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Capillary zone electrophoresis in mixed aqueous–organic media: effect of organic solvents on actual ionic mobilities and acidity constants of substituted aromatic acids IV. Acetonitrile

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Abstract

The effect of the composition of binary mixtures of acetonitrile (ACN) and water (ranging up to 80%, v/v, ACN) on the apparent pK_a values and the actual mobilities of 26 aromatic substituted benzoic acids is investigated. The (non-thermodynamic) pK_a values are determined potentiometrically (at $T=25^\circ\text{C}$ and an ionic strength, I , of 5 mmol/l). The actual mobilities are measured by capillary zone electrophoresis (phosphate buffer, pH 7 in water, $I=20$ mmol/l, $T=25.0^\circ\text{C}$). An increase of the pK_a values with increasing concentration of ACN is found, in a magnitude comparable to mixed aqueous–methanolic and –ethanolic solvents (1.5 to 2 pK units at 80% ACN). These changes are interpreted based on the theoretical model of the transfer activity coefficient or the medium effect. The actual mobilities change only slightly with solvent composition, which is in fair agreement with the change of the solvent viscosity. It is found that Walden's rule (supposing the constancy of the product of mobility, μ , and viscosity, η) applied for the solvent systems investigated in the series of papers dealing with binary aqueous mixtures with methanol, ethanol, 1-propanol and acetonitrile as cosolvent, and to the anions under consideration is obeyed within $\pm 20\%$. An extension of this rule ($\mu\eta^{0.9}=\text{constant}$) leads to products that are constant within +5 and –9% over the concentration range of up to 60% organic solvent. The effect of the substituents (methyl, nitro, chloro, hydroxy derivatives) on the change of the actual mobilities are most pronounced for the hydroxy-substituted benzoates, especially for those with the OH group in position 3 to the carboxylate group. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the introduction of capillary electrophoresis (CE) one of the important goals was to evolve parameters allowing the modification of the sepa-

ration selectivity. In addition to the most common tool to adjust resolution, namely the pH of the buffering background electrolyte (BGE), a number of other possibilities have been proposed and developed, such as the use of complexation agents (e.g. so-called inclusion-complex forming additives like cyclodextrins, not only for the very effective sepa-

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ration of chiral compounds), the application of sieving matrices for size-specific separations, the application of lipophilic or ion-exchange interactions with soluble pseudo-stationary phases, etc., and more recently even the development of hybrid methods like micellar electrokinetic chromatography or electrochromatography. Among all the possibilities to generate or enhance selectivity, the potential of organic solvents has been demonstrated since the beginning of CE [1]. These solvents have been applied either pure or in aqueous mixtures.

Organic solvents have two main influences on the selectivity of electromigration separation (we do not consider the effect on the electroosmotic flow here), namely the effect (i) on the actual mobility and (ii) on the ionization constant of weak acids or bases. In a series of previous papers, these effects have been described and discussed for the most frequently used protic solvents, the lower alcohols, in binary aqueous–organic mixtures [2–4]. We conclude this series with three other papers; the present contribution deals with the aprotic, dipolar solvent acetonitrile (ACN) which is commonly used in reversed-phase HPLC. Other members of this important class, e.g. dimethyl sulfoxide, *N*-methylformamide, or *N,N*-dimethylacetamide unfortunately have restricted applicability in CE with UV detection due to their high absorbance in the usually operated wavelength range. Nevertheless, according to their potential importance, e.g. when using an electrical conductivity detector, these solvents have been the topic of our investigations described elsewhere [5–8], and are still the subject of current work [5]. The last paper in this series of mixed aqueous–organic solvents in CE deals with the evaluation of the similarity of the investigated systems based on chemometry [9].

The basic concepts for the discussion and the interpretation of the effects of organic solvents, especially the change of the ionization constants have been already described previously in detail [2–5,10,11] and are therefore not given here. In the present work we are focusing on the influence of ACN on ionization constants and actual mobilities and we discuss these in the context of the effects of methanol (MeOH), ethanol (EtOH) and 1-propanol (PrOH). Special attention is directed to the discussion of the influence of these complex solvent systems on the mobility of the anionic solutes.

2. Experimental

2.1. Instrumentation

2.1.1. Electrophoresis

A programmable electrophoresis device (Model P/ACE 2100, Beckman Instruments, Fullerton, CA, USA) was used for all measurements with a UV–Vis absorbance detector operated at 214 nm. An untreated fused-silica capillary (total length 26.4 cm, length to detector window 19.6 cm \times 50 μ m I.D. \times 375 μ m O.D.; Polymicro Technologies, Bloomfield, NJ, USA) was used. During all runs a constant voltage of 10.0 kV with a linear ramp-up of 0.17 min was applied. Data collecting and analysis procedures were carried out with a Gold software 3.0 (Beckman Instruments).

CE measurements of the mobilities in duplicate resulted in a span in the one percent range or below. Currents were 11.7 μ A at 0%, 11.1 μ A at 20%, 10.3 μ A at 40%, and 8.0 μ A at 60%, v/v, ACN.

2.1.2. Potentiometric determination of the apparent pK_a

The apparent pK_a values of the chosen acids were determined by potentiometric titration on a Mettler titration device (Model DL 67, Mettler Toledo, Schwerzbach, Switzerland) with a glass–calomel electrode (DG 101-SC, Mettler Toledo), filled with aqueous KCl, 3 mol/l, saturated with AgCl. The samples used had a concentration of 10 mmol/l and were titrated with 100 mmol/l NaOH. The pK_a values were calculated according to the half-neutralization method, thus representing the measured pH at half of the equivalent point.

2.2. Chemicals

Buffer electrolytes and the organic solvent were purchased from E. Merck (Darmstadt, Germany) in p.A. grade. All analytes were obtained from EGA-Chemie (Steinheim, Germany) with the highest grade in purity available. The analytes (and also dimethyl sulfoxide, used to measure the electroosmotic flow) had a concentration of 0.1 mmol/l. Water used in all experiments was distilled twice from a quartz apparatus. Equimolar portions of NaH_2PO_4 and Na_2HPO_4 were mixed to obtain a 10

mmol/l phosphate buffer (ionic strength, $I=20$ mmol/l) which was used as the background electrolyte throughout. Apparent pH values of the mixed aqueous–organic background buffers, measured with a glass electrode at 25°C, were 7.02 at 0%, 7.41 at 20%, 7.77 at 40% and 8.00 at 60%, v/v, ACN.

3. Results and discussion

3.1. pK_a values in aqueous ACN mixtures

The apparent (non-thermodynamic) pK_a values of five aromatic acids are given in Table 1 at four different concentrations (v/v) of ACN. The concentration range covers up to about 80%, v/v, of organic solvent. The given pK_a values in pure aqueous solutions for the measured analytes (see Ref. [2]) are: 4.12 (benzoic); 4.03 (3-OH), 4.24 (3-Me); 3.82 (3-Cl) and 3.46 (3-NO₂). The symbols of the solutes consist of numbers indicating the position of the substituents in the ring, and the abbreviations Me for the methyl, NO₂ the nitro, Cl the chloro and OH the hydroxy group.

Addition of ACN leads to an increase of the pK_a values, in a similar way as observed for the lower alcohols. The effect of the solvent composition on the change of the pK_a values expressed as

$$\Delta pK_a = pK_a^{\text{mix}} - pK_a^{\text{w}} \quad (1)$$

Table 1

Non-thermodynamic, apparent pK_a values of benzoic acid and 3-hydroxy-, 3-methyl-, 3-chloro- and 3-nitrobenzoic acid in aqueous mixtures of ACN at various compositions (% v/v, of the organic solvents)

Acid	Symbol	pK_a			
		19.5%	39.1%	58.6%	78.2%
Benzoic	A	4.53	5.18	5.74	6.36
3-OH	C	4.47	5.09	5.63	6.20
3-Me	L	4.64	5.30	5.85	6.45
3-Cl	S	4.07	4.67	5.18	5.72
3-NO ₂	Y	3.68	4.18	4.67	5.16

The pK_a values are the means of measurements carried out in triplicate by potentiometric titration (with a measuring span in the 0.02 pK unit range). Temperature 25°C. $I=5$ mmol/l. The symbols of the acids are explained in Table 3.

is given in Fig. 1. The suffix mix indicates the mixed aqueous–organic solvent, and w=water.

Surprisingly, the addition of ACN leads to a much weaker effect than expected. The shift of the pK_a values stays between the one observed for MeOH and EtOH, although the alcohols are protic solvents: the increase of the pK_a values reaches about 1.5 to 2 pK units at 80%, v/v, ACN. However, this result must not be extrapolated to thermodynamic pK_a values at high concentration of the organic solvent (or low concentrations of water in the mixture), as in these cases the increase of the pK_a values of neutral acids would be far more pronounced [10,12]. In pure MeOH, for some substituted benzoic acids these pK_a values are in the range between 7.4 and 9.7; the corresponding values in pure ACN are found between 17 and 21, which means a ΔpK_a of about 16 units [10,12–14].

Two points, however, are noteworthy: (i) the pK_a values in pure aqueous solutions, as determined in our work, differ only slightly from the thermodynamic values: for similar substituted benzoic acids, our values agree within 0.1 pK units [14]. (ii) For e.g. mixed aqueous–ethanolic solvents, for which data are given in the literature, a good agreement is found between our practical and the thermodynamic pK_a values at not too high a concentration of the organic cosolvent [15,16]

To enable an adequate comparison with the results of the previously investigated solvent mixtures, the change of the pK_a values is described as a function of the organic solvent concentration (in %, v/v) by the same third order regression. The resulting values of the regression coefficients are shown in Table 2 for the five acids. The standard deviations of the estimates obtained by the curve fit are not given here, as they are in the same range as those obtained from the corresponding calculations for MeOH, EtOH and PrOH (see Refs. [2–4]). It should be pointed out that linear regression of the data leads to correlation coefficients with one or two 9's less after the decimal point, which justifies the application of a third-order regression.

The negative values of a_3 for ACN are larger than those for PrOH, and are similar to those of MeOH and EtOH. These negative values are caused by the inflection point of the ΔpK_a vs. % organic solvent curves, an effect which is in contrast to the results

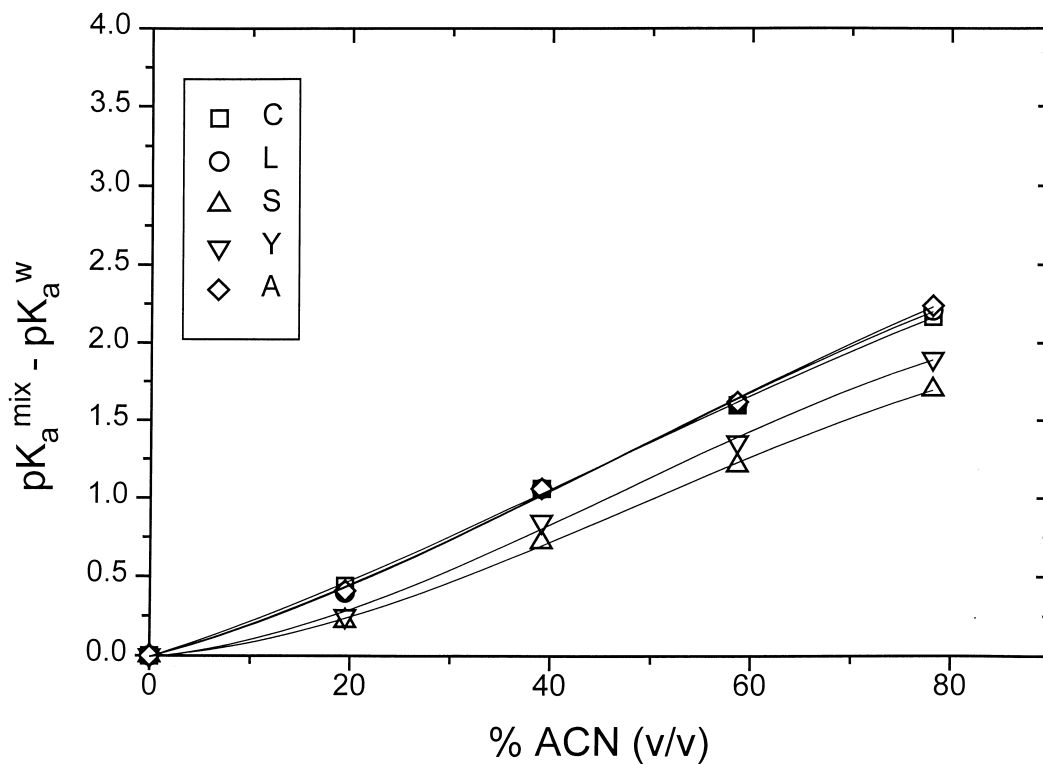


Fig. 1. Effect of the composition of the aqueous mixtures of ACN (mix) on the apparent, mixed-mode pK_a values of five meta-substituted benzoic acids, compared to water (w). The ΔpK_a values are defined in Eq. (1). The pK_a values were determined by potentiometric titration. $I=5$ mmol/l. $T=25^\circ\text{C}$. Symbols of the acids according to Table 1.

obtained for the thermodynamic pK_a values (see the discussion in the previous papers [2–4]).

The increase of the pK_a values upon addition of ACN can be interpreted in an appropriate way by the concept of the medium effect, $\log_m \gamma$. This term

relates the total change of the pK_a value to the stabilization of the individual particles involved in the acido–basic equilibrium. For the case under consideration, where the solutes are neutral acids of type HA, the change in pK_a is formulated by

$$\Delta pK_a = \log_m \gamma_{H^+} + \log_m \gamma_{A^-} - \log_m \gamma_{HA} \quad (2)$$

Table 2

List of regression coefficients from the third order polynomial fit of ΔpK_a vs. organic solvent concentration (% , v/v) according to $\Delta pK_a = a_0 + a_1c + a_2c^2 + a_3c^3$

Acid	a_1 (10^{-2})	a_2 (10^{-4})	a_3 (10^{-6})
A	1.77	2.97	-2.01
C	2.00	2.30	-1.68
L	1.69	3.29	-2.35
S	0.445	4.66	-3.13
Y	0.624	5.11	-3.58

The symbols of the acids are explained in Tables 1 and 3. The correlation coefficients, r , are larger than 0.999.

This concept has already been applied to mixed aqueous–alcoholic solvents and has been the topic of recent papers of the authors. Thus, the present work only stresses briefly the major reasons for the change of the pK_a values in ACN. The one is given by the lower basicity of ACN compared to water (reflected in positive values for $\log_m \gamma_{H^+}$), which leads to an increase of the pK_a values of neutral acids (by a mean value of about 4 pK units in pure ACN). Another deals with the significantly low ability of ACN to solvate and stabilize anions (reflected in

large positive values for $\log_m \gamma_{A^-}$). These two effects cause the drastic increase in the pK_a values of the acids of type HA (see above) at least in pure organic solvents. However, in mixed aqueous–organic solvents these effects are far less pronounced due to the dominating properties of water. Probably it is worth mentioning that, especially in the aqueous ACN mixtures, the effect of the strongly increased solubility of the neutral, free acid HA on the total increase of the pK_a values ($\log_m \gamma_{HA}$ in Eq. (2)) should not be underestimated (cf. e.g. the data in Ref. [5]).

3.2. Mobilities in aqueous mixtures with ACN

The actual mobilities of the 26 anions in water–ACN mixtures with an organic solvent concentration up to 60%, v/v, are given in Table 3. Measurements

at higher ACN content were not possible due to the limited solubility of the buffering BGE.

Addition of 20%, v/v, ACN leads to an only slight decrease of the mobilities, which is well in contrast considering the results obtained with the alcoholic solvents. In all cases even an increase of the actual mobilities at higher ACN concentrations after passing through a minimum is observed, reaching the same values or slightly higher ones than in pure aqueous solutions. Such a moderate change of the mobility is in accordance with the slight variation of the viscosity of the mixed ACN–water solvent (see Ref. [17] for comparison).

For practical purposes it may be concluded that ACN added to the BGE can be favorable in CE if approximately the same change in the pK_a values of analytes as those under consideration like in mixed aqueous methanolic or ethanolic solvents is intended, but mobilities much higher than obtained in the

Table 3

Actual mobilities, $\mu_{act,i}$, of the anionic solutes in different ACN–water mixtures (concentration of ACN given in %, v/v) measured by CZE

Symbol	Name	$\mu_{act,i}$ ($10^{-9} \text{m}^2 \text{V}^{-1} \text{s}^{-1}$)			
		Water	20% ACN	40% ACN	60% ACN
A	benzoic	33.27	30.76	31.93	33.73
B	2-OH	36.29	31.12	33.57	39.10
C	3-OH	31.17	26.28	27.29	30.61
D	4-OH	31.08	25.75	25.84	26.53
E	2,3-diOH	32.62	27.58	29.24	32.44
F	2,4-diOH	32.53	26.36	27.86	30.58
G	3,4-diOH	29.68	23.61	23.87	24.99
H	3,5-diOH	28.97	22.86	24.00	24.74
I	2,4,6-triOH	34.00	26.59	28.66	34.19
J	3,4,5-triOH	27.69	22.53	22.90	23.56
K	2-Me	31.59	28.93	29.22	31.67
L	3-Me	31.53	28.34	29.14	30.36
M	4-Me	31.51	28.11	28.97	31.16
N	2,4-diMe	29.21	26.26	27.35	30.37
O	2,5-diMe	29.36	26.66	27.92	30.94
P	3,4-diMe	29.39	26.28	27.65	29.41
Q	3,5-diMe	28.94	26.99	27.50	30.97
R	2-NO ₂	32.78	29.48	29.74	33.24
S	3-NO ₂	32.27	28.92	28.53	32.97
T	4-NO ₂	32.65	28.71	28.63	32.59
U	3,4-diNO ₂	31.03	27.37	28.24	31.83
V	3,5-diNO ₂	30.63	27.85	29.07	32.76
W	2,4,6-triNO ₂	28.42	25.85	27.77	31.49
X	2-Cl	32.34	29.43	31.11	33.31
Y	3-Cl	32.63	29.19	30.23	33.28
Z	4-Cl	32.26	28.75	29.58	32.42

Ionic strength: 20 mmol/l; temperature: 25.0°C. The data for 0% ACN are the same as in Ref. [2].

alcoholic solvents are desired, e.g. for reasons of short analysis time. With e.g. 60% ACN, mobilities may be larger by up to a factor of two as compared to MeOH at the same concentration.

3.3. Product of mobility and viscosity (Walden product analogue)

In Fig. 2 the change of the mobility when connected to the solvent viscosity is shown. It is the analogue to the Walden product, $\mu\eta$. This product is related here to the product in the pure aqueous solvent, and the change, ρ , (in percent) is expressed by

$$\rho = 100[(\mu_{\text{act},i}\eta)^{\text{mix}} - (\mu_{\text{act},i}\eta)^{\text{w}}]/(\mu_{\text{act},i}\eta)^{\text{w}} \quad (3)$$

The anions are sorted according to their substituents: methyl, nitro and chloro substitution on the one hand, hydroxy substitution on the other hand. For the non-OH substituted anions the values for ρ decrease steadily and slightly with increasing ACN concentration, and are between about 5 to 15% lower at 60% ACN as compared to water. The OH-substituted anions exhibit a steeper decrease of ρ at low, and values remain almost constant at higher ACN content, with solutes D, G, H and J as exceptions (see below).

3.4. Comparison of the relation between mobility and solvent composition in the mixed aqueous–organic systems

3.4.1. Average changes, mean ρ , of the relative Walden product analogues

In Fig. 3 a comparison is given for the values of the relative Walden product analogues, mean ρ , averaged for a particular solvent composition over all solutes (again grouped into anions without OH substituents, and those with OH groups on the aromatic ring). The discussion is not restricted to ACN but includes also the effects observed in the aqueous–alcoholic solvents consisting of MeOH, EtOH and PrOH.

The plots of average ρ as a function of the alcoholic cosolvent tempt to postulate a trend: all values of the nitro-, chloro- and methyl-substituted anions increase upon addition of the particular

alcohol. However, they decrease when ACN is added. The shift of the maxima of the mean ρ coincides with the shift in viscosity of the mixed alcoholic solvents (see Fig. 3a): the sequence MeOH (maximum viscosity at 45% alcohol), EtOH (at 53%) and PrOH [at 60%, all (v/v)] is obeyed [17]. The maximum of the relative product is always about 10–15% (v/v) alcohol lower than the viscosity maximum.

In the alcoholic mixtures these compounds have mobilities which are less reduced than caused only by the solvent viscosity at up to 60%. In contrast to the mixed ACN-containing solvent, it appears that for this class of anions the hydrodynamic radii apparently first decrease on average with increasing concentration of alcohol. In fact, concerning the hydrodynamic radii, solvation effects (according to the so-called solvent-berg model, cf. e.g. Ref. [18]) will be decisive; this is the limitation of Walden's rule. This rule treats the solvent as a continuum. Theories for mobilities with this postulate go back to the dielectric friction model introduced by Born [19], further developed by a number of authors [20–27]. This theoretical approach will be briefly mentioned below. However, it also fails to give a quantitative description of the ion transport especially in polar solvents like water or the lower alcohols. Advanced theories based on microscopic models – taking into account ion-solvent interactions, the structure of the solvent immediately adjacent to the ion and the motion of the solvent molecules – are effective to estimate only the trends of the mobility in various solvents [28,29]. They have been restricted to simple solutes like alkali or halide ions.

For the compounds under discussion the positive deviation of the change of the relative Walden product analogues in the mixed alcoholic solvents indicate that the hydrodynamic radii become smaller on average upon addition of the alcohols to the aqueous solution, probably due to a loss of water molecules in the hydration shell of the anion. We rather concentrate on the solvation of the negatively charged carboxylate group than on interactions with the aromatic ring, or with the nitro, chloro or methyl substituents.

From the experimental results it may be derived that at higher alcohol contents the organic solvent molecules are probably implemented into the solva-

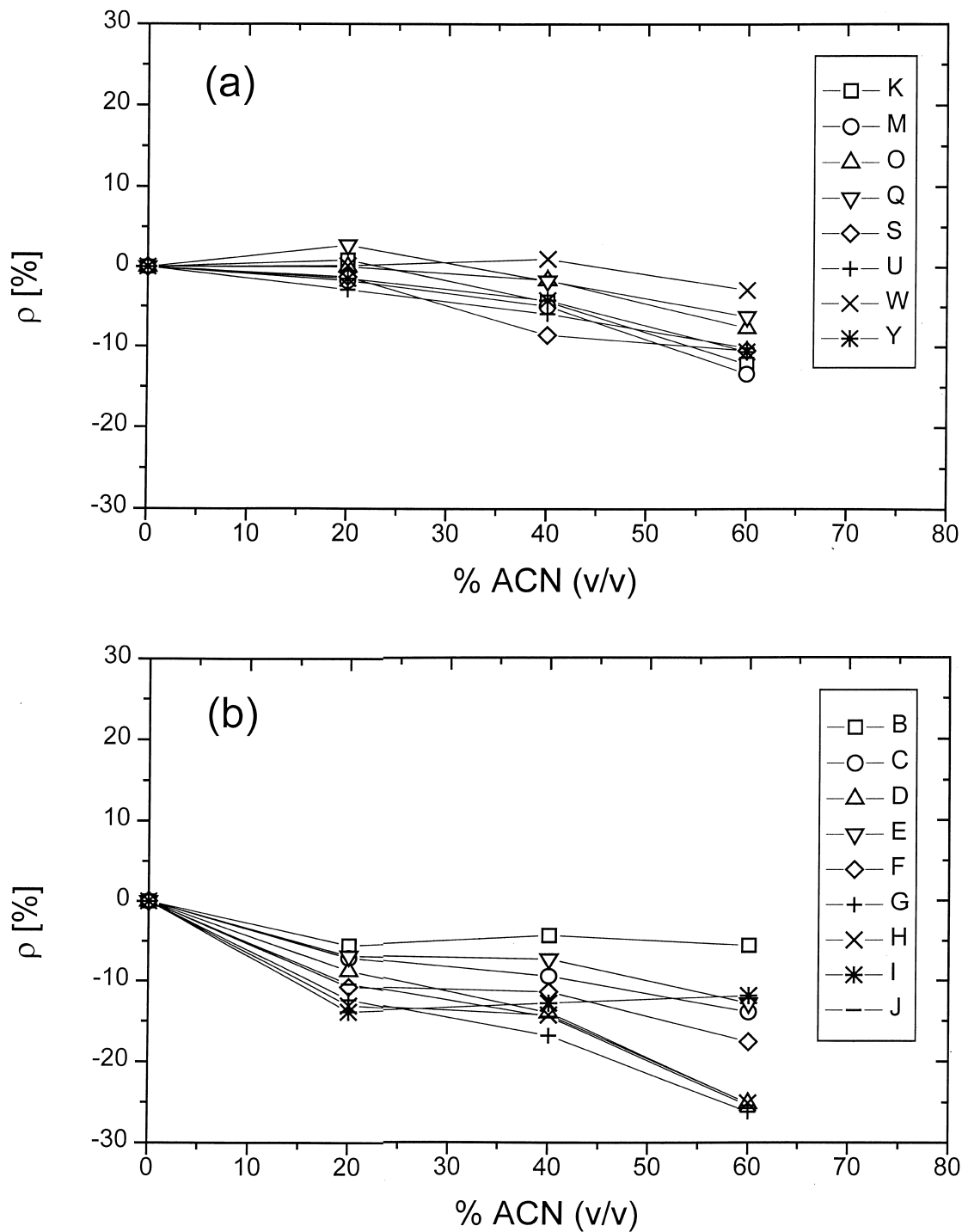


Fig. 2. Relative changes of Walden's products for the two different groups of anions in the various solvents; (a) non-hydroxy substituted, (b) hydroxy-substituted anions. The symbols of the anions are according to Table 3 (for (a) every second anion from this Table is taken). The relative changes are expressed by $\rho = 100[(\mu_{\text{act},i})^{\text{mix}} - (\mu_{\text{act},i})^{\text{w}}] / (\mu_{\text{act},i})^{\text{w}}$ (%); suffix mix and w stands for mixed aqueous–organic solvent or water, respectively.

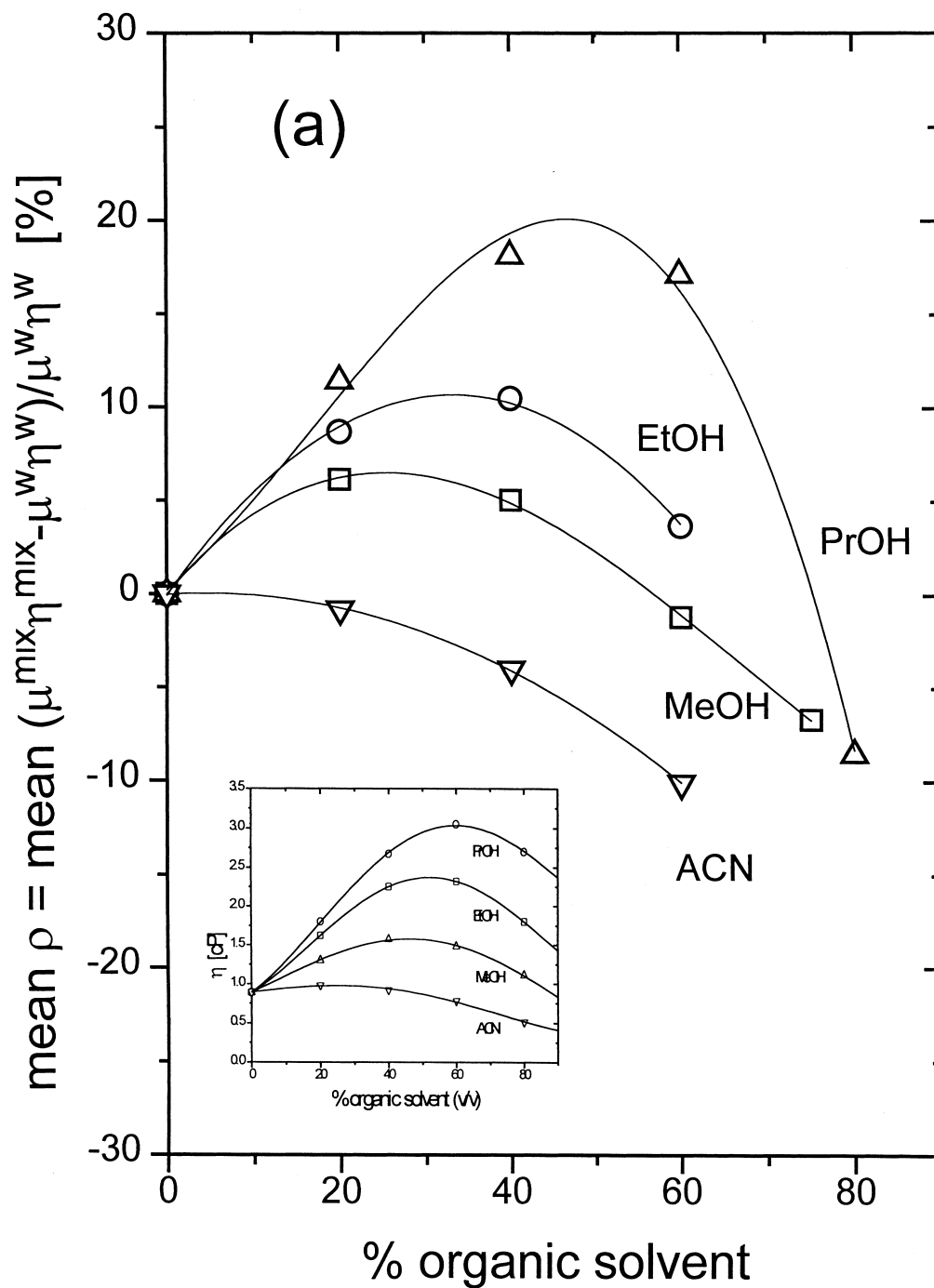


Fig. 3. Average values, $\text{mean } \rho$, of the relative change of the product of actual mobility, $\mu_{\text{act},i}$, of the solutes with the solvent viscosity, η , in the mixed aqueous–organic systems consisting of MeOH, EtOH, PrOH or ACN, respectively. (a) average for all methyl-, chloro- or nitro-substituted anions; (b) average for all hydroxy-substituted anions. For the values in the alcoholic systems see Refs. [2–4]. The graph of the viscosity as a function of the solvent composition is included in (a).

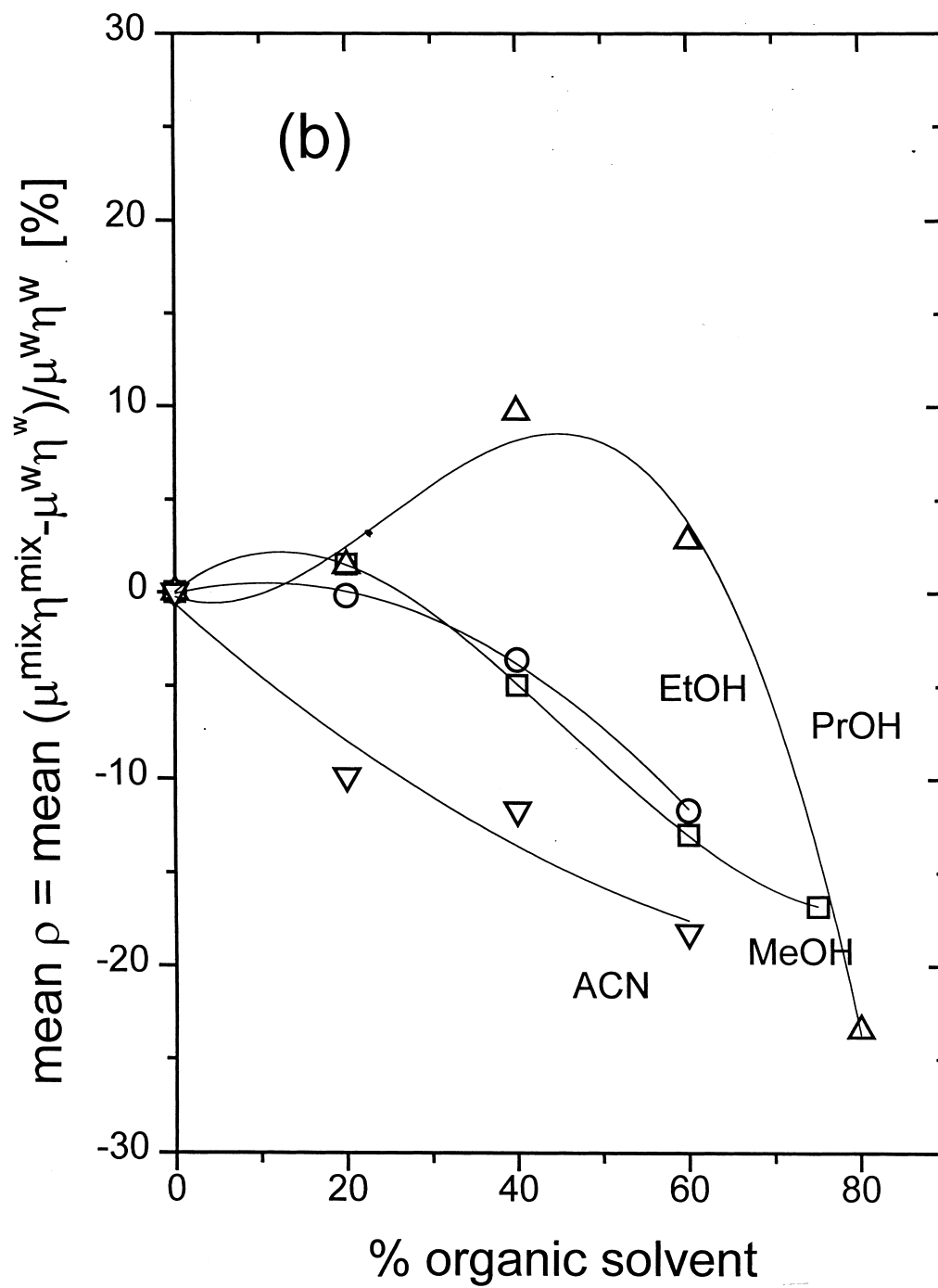


Fig. 3. (continued)

tion shell on the anionic charge center, thus increasing the hydrodynamic radii of the solvated anions, and decreasing in this way the relative Walden product analogues. Such an assumption seems plausible considering the relative effects of the different lower alcohols: with MeOH (the solvent most similar to water) solvation occurs at the lowest concentration of all three alcohols under discussion [at the maximum of the mean ρ vs. % alcohol curve, at about 30% (v/v) MeOH]. However, insertion of the alcohol molecule into the solvation shell of the ion does not mean that the anion is stabilized compared to the aqueous solution: the contrary seems to take place as the pK_a values of the solutes increase in all cases upon increasing the alcohol concentration. It should be mentioned in this context that alcohol molecules will not be present in the solvation shell at the same molar ratio as in the bulk solvent: they will be underrepresented because water has the ability of preferential solvation of the anions compared to alcohols.

For the OH-substituted solutes a different behavior is observed. Here less changes are found for all mixed solvents containing alcohol at a concentration up to 20% (v/v) in comparison with water (note that the mean ρ values are under consideration; the individual values of ρ of the different solutes change of course as discussed above and in Refs. [2–4]). OH-substitution seems to result in an increase in the average hydrodynamic radii upon addition of alcohol. One reason may lie in the fact that the OH groups of these solutes interact more strongly with the solvent molecules due to additional dipole–dipole interactions and hydrogen bonding.

Whereas a plausible interpretation of the effect of the organic solvent can be given for the alcohols, it is not possible to give such a straightforward explanation for ACN since all solutes show decreasing mean ρ values upon addition of this dipolar, aprotic solvent. As long as we restrict the discussion on the viscosity of the solvent and on the seeming variation of the hydrodynamic radii, problems for the interpretation of the change of the mobility with ACN concentration arise. It follows from all investigations of the pK_a values, and the values of the standard free energy of transfer of the single ionic species, that ACN is a much worse solvator for anions than water and all alcohols. This means that ACN is hardly able

to substitute water molecules in the solvation shell of the anions, and thus the hydrodynamic radii will not be increased as no replacement of water by bulky organic solvent molecules occurs.

If the number of water molecules in the primary solvation shell are decreased due to the decreasing concentration of water with increasing ACN content of the binary mixture, even a decrease of the hydrodynamic radii should be expected, leading to an increase of the relative Walden product analogue as well. However, the contrary is found experimentally. It also seems evident that a lipophilic interaction between the ACN molecules in the solvent and the aromatic ring of the solutes, or their substituents, respectively, is not the source of the overproportional decrease of the mobility, because the less lipophilic OH-substituted anions show an even more pronounced effect than the more lipophilic Me-, Cl-, and NO₂-substituted solutes. It must be therefore concluded that not such a simple explanation of the effects for ACN as compared to those of the alcohols can be offered. An extension of the Walden rule might lead to a better constancy of the mobility when the effect of the viscosity is less overestimated. It should be pointed out, however, that the values of the mobilities even simply corrected by the viscosity (according to Walden's rule) are changing on the average within a window of only $\pm 20\%$, although large changes of the mobilities in the different solvent systems are observed (up to 400% compared to water). This allows as a first step a fair prediction of the mobility in the various aqueous organic solvent mixtures.

3.4.2. Extended Walden products, $\mu\eta^p$

As the viscosity is a property of the bulk solvent, it is plausible that the ionic mobility as a molecular property seems not to depend directly on the viscosity, a fact that has already been pointed out some decades ago [30,31]. For some organic nonelectrolytes (e.g. glycerol or sucrose [32–34]) the experimental results of limiting ionic mobility and viscosity were better described by the equation

$$\mu_0\eta^p = \text{constant} \quad (4)$$

where the exponent p deviates from unity in most cases; it was less than one (around 0.7) for alkali

metal and halide ions. This means that Walden's rule overestimates the role of the solvent viscosity. For the solutes and solvents investigated, a better consistency between mobility and viscosity is observed when the power of η is not unity. The confirmation of this assumption is given in Fig. 4 where the modified values of the products of averaged actual mobility and viscosity are shown for exponent $p = 0.9$. For better comparison with the values for ρ in the different solvent systems also, this extended Walden product is related to that in the purely aqueous solvent, according to

$$\text{relative } \mu_{\text{act,av}} \eta^{0.9} = 100 [(\mu_{\text{act,av}} \eta^{0.9})^{\text{mix}} - (\eta_{\text{act,av}} \eta^{0.9})^{\text{w}}] / (\eta_{\text{act,av}} \eta^{0.9})^{\text{w}} \quad (5)$$

Only the non-hydroxy substituted anions are taken for this illustration, because it follows from all investigations that the OH substituted solutes behave differently in many aspects. Therefore the averaged actual mobilities, $\mu_{\text{act,av}}$ in Eq. (5) are the mean values for the compounds K to Z from Table 3.

From the comparison of Fig. 3 with Fig. 4 it can

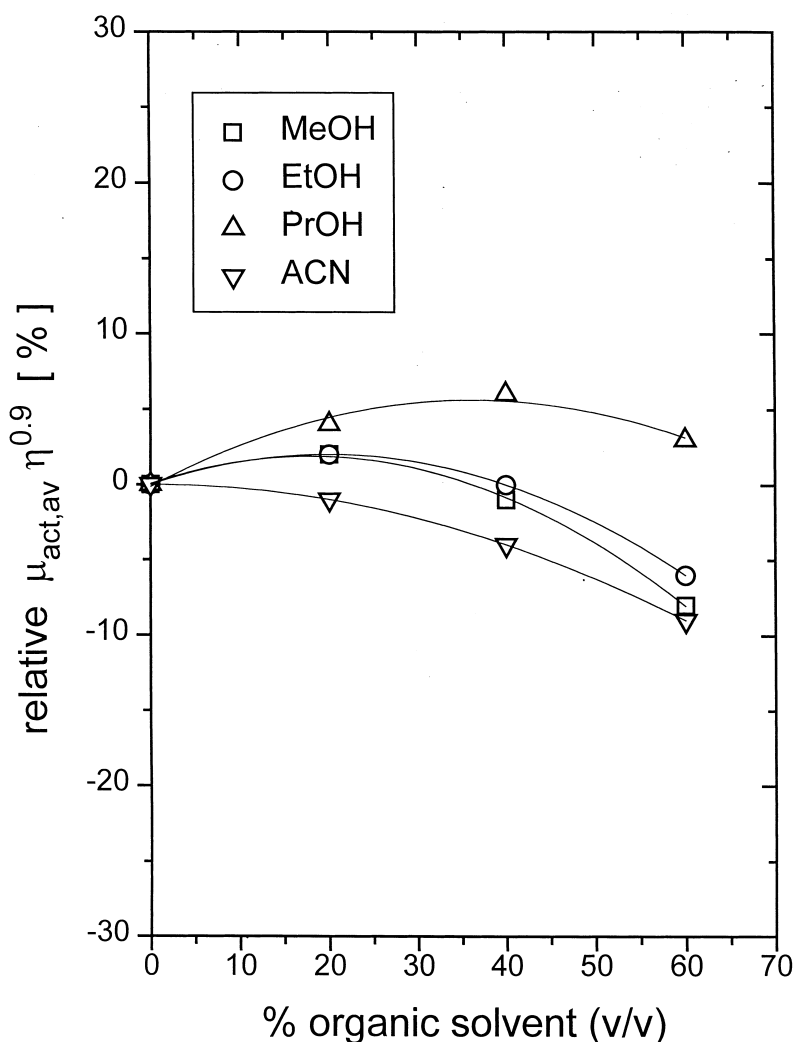


Fig. 4. Product of the average actual mobility and solvent viscosity, relative $\mu_{\text{act,av}} \eta^{0.9}$, related to the composition of the aqueous mixtures of the lower alcohols or ACN, respectively. Data shown are only for the non-hydroxy-substituted anions. For details, see Eq. (5) and text.

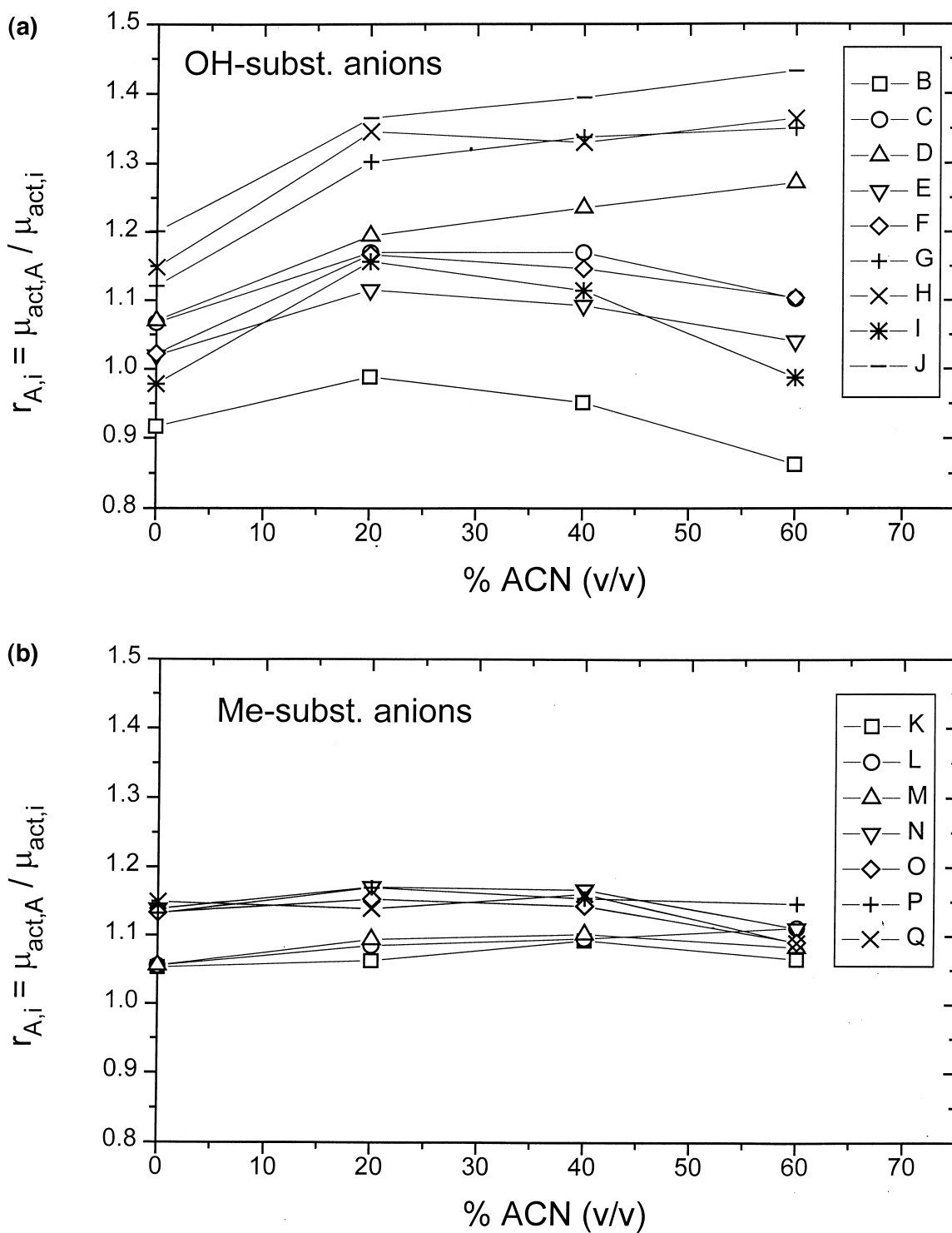


Fig. 5. Change of the actual mobility (expressed by $r_{A,i} = \mu_{act,A} / \mu_{act,i}$) of the solutes, i , with different substituents related to benzoate, A. Symbols of solutes as in Table 3.

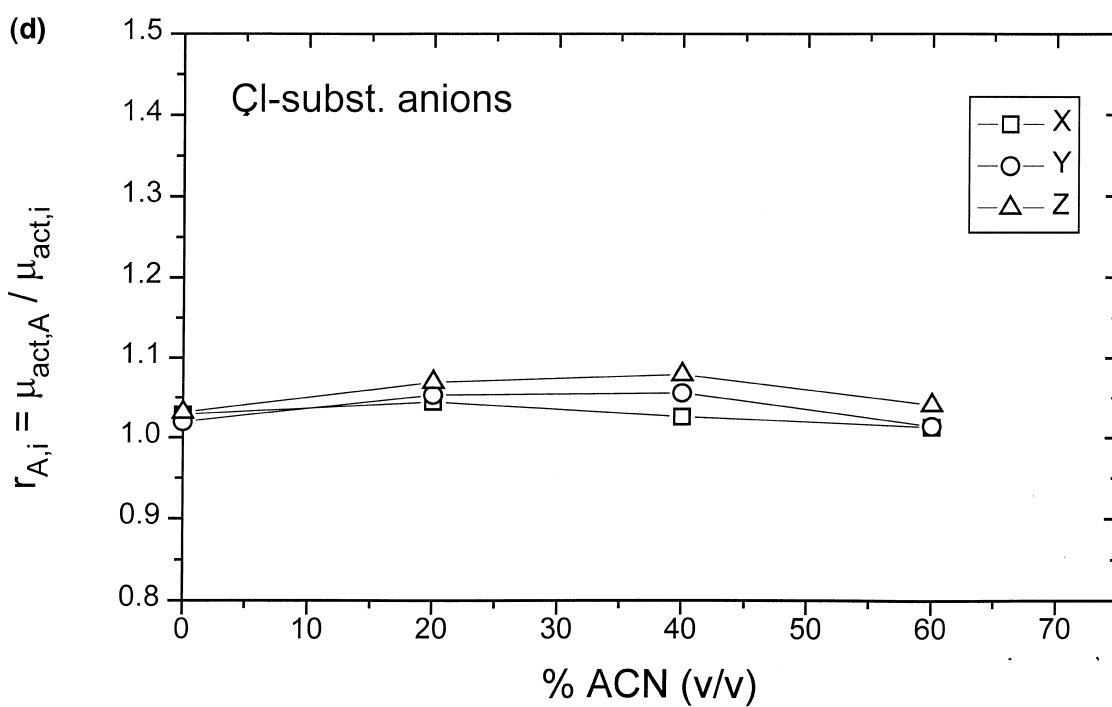
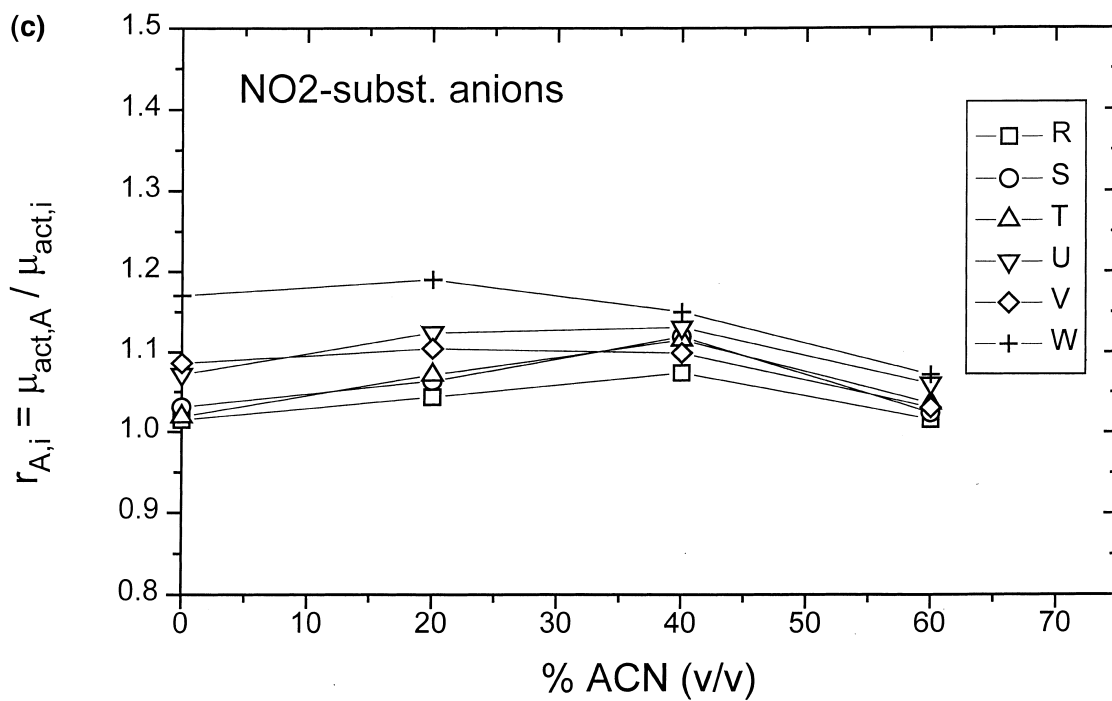


Fig. 5. (continued)

be deduced that the variation of the product is reduced here for all solutes under consideration to values changing only within +6 and –9%, a range which is smaller by nearly a factor of three compared to the normal Walden product.

To point out the complexity of ion movement in solvents like those under discussion, that model is mentioned which theoretically describes the mobility, taking into account the orientation of the dipolar solvent molecules in the vicinity of the ion during its migration through the liquid. The solvent molecules need a certain relaxation time, τ , to disorient behind the moving ion. During this time, a relaxation force acts on the ion in addition to the frictional force stemming from the viscosity. Taking into account these forces, the ionic mobility can be expressed by [18,20–22,26,27]

$$\mu\eta = \frac{ze_0}{a\left(r + \frac{s}{\varepsilon}\right)} \quad (6)$$

Here z is the ionic charge number, e_0 the electron charge unit, a is a factor depending on the geometry of the ion (for spherical particles it is 6π), s is a factor depending e.g. on the relaxation time and on the third power of the ion radius, and ε is the dielectric constant. It can be deduced that the product of viscosity and mobility depends (besides the radius of the solvated ions, which may vary itself) on the relaxation time of the solvent molecules and the dielectric constant.

The dielectric constant increases for the mixed solvents (with a certain composition) in the same sequence PrOH – EtOH – MeOH, ACN, leading to an increase of the products (Eq. (5)) in the sequence. This is in fact in contrast with our results (at least for the non-hydroxy substituted anions). However, as it is hardly possible to estimate all the parameters occurring in Eq. (5) (note also that the dielectric constant in the vicinity of the ion is not necessarily identical with that of the bulk liquid) and their variation with the solvent composition in detail, it is no surprise that in the complicated solvent systems there still remains a lack in interpretation of the effects.

3.5. Effect of the substituents on the change of the actual mobilities

The influence of the organic solvent on the

mobility is depicted in Fig. 5 according to the type of substituents of the solutes. For better visualization of the substituent effect, the actual mobilities are related to that of the unsubstituted benzoate according to $r_{A,i} = \mu_{act,A} / \mu_{act,i}$; A stands for benzoate. It can be seen that the mobility ratio (which is a kind of a selectivity coefficient) remains about equal for methyl-substitution, and becomes in general even smaller for the nitro-substituted solutes upon addition of ACN. Chloro derivatives show a slight increase of the selectivity coefficient. The OH-substituted solutes exhibit the largest effect from all anions under consideration, because as a general tendency the selectivity range is widened if ACN is a constituent of the solvent. Especially the following analytes behave much more differently than the non-OH anions: 4-OH, 3,4-OH, 3,5-OH, 3,4,5-OH (D, G, H, J). Noticeably three of these four compounds (namely G, H and J) form a subunit with high mutual similarity and with high dissimilarity to the other solutes also in the aqueous–methanolic solvent systems, as shown by cluster analysis [2]. These substances all have the OH group in meta position to the carboxylate. This finding is in clear accordance with that observed for the aqueous–alcoholic solvent systems.

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