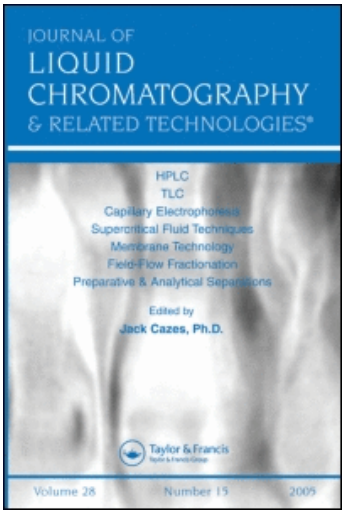

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MIGRATION BEHAVIOR MODELING OF ANIONIC SPECIES IN A HYDROORGANIC BACKGROUND ELECTROLYTE

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ABSTRACT

The migration of benzoate derivatives in a hydroorganic background electrolyte (BGE) was predicted using a novel mathematical model. In capillary electrophoresis (CE), with an acetonitrile (ACN)/buffer mixture as BGE, the influence of pH and the ACN cluster fraction can be quantitatively described by a general equation which was used to study the separation optimization. The cluster solute solvation energies in an ACN/buffer mixture over a 0.50-0.80 buffer fraction were calculated.

The energetics of the ACN cluster exchange process in the BGE was investigated in relation to the difference in pK_a (ΔpK_a) between a solute used as reference and the other solutes. A linear correlation was found between the Gibbs free energy change of the solvent exchange process and ΔpK_a confirming that the solute solvation by ACN clusters was enhanced for the lesser polar solutes.

Enthalpy-entropy compensation revealed that the solute solvation mechanism was independent of both the benzoate derivative structure and the BGE ionic strength.

INTRODUCTION

The vast majority of capillary electrophoresis (CE) separations have been performed using buffers as background electrolytes (BGE). The addition of organic solvents to the BGE has been studied in capillary zone electrophoresis[1-3] (CZE) and micellar electokinetic chromatography[4,5] and the concentration of organic modifier rarely exceeded[6,7] 40%.

Wright and co-workers[6] evaluated acetonitrile, formamide, methanol, DMF, and DMSO, without the addition of supporting electrolytes as solvents for non aqueous CE separations. The exact structure of an organic modifier (OM) in a mixture with water has been the subject of much theoretical, and experimental interest.[7-16] Its real nature depends on the hydrogen bond which exists between the OM and the water. Methanol interacts with water to form clusters of methanol-water.[14-16]

For acetonitrile (ACN), which creates few hydrogen bonds, a model was developed to describe the existence of pockets of ACN called clusters.[7] When a weak polar solute is introduced into such a mixture, it is solvated preferentially by the OM and/or the clusters. For chromic acid ions, the different solvation energies have been evaluated in methanol/water systems at different temperatures.[17] The same data have also been determined in an ACN/water mixture for a series of benzodiazepines and alkylbenzoate esters using a high performance liquid chromatography technique.[18]

The electrolyte buffer is the most flexible variable in CE.[19-21] The pH, the concentration, and the type of buffer can all significantly influence the mobility of a solute. The effect of pH on the mobility of weakly acidic and basic solutes has been described in the literature.[22-26] Buffer concentration and ionic strength have been noted to have significant effect on solute mobility. Higher ionic strength buffers and organic modifier have been used to concentrate or "stack" sample components on the capillary.[27,28] However, an understanding of the effects of pH buffer, its ionic strength, and OM concentration on solute mobility is lacking.

Only a few studies have reported the effect of buffer on the mobility. Many of the studies which purported to discuss this effect only report the effect of buffer concentration on apparent mobility.[29-31] Apparent mobility is related to both the solute and the electroosmotic mobility. The ionic strength effect on the larger electroosmotic flow mobility overwhelms and obscures the ionic strength

effects on the solute mobility. The most widely used model considers that the effective electrophoretic mobility μ_e of a solute is a weighted average of the μ_e of its different forms in the BGE.[21,32,33]

This work explains the influence of pH, OM, and ionic strength on solute effective electrophoretic mobility using a novel theoretical model.

Mathematical Model

Migration Equation for Benzoate Derivative

In a hydroorganic mixture, the ACN molecules are organized in pockets or loosely defined clusters.[11-13] An equilibrium model has been developed to describe this molecular association:[7]

$$n(ACN) \leftrightharpoons U \quad (1)$$

$$U = (ACN)n \quad (2)$$

n is the ACN molecule number in a cluster.[7]

For an anionic species, the migration is described, in an ACN/buffer mixture as BGE by the equilibria shown in Figure 1. As this figure shows, the activity of the protons is dominated by the « non-cluster solvated » protons, while HA acid and conjugate base A^- are solvated by p_{HA}=p and p_{A^-}= p' clusters[34] in the BGE.

$$HA + pU \leftrightharpoons \langle HA \rangle \quad (3)$$

$$A^- + p'U \leftrightharpoons \langle A^- \rangle \quad (4)$$

The symbols < > indicate the ACN cluster solvated species. It could be expected[34] that p'<p on the basis of a greater affinity of the cluster solvated protonated species than the cluster solvated anion.

The equilibria between the concentration of HA and A^- (non-cluster solvated) and <HA> and <A^-> (cluster solvated) in the ACN/water mobile phase can be related by the following equations:[34]

$$A^1 + H^+ \leftrightharpoons HA \quad (5)$$

$$\langle A^- \rangle + H^+ + (p'-p)\,U \leftrightharpoons \langle HA \rangle \quad (6)$$

The equilibrium constants for Eqs.3, 4, 5 and 6 are:

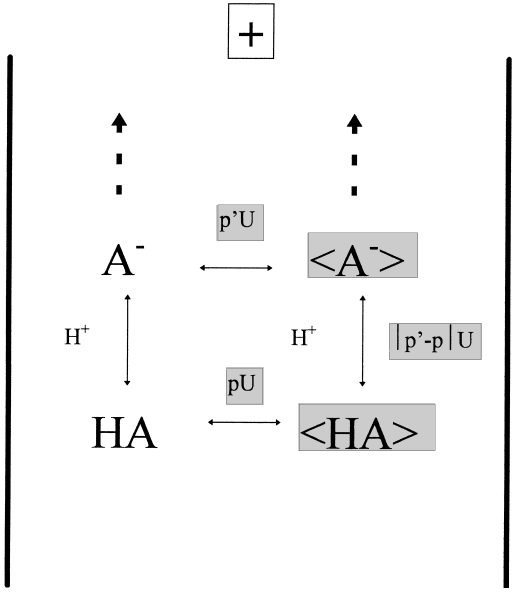

Figure 1. Proposed model of anionic species migration in CE using an ACN/buffer BGE (non-cluster ACN/water mixture in white and ACN cluster in gray tint).

$$K_{<HA>} = [<HA>]/([HA][U]^{p}) \quad (7)$$

$$K_{<A^->} = [<A^->]/([A^-][U]^{p'}) \quad (8)$$

$$K_{\alpha} = [HA]/([A^-][H^+]) \quad (9)$$

$$K_{\alpha'} = [<HA>]/([<A^->][H^+][U]^{(p'-p)}) \quad (10)$$

The forms $<A^->$ and A^- are in rapid dynamic equilibrium with one another[34] and migrate in the electric field as one uniform substance. Thus, the effective electrophoretic mobility was given by:

$$\mu_e = \alpha_{<A->}\mu_{<A->} + \alpha_{A-}\mu_{A-} \quad (11)$$

where α_{A-} and $\alpha_{<A->}$ are the molar fraction of the individual forms A^- and $<A^->$.

Thus, using the constants 7, 8, 9, and 10 and Eq.11, the effective electrophoretic mobility μ_e for the benzoate derivatives is

$$\mu_e = \mu_{<A->}/(1+K_\alpha[H^+]/K_{<A->}[U]^{p'}+[U]^{p'}/K_{<A->}+K_{\alpha'}[H^+][U]^{(p'-p)})+\mu_{A^-}/(1+K_\alpha[H^+] +K_{\alpha'}[H^+][U]^{(p'-p)}+K_{<A->}[U]^{p'}) \quad (12)$$

μ_{A^-} and $\mu_{<A->}$ are the limiting electrophoretic mobility of the benzoate derivatives and its solvated species. Equation 12 can be used to describe the effective electrophoretic mobility of an ionizable solute. The unknown constants can be calculated according to this model by using weighted non linear regression.[18,34,37]

Intrinsic Selectivity Optimization

The effective electrophoretic selectivity, α_e, between two solutes defined as the ratio of their effective electrophoretic mobilities was used as a picture of the role of both ACN fraction and pH on the separation quality.

The entire separation quality of 12 benzoate derivatives was assessed by means of a response function ξ defined as:[27]

$$\xi = \mathrm{Min}(\alpha_e) \quad \text{if} \quad \mathrm{Min}(\alpha_e)<\alpha_l$$

$$\xi = \alpha_l+1/t_a \quad \text{if} \quad \text{not} \quad (13)$$

where $\mathrm{Min}(\alpha_e)$ is the effective selectivity for the worst separated pair of peaks on the electropherogram. α_l was called the limit effective selectivity and is the minimum value of the selectivity accepted. In our application, α_l was 1.05. Therefore, if the effective selectivity for the worst separated pair of peaks on the electropherogram was lower than the chosen limit effective selectivity, then the ξ function would be equal to the effective selectivity. If not, separation conditions were obtained and then the analysis time t_a intervened in the form $1/t_a$.

The analysis time t_a depends on the apparent selectivity μ_a of the last peak on the electropherogram by the equation:

$$t_a = L_t L_d/(V\mu_a) \quad (14)$$

where L_t is the total capillary length and L_d is the capillary length to the detector and V the applied voltage. The ξ function was maximal when both efficient separation conditions and a minimal analysis time were obtained.

Simplex Optimization

To optimize the ξ function a simplex method[27] was used. The ξ value was calculated for m set of starting conditions, where m was given by the number of factors to be optimized (ACN fraction and pH) plus 1. Therefore, in this case, m was three. The point corresponding to the lowest value of ξ was then reflected in relation to the surface defined by the three other points to give a fourth set of starting conditions.

Once again, the point with the lowest ξ was reflected and the process repeated sequentially until the same values for pH and ACN fraction continued to be selected.

Solute Solvation Energies in an ACN/Water Mixture

$\Delta G°_{<A->}$, $\Delta H°_{<A->}$, $\Delta S°_{<A->}$ are the Gibbs free energy, enthalpy, and entropy for the anionic species solvation by the ACN clusters.

These energies can be determined using the well known thermodynamic equation:

$$\ln K = - \Delta H°/(RT) + \Delta S°/R \quad (15)$$

For an equilibrium physicochemical process of the K constant:

$$\ln K = -\Delta G°/(RT) \quad (16)$$

$$\partial(\Delta G/T)/\partial T = -\Delta H/T^2 \quad (17)$$

EXPERIMENTAL

Apparatus

CE separations were carried out using an automated CE apparatus (Beckman, Pace 550, Paris, France). The capillaries used were 57 cm (50 cm to the detector) 75 μm i.d. The following conditions were applied: capillary thermostated at 25°C unless otherwise specified; UV detection at 214 nm; 2s pressure injection of benzoate derivative solution dissolved in the BGE. The voltage used was 30 kV.

Reagents

Sodium benzoate salt (1) and its derivatives: 2-amino-(2), 3-amino-(3), 4-amino-(4), 2-nitro-(5), 3-nitro-(6), 4-nitro-(7), 2-chloro-(8), 3-chloro-(9), 4-

chloro-(10), 3-hydroxy-(11), 4-hydroxy-(12) were obtained from Merck (Nogent-sur-Marne, France). Fresh samples were prepared daily at a concentration of 10^{-4} M.

All chemicals employed were of analytical grade. Water was obtained from an Elgastat option water purification system (Odil, Talant, France), fitted with a reverse osmosis cartridge. Potassium phosphate buffers were prepared from potassium phosphate and potassium dihydrogen orthophosphate. Potassium hydroxide and phosphoric acid were used to adjust the pH buffer.

Buffer series were prepared over a range of ionic strengths from 0.01 M to 0.1 M by dilution of the stock buffer solutions (0.1 M). Its pH was adjusted to one of the following pH values : 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10, and 10.5. Each buffer was allowed to stand at ambient temperature and its pH was measured after standing for 1, 2, and 4 hours. No pH fluctuations were observed and the pH of each buffer was within 0.4% of the desired value.

The BGE consisted of a mixture of acetonitrile and the potassium phosphate buffer. The variation range of the potassium phosphate buffer fraction in the BGE was 0.50 to 0.80. Each solute of a concentration of 10^{-4} M dissolved in the BGE was injected and the migration times were measured**.**

Temperature Studies

Compound migration times were determined over the temperature range 25° to 55°C. It is to be noted that the maximal temperature for the experiments had to be 20° to 30°C lower than the boiling point of the organic modifier (82°C for ACN)[38]. The electrophoretic system was allowed to equilibrate at each temperature for at least 1 hour prior to each experiment.

To study this equilibrium process, the migration time of benzoate was measured every hour for seven hours and again after 20, 21, and 23 hours. The maximum relative difference of the migration time of this compound between these different measurements was always 0.4%, making the electrophoretic system sufficiently equilibrated for use after 1 hour.

All the solutes were injected, in triplicate, at each temperature, pH, and phosphate buffer fraction value

Determination of Effective Mobility

The effective mobility μ_e of an analyte was calculated from the migration time of the analyte (t_m) and the migration of the electroosmotic flow (t_{eof}) using the following equation:

$$\mu_e = \frac{L_t L_d}{V}\left(\frac{1}{t_m} - \frac{1}{t_{eof}}\right) \quad (18)$$

t_{eof} was determined using a neutral marker as mesityl oxide.

RESULTS AND DISCUSSION

Validation of the Benzoate Derivative Migration Model (Eq. 12)

A migration time at 25°C and I = 0.1 M for each of the solutes was determined for a wide variation range of buffer fractions Φ ($0.50 \leq \Phi \leq 0.80$) in the ACN/buffer mixture and pH ($5 \leq pH \leq 10.5$). Thirty one Φ values and 12 pH values were included in this range. For each Φ value, the corresponding value of the cluster concentration had been previously determined[7,34,37]. All the experiments were repeated three times.

The coefficient variations of the μ_e value were < 1% in most cases, indicating a high repeatability and good stability of the electrophoretic system. Using a weighted non linear (WNLIN) regression,[18,37] the data were fitted to eq. 12. The correlation between predicted and experimental μ_e values was excellent for the model. The slope and r^2 values were equal to 1.000 and 0.994, respectively (Figure 2).

Intrinsic Selectivity Optimization

In all cases, whatever pH and ACN fraction values, the 12 benzoate derivatives were arranged in the same order on the electropherogram. The μ_a logarithm for the last compound was modeled by a two-order polynomial:[27]

$$\ln\mu_a = a_0 + a_1\ln\Phi + a_2\ln pH + a_{11}(\ln\Phi)^2 + a_{22}(\ln pH)^2 + a_{12}(\ln\Phi)(\ln pH) \quad (19)$$

where a_0, a_1, a_2, a_{11}, a_{22}, a_{12}, are constants. The correlation coefficient was 0.999. The student t-test confirmed that μ_a was dependent on both pH and Φ values. Knowing the variation of the effective electrophoretic mobility (eq. 12) of the 12 solutes and the analysis time with pH and Φ (eqs. 14 and 19), the ξ values (eq. 13) can be given for different values of the two factors.

The results of the simplex process are given in Table 1. The corresponding electropherogram is given in Figure 3. The results confirmed the interest to use hydroorganic BGE to preserve capillary efficiency.[27]

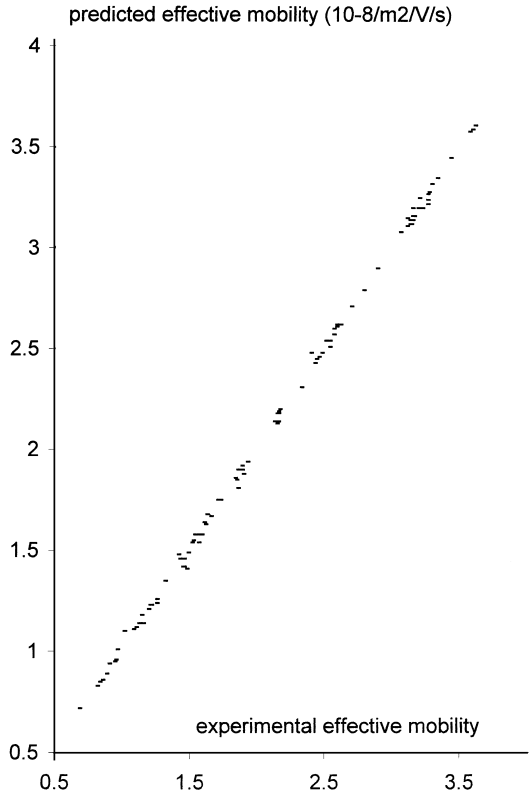

Figure 2. Correlation between the predicted (eq.12) and the experimental electrophoretic mobilities for the twelve benzoate derivatives. The slope is 1.000 with a correlation coefficient of 0.994, as determined by linear regression.

Energetics of Species ACN Cluster Solvation in Model System

To investigate the dependence of the temperature on the migration model, the previous experiments carried out at 25°C and I = 0.1 M were repeated at 6 other temperatures (20°C, 30°C, 35°C, 40°C, 45°C, and 50°C). The model parameters (eq.12) corresponding to each temperature were determined. The different van't Hoff plots (eq.15) for all the samples, as well as the different chemical solvation processes, were determined.

The correlation coefficients for the linear fits were in excess of 0.987. The typical standard deviation of slope and intercept were, respectively, 0.003 and 0.01. When the solute benzoate acid was taken into consideration, the enthalpy

Table 1

Results of the Simplex Process

pH	ACN Fraction	ξ
5.10	0.20	1.00
5.40	0.25	1.00
5.45	0.28	1.00
5.54	0.33	1.00
7.45	0.20	1.00
6.38	0.35	1.01
7.58	0.28	1.00
8.00	0.35	1.02
8.58	0.31	1.03
9.14	0.37	1.04
9.25	0.25	1.02
10.14	0.33	1.05
9.45	0.44	1.06
10.44	0.38	1.05
10.50	0.49	1.04
9.84	0.48	1.04
9.74	0.46	1.05
9.80	0.52	1.07
9.90	0.48	1.08
9.92	0.41	1.11
9.94	0.43	1.12
9.92	0.51	1.09
9.95	0.46	1.11
9.74	0.44	1.11
9.70	0.48	1.10
9.71	0.46	1.12
9.70	0.45	1.13
9.73	0.44	1.13
9.70	0.44	1.13
9.71	0.44	1.13
9.74	0.47	1.13
9.70	0.44	1.13

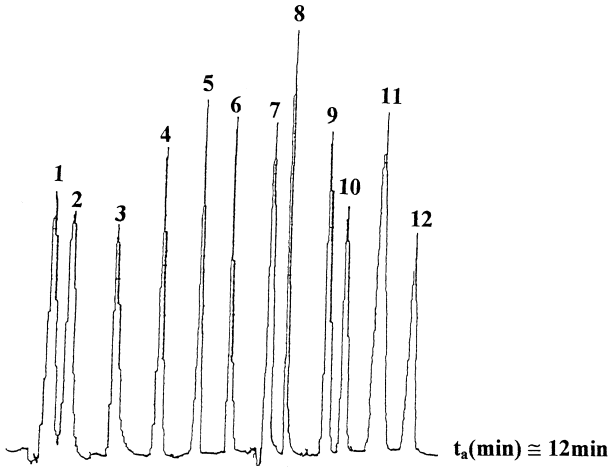

Figure 3. Representative optimal chromatogram of the 12 benzoate derivatives in the optimum conditions: pH=9.70, acetonitrile fraction=0.44, applied voltage=30kV. Number above peaks refers to the 12 compounds: (1) sodium benzoate salt and its derivatives, (2) 2-chloro-, (3) 2-nitro-, (4) 4-nitro-, (5) 3-nitro-, (6) 4-chloro-, (7) 3-hydroxy-, (8) 4-amino-, (9) 4-hydroxy-, (10) 2-amino-, (11) 3-chloro-, (12) 3-amino-.

and entropy of solvation by the ACN clusters of the A^- species were -1.5 kcal/mol and 10.3 cal/mol/K. These values, again, agreed with the values reported in the literature.[16,18,34]

Also, in the case of equilibrium between two species, A and B were noted:

$$<A> + B \leftrightharpoons A + <B> + (p_B - p_A)U \quad (20)$$

The energetics of this solvent exchange process can be investigated in relation to the difference in pK_a (ΔpK_a) between the solute A used as a reference and solute B. The equilibrium constant K_{ex} of this solvent exchange process is:

$$K_{ex} = K_{<A>} / K_{<B>} \quad (21)$$

where $K_{<A>}$ (respectively $K_{<B>}$) are the constants of the equilibrium $A + p_AU° <A>$ (respectively $B + p_BU° <B>$). Values for $K_{<A>}$ and $K_{<B>}$ at 25°C were obtained as described above.

The values of the Gibbs free energy change ΔG_{ex}, corresponding to the equilibrium of the solvent exchange process (Eq. 20), were calculated from

Eq.16. The solute reference was chosen as benzoate = A. A linear correlation between ΔG_{ex} and ΔpK_a was found for the derived benzoate system:

$$\Delta G_{ex} = \beta \Delta pK_a \text{ with } \beta \# + 1.65 \quad (22)$$

The correlation coefficient was equal to 0.986 (Figure 4).

$\Delta G_{ex} = 0$ obviously for benzoate ($\Delta pK_a = 0$), $\Delta G_{ex} > 0$ for more basic species than benzoate ($pK_{a,B} > pK_{a,A}$) and $\Delta G_{ex} < 0$ for less basic species ($pK_{a,B} < pK_{a,A}$) than benzoate. This result confirms that the solute solvation by the ACN clusters was enhanced for the lesser polar solutes.

Effect of Ionic Strength

To assess the dependence of the ionic strength on μ_e, the previous experiments were carried out at 9 ionic strength values 0.01 M, 0.02 M, 0.03 M, 0.04 M, 0.05 M, 0.06 M, 0.07 M, 0.08 M, 0.09 M. As expected, the mobility decreased as I increased.[39] The model parameters (eq. 12) corresponding to each temperature and ionic strength were determined. The different Van't Hoff plots (eq.15) for all samples as well as the different chemical processes were determined.

The correlation coefficients for the linear fits were in excess of 0.981. The typical standard deviation of slope and intercept were, respectively, 0.004 and 0.02. For the solute benzoate, the enthalpy, entropy, and Gibbs free energy of solvation for the different ionic strengths are given in Table 2.

$\Delta H°_{<A>} < 0$ shows that the solute preferred to be solvated by the ACN clusters. $\Delta S°_{<A->} > 0$ would appear to be in apparent contradiction with the apparent loss of freedom of the solute during the solvation process. This phenomenon can be explained by a contribution from the hydrophobic interaction.[40-42]

It has been known for many years that increasing the ionic strength of a bulk solvent increases its surface tension and the energy required for cavity formation.[43] Thus, there is a loss of solvent entropy in the first hydration shell in the water structure, and a reduction in the energy of solute medium solvation interactions. Also, there is an increase in the hydrophobic interaction[44,45] by enhancement of the BGE surface tension which explains the thermodynamic parameter variation, i.e., $\Delta H°_{<A->}$ decreased and $\Delta S°_{<A->}$ increased as I increased.

Enthalpy-Entropy Compensation Study

Investigation of the enthalpy-entropy compensation temperature is an extra thermodynamic approach to the analysis of physico-chemical data.[47]

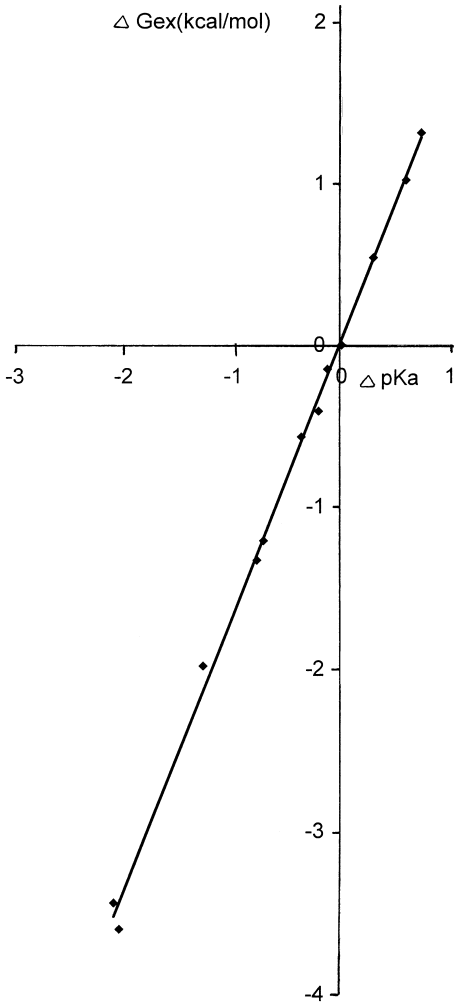

Figure 4. Solvent exchange process free energy ΔG_{ex} for the derived benzoates as a function of ΔpK_a using the benzoate anion as a reference. Correlation coefficient r=0.988 and slope β=+1.65.

Mathematically, enthalpy-entropy compensation can be expressed by the formula:

$$\Delta H^{\circ} = \beta \Delta S^{\circ} + \Delta G^{\circ}_{\beta} \qquad (23)$$

Table 2

Thermodynamic Parameters $\Delta H°_{<A->}$ (kcal/mol), $\Delta S°_{<A->}$ (cal/mol/K) and $\Delta G°_{<A->}$ (kcal/mol) at Different Ionic Strengths I for Benzoate

I	$\Delta H°_{<A>}$ (kcal/mol)	$\Delta S°_{<A>}$ (cal/mol/K)	$\Delta G°_{,A>}$ (kcal/mol)
0.01 M	-0.4(0.01)	5.7(0.02)	-2.1(0.01)
0.02 M	-0.5(0.02)	6.2(0.01)	-2.3(0.02)
0.03 M	-0.6 (0.03)	6.6 (0.01)	-2.6(0.03)
0.04 M	-0.7(0.02)	7.2(0.02)	-2.9(0.01)
0.05 M	-0.8(0.01)	7.7(0.01)	-3.1(0.01)
0.06 M	-1.0(0.02)	8.2(0.01)	-3.4(0.01)
0.07 M	-1.2 (0.01)	8.6 (0.01)	-3.7(0.02)
0.08 M	-1.3(0.01)	9.1(0.02)	-4.1(0.01)
0.09 M	-1.4(0.02)	9.9(0.01)	-4.4(0.02)
0.10 M	-1.5(0.03)	10.3(0.03)	-4.6(0.01)

Where $\Delta G°_{\beta}$ is the Gibbs free energy of a physicochemical interaction at a compensation temperature, β. $\Delta H°$ and $\Delta S°$ are, respectively, the corresponding enthalpy and entropy. According to Eq. 23, when enthalpy-entropy compensation is observed with a group of compounds in a particular chemical interaction, all the compounds have the same free energy $\Delta G°_{\beta}$ at temperature β.

Rewriting Eq. 15, using Eq., 23 gives:

$$\ln K_{\langle A-\rangle} = \ln K_{\langle A-\rangle\beta} - \frac{\Delta H^{o}_{\langle A-\rangle}}{R}\left(\frac{1}{T} - \frac{1}{\beta}\right) \tag{24}$$

where

$$\ln K_{\langle A-\rangle\beta} = -\frac{\Delta G^{o}_{\langle A-\rangle\beta}}{R\beta} \tag{25}$$

A plot of $\ln K_{\langle A-\rangle}$ (T = 25°C) calculated for each of the solutes against $-\Delta H°$ for the different values of the ionic strength was drawn. The correlation coefficients for the linear fits were at least equal to 0.961.

The high degree of correlation can be considered adequate to verify enthalpy-entropy compensation. This indicates that the solute solvation mecha-

nism in the BGE was the same for various benzoate derivatives using a similar electrophoretic system. Enthalpy-entropy compensation was also used to test the solvation mechanism of benzoate derivatives when the ionic strength in the BGE changed.

For a set of compounds where there is enthalpy entropy compensation, the slope ln $K_{<A->}$ vs-$\Delta H°$ will be the same for the same type of reaction.[47] The relative difference in the slope values obtained for all ionic strengths was inferior to 4%, thus, indicating that the solvation mechanism for the solutes was the same whatever the BGE ionic strength.

CONCLUSION

An equation was proposed to describe the effective migration of benzoate derivatives in CE using hydroorganic BGE (0.50-0.80 buffer/ACN (v/v)). The experimental value of the effective migration obtained by varying the ACN fraction in the BGE and pH of the buffer provided a verification of the predictive theoretical treatment. Also, using this mathematical model, the intrinsic selectivity of the 12 species and the analysis time were both optimized with a new response function developed in our laboratory.

These migration data were also used to calculate the thermodynamic parameters for the benzoate derivatives ACN cluster solvation in the BGE. A linear relation was obtained between the Gibbs free energy changes in the ACN cluster exchange process and the difference in the pK_a values for the benzoate derivatives, which were consistent with an ACN cluster solvation under the dependence of the relative polarity of the solute.

Enthalpy-entropy compensation revealed that the ACN cluster solute solvation mechanism was independent of both the molecular structure and the BGE ionic strength.

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