'_{cB} = k'_{0B} \exp(-z_B F\psi_0/RT) \tag{2}$$

where k'_{0B} is the capacity factor of solute B in the absence of a hydrophobic pairing ion, F is the Faraday constant, R is the gas constant and T is the absolute temperature.

When an organic modifier of concentration φ is added to the eluent, both k'_{0B} and ψ_0 change. In the absence of pairing ions, k'_{0B} varies with φ as

$$k'_{0B}(\varphi) = \Phi \exp[-\Delta G^0_B(\varphi)/RT] \tag{3}$$

where Φ is the phase ratio and ΔG^0_B is the free energy of adsorption of solute B.

ψ_0 is related to the surface concentration, n_A, of the adsorbing hydrophobic pairing ion according to eqn. 4, obtained by solving the linearized Poisson–Boltzman equation for cylindrical surfaces (*i.e.*, idealized porous particles)[14,15]:

$$\psi_0 = (z_A n_A F I_0)/(\kappa \varepsilon_0 D_e I_1) \tag{4}$$

where z_A is the charge of pairing ion A, κ is the reciprocal Debye length, I_0 and I_1 are the modified Bessel functions of the first kind of order zero and one, respectively, ε_0 is the permittivity of vacuum and D_e is the dielectric constant of the eluent. When n_A is much lower than the monolayer capacity of the stationary phase, n_0, the surface potential-modified adsorption isotherm of the pairing ion becomes

$$n_A = n_0 K_{As} c_A \exp(-z_A F \psi_0 / RT) \tag{5}$$

where K_{As} is the adsorption constant and c_A is the mobile phase concentration of the pairing ion. K_{As} depends on the type and concentration of the organic modifier:

$$K_{As} = \exp[-\Delta G^0_A(\varphi)/RT] \tag{6}$$

where $\Delta G^0_A(\varphi)$ is the free energy of adsorption of the pairing ion. With this, k'_{cB} as a function of c_A becomes

$$\frac{z_A}{z_B} \ln\left(\frac{k'_{cB}}{k'_{0B}}\right) + \ln\left[-\frac{RT}{z_A z_B F} \ln\left(\frac{k'_{cB}}{k'_{0B}}\right)\right] = \ln\left[\frac{I_0 F}{I_1 \kappa \varepsilon_0 D_e} c_A\right] + \ln(n_0 K_{As}) \tag{7}$$

This expression is valid only for non-zero pairing ion concentrations.

In order to include the concentration of the organic modifier in eqn. 7, let us approximate the second term on the left-hand side as

$$\ln[\ln(k'_{cB}/k'_{0B})] \approx \ln(k'_{cB}/k'_{0B}) - 1 \tag{8}$$

The relative error of this approximation is less than 25% when $1.6 < k'_{cB}/k'_{0B} < 6$. A relative retention change of this magnitude corresponds to a pairing ion surface concentration change of 10–100 μmol/g[16], meaning that the expressions derived here are valid only at non-zero mobile phase concentrations and low surface concentrations of the pairing ion, and for a 2–6-fold relative change in solute retention. As such, they are considered first-order approximations which, nevertheless, reveal the relative significance of the different parameters in the control of solute retention and separation selectivity in RP-IPC.

For the sake of clarity, separate expressions are obtained for the oppositely charged ($k'_{cB} > k'_{0B}$) and the similarly charged ($k'_{cB} < k'_{0B}$) ionic solutes. When there is a unit charge of identical sign on both the pairing ion and the solute ion (*i.e.*, $z_A = z_B = \pm 1$), eqn. 7 can be rewritten (for $c_A > 0$) as

$$\ln k'_{cB} = \ln k'_{0B} - \tfrac{1}{2} \ln\left[\frac{I_0 F^2 \exp(1)}{I_1 \kappa \varepsilon_0 D_e RT} c_A\right] - \tfrac{1}{2} \ln(n_0 K_{As}) \tag{9}$$

When there is a unit charge of opposite sign on both the pairing ion and the solute ion ($z_A = -z_B = \pm 1$), eqn. 7 can be rewritten (for $c_A > 0$) as

$$\ln k'_{cB} = \ln k'_{0B} + \tfrac{1}{2} \ln \left[\frac{I_0 F^2 \exp(1)}{I_1 \kappa \varepsilon_0 D_e RT} c_A \right] - \tfrac{1}{2} \ln (n_0 K_{As}) \qquad (10)$$

Both equations consist of three terms, the sum of which gives the retention of an ionic solute as a function of the mobile phase concentrations of both the pairing ion and the organic modifier. "Regular" RPC solute retention is decreased (eqn. 9) or increased (eqn. 10) by the addition of a pairing ion (second and third terms).

In order to evaluate eqns. 9 and 10, the dependence of their terms on the type and concentration of the organic modifier and the concentration of the pairing ion was studied. As the ionic strength of the mobile phase influences the coefficient of c_A in the second term, its value was kept constant throughout this study.

EXPERIMENTAL

The test solutes were obtained from Janssen (Beerse, Belgium). Sodium octylsulfonate ($OctSO_3$) and decylsulfonate ($DecSO_3$) were purchased from Merck (Darmstadt, F.R.G.). Distilled, deionized water, HPLC-grade organic solvents methanol (CH_3OH), acetonitrile (ACN), tetrahydrofuran (THF) and analytical-reagent grade buffer components were used for eluent preparation. The mobile phase concentration of the organic solvent was varied in the ranges 0–40% (v/v) for methanol, 0–28% (v/v) for ACN and 0–25% (v/v) for THF. The aqueous buffer (pH 2.1) contained 25 m*M* H_3PO_4, 25 m*M* NaH_2PO_4 and various concentrations of sodium bromide and sodium octylsulfonate (ion-pairing reagent). The inorganic counter ion (sodium) concentration was kept constant at 175 m*M* by varying the concentration ratio of sodium bromide and the pairing ion. ODS-Hypersil (5 μm) stationary phase (Shandon, Runcorn, U.K.) with a BET surface area of 173 m^2/g (according to the manufacturer), was slurry packed into 120 × 4.6 mm I.D. stainless-steel columns. An LC 5560 liquid chromatograph, equipped with UV (254 nm) and refractive index (RI) detectors (all from Varian, Walnut Creek, CA, U.S.A.) and two Model 7010 six-port injection valves (Rheodyne, Cotati, CA, U.S.A.), was used. Columns were thermostated at 25°C. Both the breakthrough curves of the pairing ions (in order to determine their excess surface concentrations) and the capacity factors of the solutes could be determined by this system[11].

RESULTS AND DISCUSSION

Effects of the type and concentration of the organic modifier on the adsorption of the pairing ion

In Fig. 1, the surface concentration (n_A) of sodium octylsulfonate is plotted against the concentration of (a) methanol (0–40%), (b) ACN (0–28%) and (c) THF (0–25%) at constant eluent concentrations of the pairing ion (c_A = 1, 2, ..., 70 m*M*). The plots are similar to those for tetrabutylammonium bromide[11]: at a given c_A value, n_A decreases as the polarity of the solvent decreases (CH_3OH > ACN > THF).

In order to determine the value of the $n_0 K_{As}$ [(μmol/g)/m*M*] parameter of the

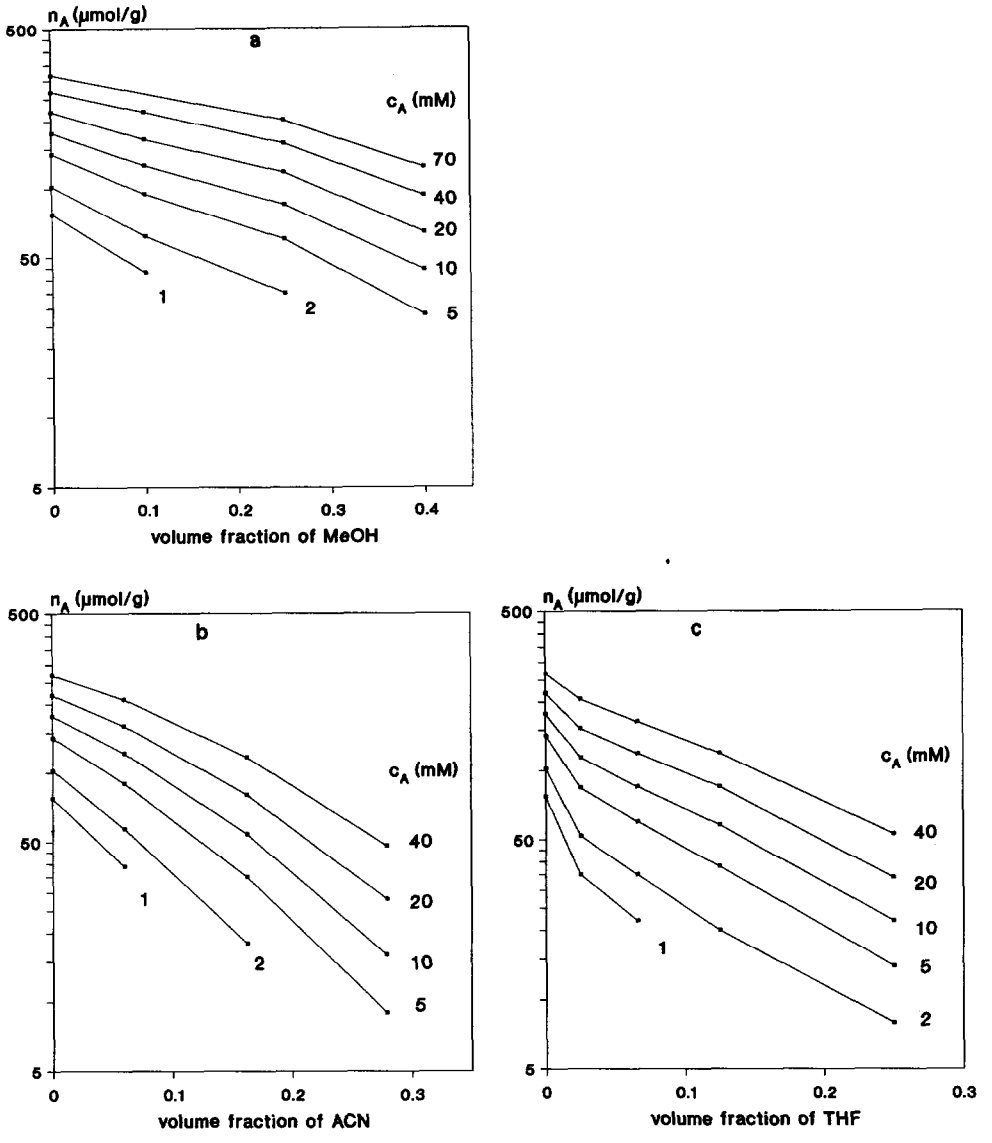

Fig. 1. Surface concentration (n_A, μmol/g) of sodium octylsulfonate as a function of the concentration of (a) methanol, (b) acetonitrile and (c) tetrahydrofuran at different eluent concentrations (c_A, m*M*) of the pairing ion. Aqueous buffer: pH 2.1, 25 m*M* H_3PO_4, 25 m*M* NaH_2PO_4,150 m*M* constant ionic strength (maintained with NaBr). Stationary phase: ODS-Hypersil (5 μm). Column temperature: 25°C. MeOH = Methanol.

adsorption isotherm of sodium octylsulfonate (eqn. 5), the surface potential values were calculated from experimental retention data of ionic solutes as described in refs. 13–18. For improved precision, an average ψ_0 value, obtained with a positively and a negatively charged solute, was used in the calculations. The ln (n_0K_{As}) values

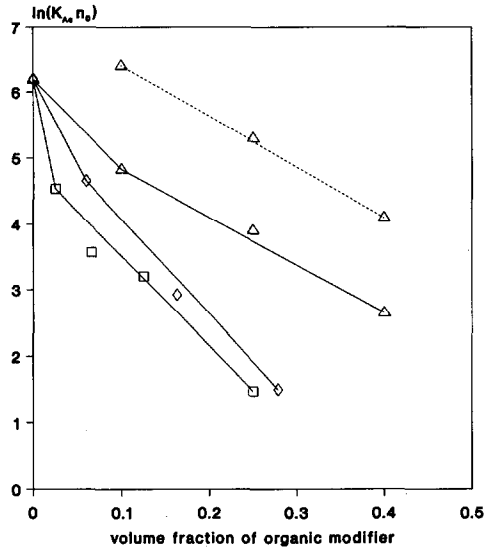

Fig. 2. The adsorption term [ln (n_0K_{As})] of sodium octyl- (solid lines) and decylsulfonate (dashed line) as a function of the (△) methanol, (◇) acetonitrile and (□) tetrahydrofuran concentrations in the eluent. Conditions as in Fig. 1.

calculated from Fig. 1a–c and the ψ_0 values of octylsulfonate are plotted in Fig. 2 against φ for methanol, ACN and THF as organic modifier. Fig. 2 also contains data for sodium decylsulfonate as ion pairing reagent and methanol as modifier. The octyl- and decylsulfonate plots differ only in their intercepts, but not in their slopes.

After an initial, steep decrease in water-rich eluents, ln (n_0K_{As}) decreases almost linearly with φ (over a limited concentration range), permitting the use of the following approximation (for $n_0K_{As} > 0$):

$$\ln (n_0K_{As}) = C - D\varphi \tag{11}$$

where C and D are constants for a given pairing ion–organic modifier combination. Coefficients C and D, calculated by linear regression from Fig. 2, are listed in Table I.

TABLE I

SLOPE (D) AND INTERCEPT (C) VALUES AND CORRELATION COEFFICIENTS (r) OF THE ln (n_0K_{As}) *vs.* φ RELATIONSHIP FOR SODIUM OCTYLSULFONATE ($OctSO_3$) AND DECYLSULFONATE ($DecSO_3$) WITH METHANOL, ACN AND THF AS ORGANIC MODIFIERS

Modifier	φ	*Pairing ion*	C	D	r
CH_3OH	0.1–0.4	$OctSO_3$	5.61	−7.26	0.996
CH_3OH	0.1–0.4	$DecSO_3$	7.18	−7.66	0.999
ACN	0.06–0.28	$OctSO_3$	5.42	−14.33	0.995
THF	0.02–0.13	$OctSO_3$	4.69	−12.8	0.937

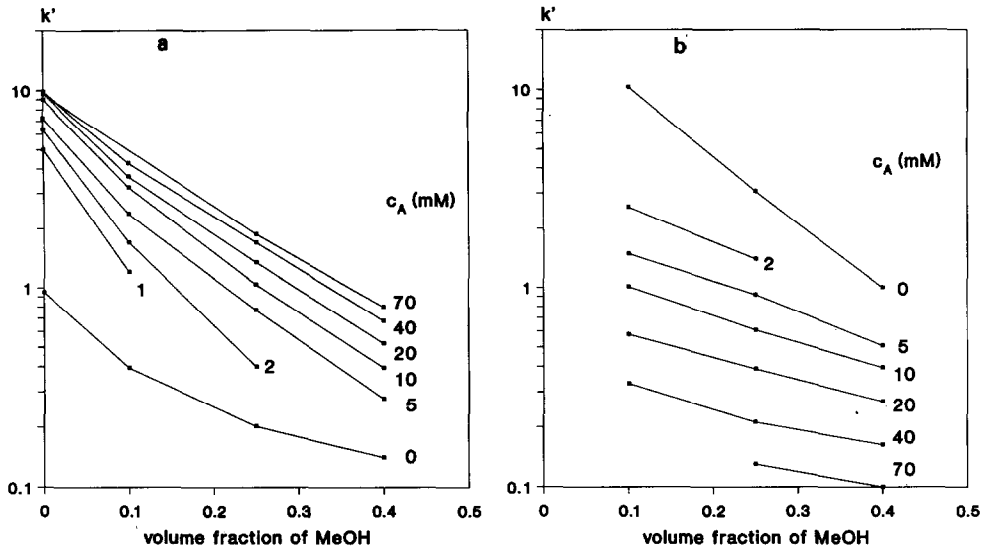

Fig. 3. Retention of the (a) octopamine and (b) 2-naphthalenesulfonate ions as a function of the methanol concentration of the eluent at c_A = 0, 1, 2, ..., 70 m*M* concentration of sodium octylsulfonate.

Effects of the concentration of the organic modifier on the retention of charged solutes

In Fig. 3, the k' vs. φ data for the positively charged octopamine and negatively charged 2-naphthalenesulfonate ions are shown for octylsulfonate as pairing ion at c_A = 0, 1, ..., 70 m*M* and methanol as organic modifier. Octopamine becomes more retained and 2-naphthalenesulfonate less retained in the presence of the pairing ion. The retention shifts are larger ($\Delta \ln k' \approx 1$) at low φ ($0 < \varphi < 0.1$), and smaller ($\Delta \ln k' \approx 0.6$) at larger φ ($0.1 < \varphi < 0.4$).

According to the electrostatic model of RP-IPC, these retention differences are related to the surface potential. ψ_0, in turn, depends on both n_A and D_e (eqn. 4). As the organic modifier affects n_A, κ and D_e, and through them ψ_0, plotting ln k' from Fig. 3 as a function of φ at constant n_A (determined from the adsorption isotherms in Fig. 1a–c) should reveal the relative roles of n_A and D_e. The retention plots shown in Fig. 4 are almost parallel, suggesting that solute retention depends primarily on the surface concentration of the hydrophobic pairing ion. The dielectric constant-related variations of k', predicted by eqn. 4 (through κ and D_e), more or less compensate each other. Analysis of the analogous retention plots obtained with acetonitrile and tetrahydrofuran gave similar results.

Simultaneous effects of the pairing ion and the organic modifier on the retention of ionic solutes

The concentration of the organic modifier can be introduced into eqns. 9 and 10 as an explicit variable by noting that ln k'_{0B} is a linear function of φ (eqn. 1), ln ($n_0 K_{As}$) is a linear function of φ (eqn. 11) and the dielectric constant-related effects of the eluent largely cancel each other (Fig. 4), *i.e.*, the coefficient of c_A in eqns. 9 and 10 is constant (K_1).

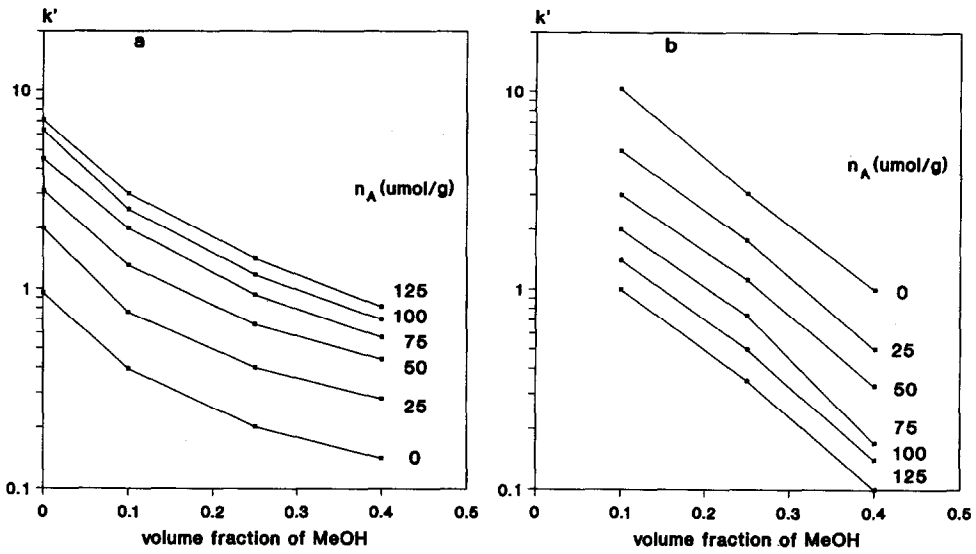

Fig. 4. Retention of (a) octopamine and (b) 2-naphthalenesulfonic acid as a function of the methanol concentration of the eluent at zero and constant (n_A = 25, 50, ..., 125 μmol/g) stationary phase concentrations of sodium octylsulfonate.

Substitution of eqns. 1 and 11 into eqns. 9 and 10 results in

$$\ln k'_{cB} = (\ln k'_{wB} - S\varphi) - 1/2 \ln (K_1 c_A) - 1/2 (C - D\varphi) \quad (12)$$

for solutes and pairing ions with a unit charge of identical sign and

$$\ln k'_{cB} = (\ln k'_{wB} - S\varphi) + 1/2 \ln (K_1 c_A) + 1/2 (C - D\varphi) \quad (13)$$

for solutes and pairing ions with a unit charge of opposite sign. After rearrangement:

$$\ln k'_{cB} = \ln k'_{wB} - 1/2 \ln K_1 - 1/2 \ln [\exp(C)] - 1/2 \ln c_A - (S - 1/2\, D)\varphi \quad (14)$$

when $z_A = z_B = \pm 1$, and

$$\ln k'_{cB} = \ln k'_{wB} + 1/2 \ln K_1 + 1/2 \ln [\exp(C)] + 1/2 \ln c_A + (S + 1/2\, D)\varphi \quad (15)$$

when $z_A = -z_B = \pm 1$.

Obviously, eqns. 14 and 15 apply only for $c_A > 0$. When there is no pairing ion present, eqn. 1 must be used instead of eqns. 14 and 15. In agreement with experimental data[8], both the intercept (first four terms) and slope (fifth term) of the ln k' *vs.* φ function decrease (for $z_A = z_B = \pm 1$) or increase (for $z_A = -z_B = \pm 1$) as pairing ion is added to the eluent.

The slope is independent of the concentration, but not of the hydrophobicity of the pairing ion. It is smaller by 1/2 D than the "regular" RPC slope (Eqn. 1) for $z_A = z_B$ and larger by 1/2 D for $z_A = -z_B$. The predicted slope values are compared with the

TABLE II

COMPARISON OF THE EXPERIMENTAL AND THE PREDICTED SLOPE VALUES OF THE ln k' *VS.* φ RELATIONSHIP FOR NEGATIVELY CHARGED, POSITIVELY CHARGED AND UNCHARGED SOLUTES

Eluents: 0 and 5 m*M* sodium octylsulfonate, $0.1 < \varphi_{CH_3OH} < 0.4$ ($D = -7.2$), $0.06 < \varphi_{ACN} < 0.28$ ($D = -14.4$), $0.02 < \varphi_{THF} < 0.13$ ($D = -12.8$).

Solute	$0.1 < \varphi_{CH_3OH} < 0.4$				$0.06 < \varphi_{ACN} < 0.28$				$0.02 < \varphi_{THF} < 0.13$			
	$c_A = 0$ m*M* $- S_{RP}$	$c_A = 5$ m*M* $- S_{IPC}$		*Rel. difference (%)*	$c_A = 0$ m*M* $- S_{RP}$	$c_A = 5$ m*M* $- S_{IPC}$		*Rel. difference (%)*	$c_A = 0$ m*M* $- S_{RP}$	$c_A = 5$ m*M* $- S_{IPC}$		*Rel. difference (%)*
		Exp.	*Calc.*			*Exp.*	*Calc.*			*Exp.*	*Calc.*	
Phenol	4.6	4.5	–	–	6.8	6.3	–	–	2.3	2.2	–	–
2-Naphthalene-sulfonic acid	7.3	3.5	3.7	+ 6	14.6	8.1	7.4	− 9	12.5	6.7	6.1	−10
Phenylalanine	6.1	10	9.7	− 3	12.9	18.5	20.1	+ 9	9.4	15.4	15.8	+ 3
Octopamine	4.7	8.2	8.3	+ 1	9.3	13.7	16.5	+20	6.7	11.3	13.1	+16
Tyrosine	6.7	10.2	10.3	+ 1	16.4	22.9	23.6	+ 3	17.9	22.6	24.3	+ 8
Norephedrine	4.9	10	8.5	−15	8.2	15.9	15.4	− 3				
Tryptophan	7.6	11.7	11.2	− 4	11.4	17.2	18.6	+ 7				
Morphine	7.8	10.5	11.4	+ 9								
Dopamine					15.1	19.6	22.3	+10	10.6	15.9	17	+ 7
Isoprenol									13.5	17	19.9	+17

TABLE III

D VALUES CALCULATED FROM THE RETENTION DATA FOR FIVE POSITIVELY CHARGED SOLUTES WHICH WERE OBTAINED WITHOUT AND WITH 1 m*M* SODIUM DECYLSULFONATE AS PAIRING ION IN $0.1 < \varphi_{CH_3OH} < 0.4$ AQUEOUS BUFFER ELUENTS (pH 2.1)

Solute	$c_A = 0$ *mM* $-S_{RP}$	$c_A = 1$ *mM* $-S_{IPC}$	*D*
o-Cresol	6.0	5.2	–
3,4-Dihydroxyphenylalanine	7.2	10.4	−6.4
Tyrosine	6.7	10.7	−8
Adrenaline	4.4	8.4	−8
Dopamine	5.6	10	−8.8
Phenylalanine	6.1	10.7	−9.2
Average			−8.1

experimental values in Table II for uncharged, positively charged and negatively charged solutes, with octylsulfonate as the pairing ion and methanol, ACN and THF as organic modifiers. The relative error between the predicted and experimental slope values varies between ±1 and 20%, indicating that secondary effects (*e.g.*, changes in the nature of the octadecylsilica surface due to adsorption of the pairing ion) can also contribute significantly to solute retention.

Eqn. 14 or 15 can also be used to determine the value of *D* from solute retention data obtained in the absence and presence of pairing ions. The ln *k'* vs. φ_{CH_3OH} values of five positively charged solutes obtained with and without decylsulfonate pairing ions were used to calculate the slope and *D* values listed in Table III. The average *D* value is −8.1, which agrees within 6% with *D* (−7.66) calculated from the adsorption data (Fig. 2).

It was reported[19] that there are no large selectivity differences for closely related solutes when a pairing ion is replaced with a homologous one (*e.g.*, alkylsulfonates). This observation can be rationalized by Fig. 2 and eqns. 14 and 15: only coeffcient *C*, but not coefficient *D* in eqn. 10 is changed when a pairing ion is replaced by a more hydrophobic member of the same homologous series ($D = -7.26$ for octylsulfonate and $D = -7.66$ for decylsulfonate).

According to eqns. 14 and 15, the intercept is a sum of four terms. The first, $\ln k'_{wB}$, depends only on the solute, the second, $\ln (K_1)$, depends only on the eluent, the third, $\ln [\exp(C)]$, depends on the type, but not the concentration of the pairing ion, and the fourth depends linearly on $\ln c_A$. Therefore the ln *k'* *vs.* $\ln c_A$ plots of a charged solute obtained with two different pairing ions (1 and 2) are parallel with a retention shift of

$$\Delta \ln k'_B(\varphi) = 1/2\,(C_2 - C_1) + 1/2\,(D_2 - D_1)\varphi \qquad (16)$$

The shift is negative for $z_A = z_B = \pm 1$ and positive for $z_A = -z_B = \pm 1$.

These predictions are substantiated by the ln *k'* *vs.* c_A plots of the positively charged norephedrine and the negatively charged cresol red ions in Fig. 5 with octyl- and decylsulfonate as pairing ions and methanol as organic modifier ($\varphi_{CH_3OH} = 0.4$).

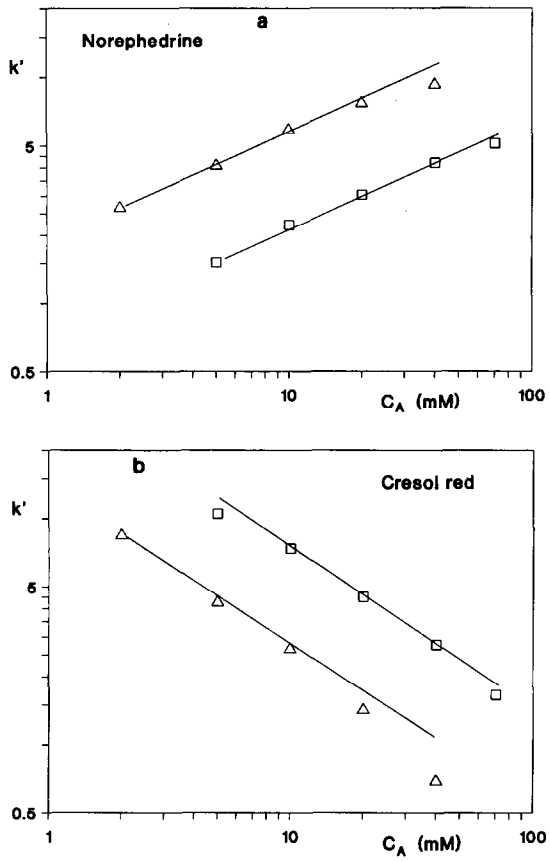

Fig. 5. Retention of (a) norephedrine and (b) cresol red as a function of the mobile phase concentration of the (□) octysulfonate and (△) decylsulfonate pairing ions in 40% methanol–aqueous phosphate buffer (pH 2.1) eluents.

These solutes were not included in the previous calculations of coefficients C and D for the two pairing ions. The slope values are 0.45 for norephedrine and −0.65 for cresol red, both slightly different from the theoretical value of 0.5. The experimental $\Delta \ln k'$ is 0.97 for norephedrine and −1.02 for cresol red, again both slightly different from the theoretical value of 0.89 (calculated from Table I and eqn. 16). The deviations are believed to stem from the linearization of the rigorously non-linear equations, as discussed in ref. 14.

CONCLUSIONS

The electrostatic retention model of RP-IPC has been extended to account for the simultaneous effects of the pairing ion and the organic modifier on the retention of ionic solutes. Retention equations were derived assuming that the relative retention changes do not exceed the 2–6-fold range (*i.e.*, the surface concentration of the pairing ion is between 10 and 100 μmol/g), there is a linear relationship between ln k' of the

solute and the concentration of the organic modifier (for $\varphi < 0.4$) in the "regular" reversed-phase mode, there is a linear relationship between the adsorption term of the pairing ion and the concentration of the organic modifier (for $\varphi < 0.4$) and changes in the dielectric constant of the eluent do not influence the surface potential significantly.

According to the extended retention equation, both the slope and the intercept of the ln k' vs. φ relationship increase for oppositely charged solutes and decrease for similarly charged solutes when a pairing ion is added to the eluent. The slope depends on the original (reversed-phase) retention behavior of the solute and the organic solvent dependence of the adsorption term of the pairing ion. The intercept depends on the original (reversed-phase) retention of the solute in water, the type of the organic modifier and the hydrophobicity and the mobile phase concentration of the pairing ion. Predictions made by the extended equations agree well, both qualitatively and quantitatively, with experimental data observed with methanol, acetonitrile and tetrahydrofuran as organic modifiers and alkylsulfonates as pairing ions.

The extended retention model indicates that solvent strength effects depend not only on the organic modifier, but also on the charge type of the solutes and the adsorption characteristics of the pairing ion. The new retention equations can be used to determine the initial conditions of eluent optimization in reversed-phase ion-pair chromatography, provided that the charge-type and the "regular" reversed-phase retention behavior of the solutes are known.

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