ISOTACHOPHORESIS IN MIXED SOLVENTS CONSISTING OF WATER, METHANOL AND DIMETHYL SULPHOXIDE

III. INFLUENCE OF THE SOLVENT COMPOSITION ON THE DISSOCIATION CONSTANTS AND MOBILITIES OF NON- AND HYDROXY-SUBSTITUTED ALIPHATIC CARBOXYLIC ACIDS

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SUMMARY

The electrophoretic properties of uncharged acids of the type HA were investigated in operational systems consisting of mixed aqueous–organic solvents. The mixed solvents applied consisted of water, methanol and dimethyl sulphoxide in which the molar fraction of water was held constant at 0.3 and those of the organic co-solvents were varied. The analytes were C_1–C_5 non- and monohydroxy-substituted *n*-alkanoic acids.

The changes in the pK values were found to be linearly correlated with the molar fraction of dimethyl sulphoxide within the mixing range considered. The changes in the pK values can be qualitatively described by the transfer activity coefficients, which are related to the solvation abilities of the solvents involved.

The mobilities and the corresponding normalized values, where the different viscosities of the particular solvents are taken into account, were determined in operational systems with apparent pH values of 8.7. No changes in the selectivities occurred within the two groups of acids. The normalized mobilities of the non-substituted acids, on the other hand, increased with increasing concentration of dimethyl sulphoxide to a smaller extent than those of the hydroxy-substituted acids. The grouping of these two classes is demonstrated by cluster analysis.

INTRODUCTION

The electrophoretic mobility of an analyte can be influenced by a variety of factors. Properties of the bulk solvent such as viscosity on the one hand affect the mobilities of all analytes in the same way, and therefore do not change the selectivity of the electrophoretic system. On the other hand, solute–solute and solute–solvent interactions can lead to pronounced specific changes in the electrophoretic properties. These interactions either determine the size of the ion, and therefore the absolute mobility m_i^0 (at infinite dilution), or the actual mobility m_i (of the totally dissociated or protonated molecule at finite concentration), or they determine the acid–base

properties of the analytes. This can lead to different changes in the pK values due to different solvation of the particles considered and can be used to adjust the effective mobility, $m_i^{eff} = \alpha m_i$, via the degree of dissociation, α.

One possibility of increasing the range of solute–solvent interactions lies in the application of non-aqueous or mixed solvents for the electrolyte systems. In previous studies[1,2] we investigated the effects of two different mixed aqueous–organic solvents, the first consisting of water (with a molar fraction $x = 0.3$) and methanol ($x = 0.7$) and the second of water ($x = 0.3$), methanol ($x = 0.4$) and dimethyl sulphoxide (DMSO) ($x = 0.3$). In these systems, the electrophoretic properties of aromatic uncharged (or molecular) acids of type HA, and of aliphatic positively charged acids, HB^+ (of the ammonium ion type), were investigated. In some cases strong changes in the migration sequence of the cations were found, which were attributed to changes in the size of the ions. The increased applicability to the separation of substituted benzenecarboxylic acids due to selective changes in their apparent pK values (pK' values) was demonstrated.

In this study, the changes in the properties of uncharged acids by variation of the composition of the mixed solvents within the mixing range mentioned above were investigated in greater detail. As solutes, homologues series of aliphatic carboxylic acids were selected. One series consisted of non-substituted acids and the other of monohydroxy-substituted acids, where interaction of the hydroxy group with polar solvents via hydrogen bonding is possible.

Four solvent mixtures were applied, in which the molar fraction of water was kept constant ($x = 0.30$) and those fractions of methanol and DMSO were varied (Table I). In contrast to previous work[1], here the mobilities of the analytes were determined at such high apparent pH (pH') values that the properties of these analytes can be considered to be influenced to only a minor extent by the degree of dissociation.

EXPERIMENTAL

Chemicals and solvents

Unless stated otherwise, the chemicals and solvents used for the electrolyte systems were of analytical-reagent grade, obtained from E. Merck (Darmstadt, F.R.G.), Fluka (Buchs, Switzerland) or Serva (Heidelberg, F.R.G.). The non-substituted, the 2-hydroxy-substituted n-alkanoic acids and 3-hydroxybutyric acid (3C4) were purchased from E. Merck, Serva or Fluka, either as free acids or as their

TABLE I

COMPOSITION OF MIXTURES OF WATER, METHANOL AND DMSO USED AS SOLVENTS FOR THE ELECTROLYTE SYSTEMS

Solvent code	Molar fraction (x)		
	Water	Methanol	DMSO
1	0.300	0.700	0.000
2	0.300	0.600	0.100
3	0.300	0.500	0.200
4	0.300	0.400	0.300

salts. 3-Hydroxypropionic acid (3C3), 4-hydroxybutyric acid (4C4) and 5-hydroxy-valeric acid (5C5) were synthesized from the corresponding lactones (Fluka, Serva). 3-Hydroxyvaleric acid (3C5) was synthesized from 2-pentenoic acid by addition of HBr and subsequent hydrolysis of the 3-bromovaleric acid to the hydroxy derivative.

Buffer substances were recrystallized three times before use. Water, methanol and DMSO were distilled twice before use.

Apparatus

The apparent pK values were determined by potentiometric titration of the free acids or their salts, using an all-aqueous combined glass–calomel electrode as described previously[1]. The initial analyte concentration was 0.01 mol/l.

The measurements of the relative step heights were carried out using an isotachophoresis instrument with a capillary (25 cm × 0.3 mm I.D.) made from polytetrafluoroethene and equipped with an electrical conductivity detector. The constant driving current was 40 μA. This instrument was also used for the determination of the mobilities of the leading and the reference ions in the mixed aqueous–organic solvents, applying a modified moving boundary method as described[1,2].

The viscosity coefficients were determined with an Ubbelohde viscosimeter and a pyknometer, thermostated to within 0.1°C.

The dielectric constants were determined with a Type DK 03 instrument (WTW, Weilheim, F.R.G.), thermostated to within 0.1°C.

Cluster analysis was carried out by a computer program[3] using the Euclidian distances of the points representing the compounds in a multi-dimensional pattern space, as discussed previously[2]. These distances were calculated from the scaled values of the differences in the normalized mobilities, given by the product of the mobility and the viscosity coefficient.

RESULTS AND DISCUSSION

pK values in mixed solvents

The apparent pK values of non- and hydroxy-substituted carboxylic acids are given in Table II, together with thermodynamic pK values in pure water, taken from the literature[4,5]. The problems of the experimentally determined apparent pK values, which include effects arising from liquid junction potentials, were discussed previously[1,2].

It can be seen from Table II that, in accordance with some literature data[6], the pK values increase by about 1.5–2 pK units when methanol is added to aqueous solutions at a molar fraction of 0.7. In this special case, the increase in pK is roughly linearly dependent on the methanol content, at least in the concentration range up to a molar fraction of 0.7. At higher concentrations, the corresponding curve becomes steeper and reaches values that are approximately 5 pK units higher in pure methanol than in water[6,7].

The increase in the pK (or pK' values) in system 1 given in Table II is in accordance with the fact that methanol and water–methanol mixtures have lower dielectric constants than water, as shown in Table III. This leads to positive values for the electrostatic part of the "medium effect", log $_m\Gamma_{HA}$, and the corresponding

TABLE II

APPARENT pK VALUES (pK') OF NON- AND HYDROXY-SUBSTITUTED ALIPHATIC CARBOXYLIC ACIDS IN MIXTURES OF WATER, METHANOL AND DMSO

The solvent codes correspond to Table I. The number after the C in the acid codes indicates the number of carbon atoms of the acid molecule and the number before the C indicates the position of the hydroxy group (e.g., 2C4 = 2-hydroxybutyric acid; C2 = acetic acid). Temperature, 25°C.

Acid	pK in water[a] (20°C)	pK' in solvent system			
		1	2	3	4
C1	3.75	5.25	5.75	6.12	6.70
C2	4.76	6.62	7.09	7.62	8.20
C3	4.87	6.78	7.26	7.84	8.44
C4	4.81	6.84	7.27	7.86	8.43
C5	4.79	6.79	7.26	7.85	8.42
2C2	3.82	5.55	6.02	6.41	7.05
2C3	3.86	5.73	6.33	6.60	7.09
2C4	–	5.55	5.79	6.40	6.92
2C5	–	5.45	5.87	6.45	6.71
4C5	4.69[b]	6.56	6.99	7.42	8.19
5C5	–	6.81	7.07	7.52	8.27

[a] From refs. 4 and 5.
[b] Value at 18°C.

standard free energy of transfer, $\Delta G^0_{t,HA}$, of the dissociation reaction of uncharged acids, HA, as given by Born's treatment:

$$\Delta pK = p_sK - p_wK = \frac{N_L e_0^2}{2RT(\ln 10)} \left(\frac{1}{r_{H^+}} + \frac{1}{r_A} \right) \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w} \right) \qquad (1)$$

where the subscripts w and s indicate water and organic or mixed solvent, respectively, e_0 = elementary charge, N_L = Loschmidt's number, T = absolute temperature, R = gas constant, r = crystallographic radius of the ion and ε = dielectric constant. $_m\Gamma_{HA} = (_m\gamma_{H^+} \cdot {_m\gamma_{A^-}})/_m\gamma_{HA}$ is related to the transfer activity coefficients, $_m\gamma_i$, of the single species, i^{8-13}.

TABLE III

DIELECTRIC CONSTANTS OF THE MIXED SOLVENTS AT DIFFERENT TEMPERATURES

The solvent codes correspond to Table I.

Temperature (°C)	Dielectric constants of mixed solvents			
	1[a]	2	3	4[a]
20	43.78	47.80	51.40	54.29
25	42.52	46.74	50.48	53.04
30	40.99	45.15	48.96	51.57

[a] From ref. 1.

The restriction to pure electrostatic work, according to Born's treatment, neglects the effects on the pK values originating from the different basicities and from the different solvation abilities of the solvents. Therefore, this simple approach does not explain the variation of the pK values in most instances. However, for some water–alcohol mixtures, this rough approach leads to results that are at least qualitatively in accordance with the observed effects. In fact, the transfer of a uncharged acid and its dissociation products from water (with a dielectric constant of 78.30 at 25°C) to, e.g., system 1 would lead to a calculated increase in the pK value of 1.1 units when values of 2 and 3 Å are assumed for the crystallographic radii of the proton (or the H_3O^+ ion) and the anion, respectively. The observed values are of about the same magnitude as the predicted values, which can be seen from Table II.

If methanol is replaced with DMSO, as is carried out in the sequence of the solvents 1–2–3–4, an aprotic dipolar solvent is introduced which (a) has a higher dielectric constant than methanol, (b) is a stronger base than both water and methanol and (c) has the lowest ability to solvate anions of all solvent constituents under consideration.

The resulting change in the pK' values with solvent composition is shown in Fig. 1, where the differences in the means of the pK' values, $\Delta \overline{pK'}$, of the carboxylic acids in the particular solvent systems, relative to system 1, are plotted against the concentration of DMSO and methanol. There is a linear increase in $\Delta \overline{pK'}$ with increasing molar fraction of DMSO (the linear correlation coefficient, r, is 0.999). This is in clear
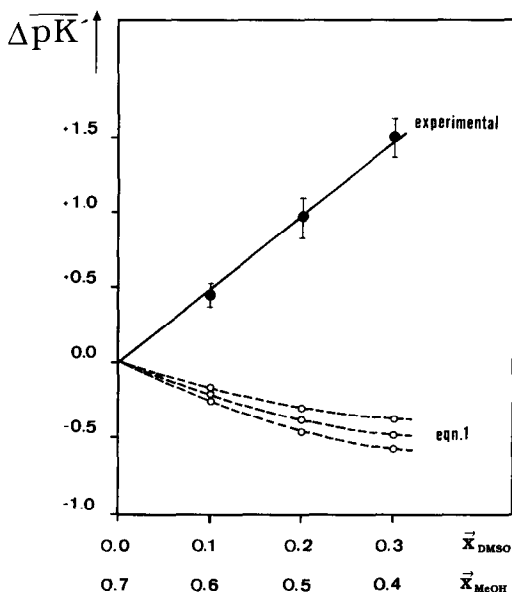

Fig. 1. Variation of the apparent pK values with the composition of the mixed solvents. $\Delta \overline{pK'}$ = differences in the means of the apparent pK values of the acids given in Table II, relative to the values in the binary mixed aqueous–methanolic solvent 1. The molar fraction of water was held constant at 0.3. ⅛, Experimental values (standard deviations indicated); ⓞ, values calculated from eqn. 1, assuming different crystallographic radii of the ions. MeOH = Methanol.

contrast to the results of the calculation according to eqn. 1, which would give negative values for $\Delta pK'$ with increasing DMSO concentration, as indicated in Fig. 1 by the broken lines. The curves shown there were calculated from eqn. 1 using the values of the dielectric constants at 25°C given in Table III. They were obtained for different crystallographic radii for the ions: upper curve, $r_{H^+} = 3$ Å, $r_{A^-} = 3$ Å; middle curve, $r_{H^+} = 2$ Å, $r_{A} = 3$ Å; lower curve, for both ions $r = 2$ Å.

Replacing the crystallographic radii in eqn. 1 by the Stokes' radii as proposed in the literature (*cf. e.g.* ref. 10) is also unable to explain the effects actually observed; only if negative values for the Stokes' radii are applied in eqn. 1, which is of no physical meaning, would the calculated values be in accordance with the experimental data.

It should be mentioned that the observed result also conflicts with an explanation based solely on the acid–base properties of DMSO. This solvent, being a stronger base than methanol, should also decrease the pK values with increasing concentration.

The effects found experimentally seem to result from the very low ability of DMSO to solvate anions, which leads to highly positive values for the medium effect on the anion. This effect overcompensates the contributions of the electrostatic work to the change in the standard free energy of transfer, and also the contribution of the medium effect on the proton, log $_m\gamma_{H^+}$.

The resulting effects of the composition of the mixed solvents on the pK' values of the uncharged acids can be summarized as follows: for the analytes under consideration, the partial replacement of water as a solvent with methanol up to a molar fraction of 0.7 leads to an almost linear increase in the pK values of about 1.5–2 units, compared with pure aqueous solutions; and the replacement of methanol by DMSO in ternary mixtures of water, methanol and DMSO leads to a further linear increase in the pK' values of about 0.5 unit per 10 mol% DMSO.

Migration properties of the anions of non- and hydroxy-substituted carboxylic acids in mixed solvents

Obviously the migration properties of the analytes are highly dependent on their acid–base properties, as the degree of dissociation in a given electrolyte system, which determines the effective mobilities, is related to the pK values. Therefore, in this work the conditions were chosen such as to suppress the effects originating from different degrees of dissociation by applying electrolyte systems with sufficiently high pH (or pH') values. The migration properties in the solvent systems at pH' 8.7 [with tris(hydroxymethyl)aminomethane as buffering counter ion] were, in a first step, determined with the aid of the step heights of the isotachophoretic analyte zones, measured with an electrical conductivity detector. They were determined at an ambient temperature of 28°C, for which the problem of the actual temperature of the analyte zones has already been mentioned[1]. This temperature can be assumed to be slightly higher than ambient. At pH' values of the leading electrolytes of 8.7, and at the higher pH' values within the analyte zones, the acids are dissociated to more than 95%, at least in the electrolyte systems consisting of solvents 1, 2 and 3. In the electrolyte with solvent 4, formic acid and the 2-hydroxy-substituted acids are dissociated to more than 99% and the other acids to a smaller extent.

The relative step heights are given in Table IV. From these values, the mobilities in the respective buffered solvent systems can be calculated. For this calculation the

TABLE IV

RELATIVE STEP HEIGHTS OF NON- AND HYDROXY-SUBSTITUTED CARBOXYLIC ACIDS
AT APPARENT pH VALUES OF 8.7 IN ELECTROLYTE SYSTEMS WITH MIXED SOLVENTS
CONSISTING OF WATER, METHANOL AND DMSO

The step heights are related to trichloroacetate as the reference ion. The leading ion was chloride (c = 0.01 mol/l). The acid and solvent codes correspond to Tables I and II, respectively.

Acid	Relative step height (× 100) in solvent			
	1	2	3	4
C1	53.7	46.2	36.8	47.3
C2	120	121	156	192
C3	143	142	199	258
C4	159	161	224	287
C5	170	178	260	326
2C2	104	100	95.5	92.1
2C3	128	124	129	127
2C4	147	145	159	159
2C5	162	159	190	190
3C3	162	167	210	221
3C4	170	178	220	237
3C5	189	196	245	255
4C5	218	239	316	376
5C5	237	256	346	393

values of the mobilities of the leading and a reference ion are required, as discussed in a previous paper[2]. However, no data for the mobilities of chloride (used as the leading ion) and trichloroacetate (used as the reference ion) in the mixed solvents were found in the literature. Therefore, these data were measured by a moving boundary method described previously[2], using an electrical conductivity detector to determine the position of the moving boundary. The results are presented in Table V. With these mobility data and with the values of the relative step heights, the mobilities of the analytes were calculated (Table VI). It can be seen that they range between approximately 18 and 32 units, and are therefore much lower than the comparable data in water, where they range between approximately 30 and 57 units. The highest values for the aqueous–organic solvents are observed in the electrolyte system with

TABLE V

MOBILITIES OF LEADING AND REFERENCE IONS IN THE ELECTROLYTE SYSTEMS
CONTAINING MIXED SOLVENTS

Temperature, 30°C. The solvent codes correspond to Table I. c = 0.01 mol/l.

Ion	Mobility (10^{-5} cm^2 V^{-1} s^{-1}) in solvent			
	1	2	3	4
Chloride	38.1	32.4	27.4	26.3
Trichloroacetate	28.2	25.1	23.7	24.1

TABLE VI

MOBILITIES OF NON- AND HYDROXY-SUBSTITUTED CARBOXYLIC ACIDS IN ELECTRO-
LYTE SYSTEMS CONSISTING OF SOLVENT MIXTURES OF WATER, METHANOL AND DMSO
AT AN APPARENT pH VALUE OF 8.7

The mobilities were derived from the relative step heights given in Table IV. The acid and solvent codes
correspond to Tables I and II, respectively. Temperature, 30°C.

Acid	Mobility (10^{-5} cm^2 V^{-1} s^{-1}) in solvent			
	1	2	3	4
C1	31.8	28.6	25.9	25.2
C2	26.6	24.0	22.0	22.4
C3	25.0	22.9	20.9	21.3
C4	24.2	22.1	20.3	20.8
C5	23.4	21.3	19.5	20.3
2C2	27.9	25.1	23.8	24.3
2C3	26.1	23.8	22.8	23.6
2C4	24.9	22.8	22.0	23.0
2C5	24.1	22.2	21.1	22.4
3C3	24.1	21.8	20.6	21.9
3C4	23.3	21.4	20.4	21.6
3C5	22.7	20.6	19.6	21.3
4C5	21.2	19.1	18.4	19.6
5C5	20.5	18.6	17.8	19.4

solvent 1; in the electrolyte systems consisting of solvents 2, 3 and 4, the mobilities of
a particular analyte differ by only 10%.

One can compare the effects of the electrolyte systems on the migration
properties of the analytes better when the different viscosities of the bulk liquids are
compensated, according to Stokes' law. The viscosity coefficients, η, of the mixed
solvents at different temperatures are given in Fig. 2. A linear increase in the viscosity
coefficients with increasing molar fraction of DMSO (and decreasing molar fraction of
methanol) is found. The linear correlation coefficient, r, is >0.999 for all three curves.

The values at 30°C were used to calculate the products $m_i\eta$, which are plotted in
Fig. 3 against the solvent composition. There is a non-linear but continuous increase of
$m_i\eta$ with increasing concentration of DMSO for all analytes. Both the non-substituted
carboxylic acids (Fig. 3a) and the hydroxy-substituted acids (Fig. 3b) show roughly
parallel curves, which means that the selectivity of the systems has not changed within
either class of analyte. This result is in accordance with predictions which can be made
based on the solvation properties of the solvents involved, especially of DMSO. The
behaviour of the uncharged acids differs from that of positively charged acids of the
ammonium type[2], where changes in the migration sequence were observed for small
ions with relatively high charge densities.

For the particular anions, the changes of in $m_i\eta$ from system 1 to system 4 are in
the range of about 50% for the hydroxy derivatives and about 25–30% for the
non-substituted acids. This means that much larger effects are found for the carboxylic
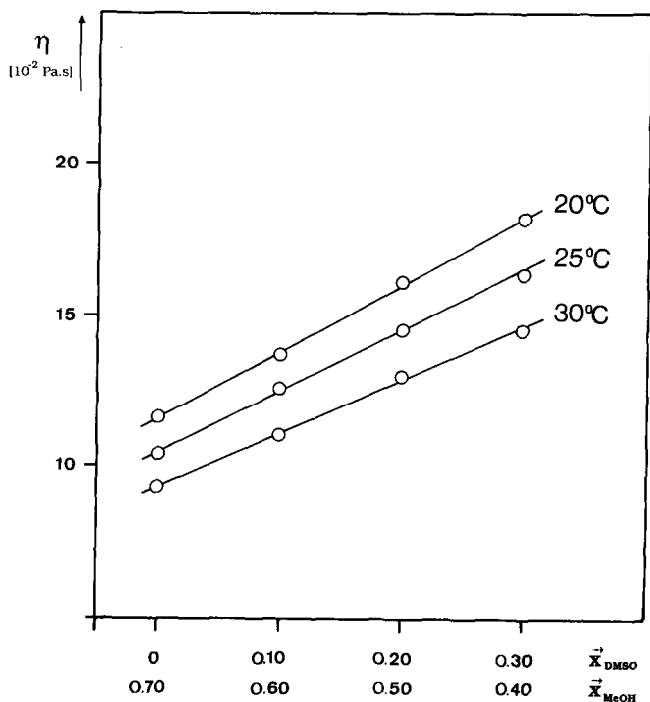acids compared with cations with low charge densities such as tetrapropylammonium

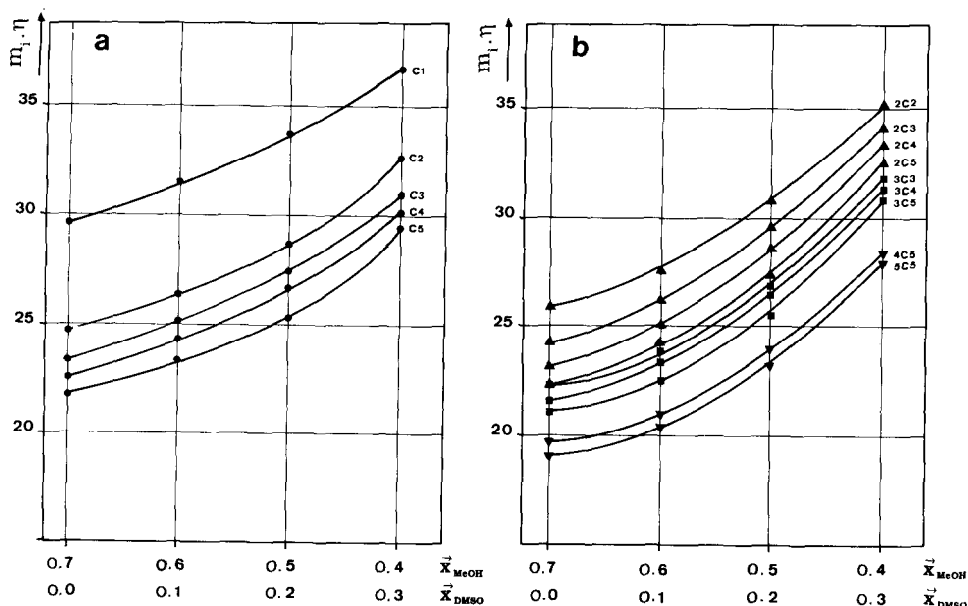Fig. 2. Viscosity coefficients, η, of the mixed solvents at different temperatures.

Fig. 3. Products $m_i\eta$ (10^{-12} N V^{-1}) of the mobilities, m_i, of the analyte anions and the viscosity coefficients, η, of the mixed solvents *versus* the composition of the operational system. (a) Non-substituted carboxylic acids; (b) hydroxy-substituted carboxylic acids. The codes for the acids correspond to Table II.

or tetrabutylammonium ions[2], for which we can assume that they are not solvated, and where only small changes ($<10\%$) were found for the particular cation.

It can be concluded from the parallel shape of the curves for 4C5 and 5C5, which have relatively high pK' values compared with those of the 2-hydroxycarboxylic acids (with lower pK' values), as shown in Fig. 3a and b, that the effect of the degree of dissociation has only a minor effect on the mobilities under the conditions given. This means that the mobilities calculated were in fact the actual mobilities of the solutes. This assumption is confirmed when the curves for the higher non-substituted acids in Fig. 3a are compared with that of formic acid, which also has lower pK' values but shows the same trend.

Although for both classes of compounds the sequence of the mobilities does not change within a given class, changes can be observed when compounds from different classes are compared. It can be seen from Fig. 3 that the curves for the hydroxy-substituted acids show a steeper increase with increasing molar fraction of DMSO than the corresponding curves for the non-substituted acids. This steeper increase leads, e.g., to the effect that C3, C4 and C5, which have about the same mobilities as 2C4, 2C5
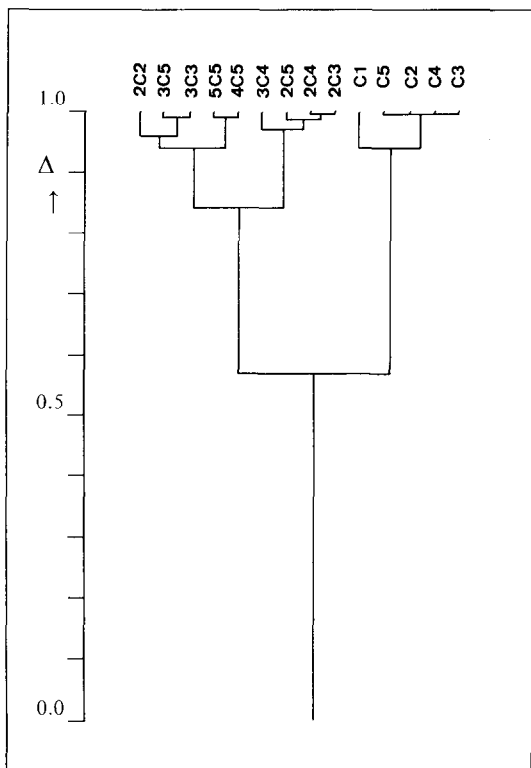

Fig. 4. Dendrogram resulting from the hierarchical clustering procedure for characterizing the electrophoretic properties of the solutes. The differences in the products $m_i\eta$ in operational systems 2, 3 and 4, relative to the values in system 1, were used as features. Δ = relative Euclidian distance. The codes for the acids correspond to Table II.

and 3C4 in system 1, and have higher mobilities than 3C5 and 4C5 in this particular system, show mobilities between 3C5 and 4C5 in system 4.

In general, similarities of species such as ions in different solvents (or electrolyte systems with different pH or solvent composition), can be characterized and evaluated by chemometric methods such as cluster analysis, as shown in previous papers[1,2,14]. The same method can be used to show the different migration properties of the compounds investigated in this study. For this procedure, the differences in the normalized mobilities, $m_i\eta$, in the particular electrolyte systems relative to system 1 were used as features. The Euclidian distances were used as a measure of resemblance. The dendrograms were constructed by an average linkage method.

The results of the clustering procedure are shown in Fig. 4. One can see the differentiation of the analytes into two main subclusters, which is clearly in accordance with the discussion given above; two groups of compounds are differentiated, based on their different migration properties. These groups formed are not dependent on the chain lengths or the pK' values, but are characterized only by their chemical structure; one group is formed by the non-substituted acids and the other group consists of all the hydroxy-substituted acids.

The electrophoretic behaviour of the hydroxy derivatives of the carboxylic acids is found to be similar to that of some of these compounds in the presence of methanol, where they also show higher mobilities, when compared with the corresponding non-substituted compounds; e.g., 2C3 and C3 have the same mobilities in water, but 2C3 has a higher mobility than C3 in 99.5% methanol[15].

These changes cannot be related to a single or predominant effect such as ion solvation by DMSO, as was shown for cations[2], and seem to have more complex sources. Considering the behaviour of the anions investigated, not only are structural changes in the mixed solvents of importance compared with the pure solvents, but also various competing solvation and desolvation reactions seem to play an important role. This leads finally to effects that cannot be explained by a simple model.

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