High ionic strength electrokinetics

Marek Kosmulski[a,*], Jarl B. Rosenholm[b]

[a]Department of Electrochemistry, Lublin University of Technology, PL-20618 Lublin, Poland
[b]Department of Physical Chemistry, Åbo Akademi University, FIN-20500 Åbo, Finland

Abstract

The electrokinetic potentials at high ionic strengths can be measured by means of electroacoustic method. The reported values are surprisingly high: up to 25 mV in 1 mol dm^{-3} 1:1 electrolyte solution. The IEP of metal oxides in concentrated solutions of 1:1 electrolytes shifts to substantially higher pH values with respect to the pristine value, although these electrolytes are inert at low concentration. The shift in the IEP is salt-specific, and it is correlated with the hard–soft character of the anion and of the cation.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Isoelectric point; Zeta potential; Electric sonic amplitude; Colloid vibration current; Concentrated electrolyte solutions

Contents

* Corresponding author. Tel./fax: +48 81 53381355.
E-mail address: mkosmuls@abo.fi (M. Kosmulski).

1. Inert electrolyte

The concept of inert electrolyte is very useful in colloid chemistry. An electrolyte is termed inert (or indifferent) when the adsorption is exclusively due to electrostatic forces; that is, the ions do not adsorb specifically. The definitions of inert electrolyte and of specific adsorption were borrowed from electrochemists, who have been successfully using them in interpretation of the course of electrocapillary curves of mercury in the presence of various electrolytes. Interestingly, electrolytes, which are inert for mercury, are not necessarily inert for metal oxides or other model colloids, and vice versa. Generally, the categorizing of an electrolyte as inert (or not inert) depends on the type of interface and not only on the nature of the electrolyte. Addition of inert electrolyte to the system brings about changes in the absolute value of the surface charge density and surface potential, but not in the sign. In contrast, specific adsorption of ions may induce a sign reversal. For more detailed discussion on inert electrolytes, as well as on specific and nonspecific adsorption, confer a book by Lyklema [1]. Alkali metal halides, nitrates V, and chlorates VII (perchlorates) behave as inert electrolytes with respect to metal oxides and many other model colloids, at least at low concentrations and near the pristine point of zero charge PZC. In the present review, we show that at concentrations >0.1 mol dm^{-3}, the behavior of the abovementioned salts with respect to the same model colloids can be far from inert. The shift in the isoelectric point IEP detected by means of the electroacoustic method is the most spectacular evidence of specific adsorption of alkali metal cations from concentrated solutions of their 1–1 salts. We also clarify a few discrepancies and arguments which appeared in the literature in this respect.

2. Potentiometric titration

Potentiometric titration is used (often together with electrokinetic methods) to study the surface-charging behavior of colloids. The pristine point of zero charge PZC of metal oxides and related materials is determined as the intersection point of surface-charging curves obtained at various ionic strengths [1]. Potentiometric titration at high ionic strengths does not pose substantial technical problems as compared with experiments at lower electrolyte concentrations. Many publications report the surface-charging curves of metal oxides and related materials obtained in 1 mol dm^{-3} solutions of 1–1 electrolytes, most often Na and

K salts. Most published papers report one common intersection point of charging curves of metal oxides obtained at inert electrolyte concentrations up to 1 mol dm^{-3}. Ionic strengths higher than 1 mol dm^{-3} were seldom visited, but the existing data do not indicate any substantial shift in the PZC in the presence of Na or K salts even at extremely high concentrations [2].

There are rather few publications reporting surface charging in concentrated solutions of lithium salts. Yates and Healy [3] report a common intersection point at pH 5.8 of charging curves of rutile obtained in 0.001, 0.01, 0.1, and 2.9 mol dm^{-3} KNO$_3$. This type of behavior indicates that KNO$_3$ behaves as inert electrolyte even at very high concentrations. The charging curves obtained in 0.001, 0.01, and 0.1 mol dm^{-3} LiCl also intersect at pH 5.8. In contrast, 1 mol dm^{-3} LiCl induced a shift in the PZC to low pH indicating specific adsorption of lithium. Breeuwsma and Lyklema [4] report a common intersection point at pH 8.5 of charging curves of hematite obtained in 0.001, 0.01, 0.1, and 1 mol dm^{-3} KCl. The charging curves obtained in 0.001 and 0.01 mol dm^{-3} LiCl also intersect at pH 8.5. With higher LiCl concentrations, the PZC shifts to lower pH, namely, 8.2 at 0.1 mol dm^{-3} LiCl and 7.9 at 0.1 mol dm^{-3} LiCl. This type of behavior is characteristic for specific adsorption of cations. Tschapek et al. [5] found an indifferent behavior of 1 mol dm^{-3} LiCl with respect to titania, but specific adsorption of Li from 1 mol dm^{-3} LiCl on alumina, while KCl (up to 1 mol dm^{-3}) was an indifferent electrolyte for the both oxides.

The above results suggest indifferent behavior of lithium salts up to about 0.1 mol dm^{-3}, and specific adsorption of Li from 1 mol dm^{-3} solutions of its salts at least on some oxides, but the shifts in the PZC were rather insignificant in comparison with the shifts in the IEP in analogous systems (which will be discussed in Section 10). On the other hand, the titration data indicate that the surface charging at high concentrations of K and Na salts follows the same pattern as that observed at low ionic strengths; that is, addition of salts affects the absolute value of the surface charge, but not its sign, apparently without any concentration limit.

3. Classical electrokinetic methods

Classical electrokinetic methods allow measurements of the ζ potential at electrolyte concentrations up to about 0.1 mol dm^{-3}. Higher ionic strengths were not accessible experimentally until very recently. The difficulties in obtaining reliable ζ potentials at high ionic strengths by

means of microelectrophoresis (the most common method used in commercial zetameters) are due to the following phenomena:

(1) The dispersions are unstable against aggregation and sedimentation (cf., Section 11).
(2) The absolute value of the ζ potential is comparable with or even lower than a typical scatter of experimental results.
(3) The electric field produces heat in the measurement cell and thus affects the physical properties of the liquid, e.g., its viscosity. Moreover, convective currents influence the flow of the particles and the liquid in the cell.
(4) The products of reactions occurring at the electrodes (solutes, gases, and solids) affect the results.

The limitations #2–4 affect also the results obtained by electroosmosis. The upper limit of electrolyte concentration for commercial zetameters is usually indicated in user manuals. Publications reporting experimental results obtained at very high ionic strengths using classical electrokinetic methods are rare, and the knowledge about the electrokinetics at high ionic strengths was chiefly based on extrapolation of the trends observed at lower ionic strengths. Over the range of ionic strengths accessible for direct measurements (0.0001–0.1 mol dm^{-3}), the increase in the ionic strength induced a decrease in the absolute value of the ζ potential, but did not affect its sign or the position of the IEP. Many examples of typical electrokinetic behavior at low ionic strengths can be found elsewhere [2].

It seemed rather obvious that at higher ionic strengths (beyond the range accessible experimentally), the absolute values of the ζ potential are even lower (close to zero), but the IEP is not affected. Mpandou and Siffert [6] reported such a behavior of titania at ionic strength up to about 1 mol dm^{-3} NaCl. A few publications report rather insignificant shifts (by a fraction of 1 pH unit) in the IEP in 0.1 mol dm^{-3} solutions of 1:1 salts, suggesting specific adsorption of alkali metal cations. Very recent designs of instruments based on electrophoresis are more suitable for studies of high ionic strength systems than the old equipment. Probably more targeted electrophoretic experiments based on the present knowledge about salt specificity would produce more significant results even with older equipment.

4. Early evidence for specific adsorption of cations from "inert" electrolytes

Some limitations of the significance of the term "inert electrolyte" were realized long before the advent of the electroacoustic method. The specific adsorption of alkali metal cations from organic solvents is beyond the scope of the present review, and it was discussed in detail elsewhere [7–10]. It was further found that even relatively small admixture of organic cosolvents to water caused abnormal electrokinetic behavior. In water–organic mixtures, the presence of 0.1 mol dm^{-3} of alkali halides induces substantial shifts in the IEP; for example, the ζ potential of anatase in 30% methanol is positive over the entire pH range [11]. The sign reversal of the ζ potential of anatase in mixed solvents is rather insensitive to the nature of the 1–1 salt. Similar sign reversal was observed for other metal oxides. The presence of 0.1 mol dm^{-3} of CsCl induces a substantial shift in the IEP of silica to high pH even in pure water [12]. Somewhat less-pronounced shifts in the IEP of silica were observed in the presence of Rb and K salts (and Li and Na salts have very little or no effect at all). In contrast with silica, the shift in the IEP of metal oxides in 0.1 mol dm^{-3} salt solutions is rather insignificant.

5. Electroacoustic method

The instruments based on the electroacoustic method became available in the 1990s, and their popularity is steadily growing. These instruments are designed to measure the ζ potential and the particle size. The theory for Acustosizer was developed by O'Brien [13,14].

The ESA signal is expressed by the equation:

$$\text{ESA} = A(\omega)\phi(\Delta\rho/\rho)<\mu_D>Z \tag{1}$$

where $A(\omega)$ is a frequency-dependent instrument constant, ϕ is the volume fraction of the solid, ρ is the specific density of the liquid, $\Delta\rho$ is the difference in specific density between the solid and the liquid, Z is another instrument constant, and $<\mu_D>$ is the particle-averaged dynamic mobility, given by

$$\mu_D = (2\varepsilon\zeta/3\eta)G(\omega a^2/v)[1 + f(\lambda, \omega')], \tag{2}$$

where the function G is defined as

$$G(\alpha) = \left[1 + (1+i)(\alpha/2)^{1/2}\right] \Big/ \Big[1 + (1+i)(\alpha/2)^{1/2}$$
$$+ i(\alpha/9)(3 + 2\Delta\rho/\rho)\Big] \tag{3}$$

and

$$f(\lambda, \omega') = \left[1 + i\omega' - (2\lambda + i\omega' \, \varepsilon_p/\varepsilon)\right]$$
$$\Big/\left[2(1 + i\omega') + (2\lambda + i\omega' \, \varepsilon_p/\varepsilon)\right] \tag{4}$$

and

$$\omega' = \omega\varepsilon/K^\infty \tag{5}$$

and

$$\lambda = K_s/(K^\infty a). \tag{6}$$

In the above equations, K_s is the surface conductance in the double layer, K^∞ is the solution conductivity, a is the particle radius, and $v \, (=\eta/\rho)$ is the kinematic viscosity.

The principle of operation of Acustosizer (applied electric field results in an ultrasound signal that is measured and analyzed) was described in detail by O'Brien et al. [15]. The principle of operation of DT-1200 (applied ultrasound field results in an electric signal, colloid vibration current CVI, that is measured and analyzed) was described in detail by Dukhin and Goetz [16].

6. Correction for the electrolyte signal

A salt solution produces an ESA (or CVI) signal roughly proportional to the salt concentration. At low salt concentrations, the contribution of the salt to the total ESA signal is negligible (at sufficiently high solid load), but at high salt concentration, it becomes significant and has to be corrected for. The ratio of the ESA signal from the dispersion to the signal from the solution can be improved by increasing the solid-to-liquid ratio, but only to limited extent because very concentrated dispersions are viscous and difficult to handle. Then, the electrolyte correction problem cannot be avoided. Commercially available instruments have an electrolyte background correction procedure built in the software. When the ζ potential is close to zero, it is obtained as a difference between two large and almost equal numbers (signal from the dispersion and signal from the electrolyte, each burdened with certain error), thus the value and even the sign of the difference are very uncertain.

7. Instrument calibration

Acustosizer was not originally designed to work with very high electrolyte concentrations. A special calibration procedure (cf., Section 10.3 for details) was then proposed for high salt concentrations, but for sake of simplicity, normal factory calibration is preferred even for relatively high salt concentrations when it does not cause a substantial error in the results. The problem of limited validity of the factory calibration was mentioned already in the first electroacoustic study at high ionic strength by Kosmulski and Rosenholm [17]. Here, we will discuss the concentration range for which the normal factory calibration is acceptable (and possible consequences of working outside normal operation range of the instrument) in some more detail. This will allow objective assessment of published results, most of which were obtained with factory calibration. In contrast, according to the manufacturer [18], DT-1200 does not need high-ionic-strength calibration; that is, the instrument calibrated by means of a low-ionic-strength standard produces proper values of the ζ potential even at very high ionic strengths. Thus, further discussions in this section refer solely to Acustosizer.

Johnson et al. [19] discussed the significance of the results reported in Ref. [17] in terms of the calibration procedure (conventional low-ionic-strength calibration ver-

sus a special high-ionic-strength calibration designed by Rowlands et al. [20]). To this end, the results obtained using two different calibration procedures at otherwise identical experimental conditions are compared. In the presence of 1 mol dm^{-3} CsNO$_3$, the ζ potential obtained with high-ionic-strength calibration was two times higher in absolute value than the ζ potential obtained with low-ionic-strength calibration. But in the presence of 0.3 mol dm^{-3} CsNO$_3$, the difference in ζ potential between the above two calibration procedures was less than 10%. The extent of the difference between the results obtained using two calibration methods is salt-specific, and the experimental results are explicitly reported only for CsNO$_3$. Johnson et al. [19] mentioned that the salt selected for presentation shows "*substantially greater*" discrepancy between the results obtained using two calibration methods than LiNO$_3$. The original paper by Rowlands et al. [20] addressed this question in more explicit way. Figs. 1 and 2 in Ref. [20] show that the ESA signal of NaCl and KCl solutions is smaller by an order of magnitude then the ESA signal of CsCl solution of the same conductance over the frequency range 0.3 to 11.15 MHz. This is because—according to Eq. (1)—the ESA signal of a salt solution is proportional to the product of two instrument constants (of which one is frequency dependent) and the following salt-dependent factor

$$\gamma = \Sigma \phi_j (\Delta \rho_j / \rho) <\mu_D>_j \tag{7}$$

where the sum is taken over all ions j in solution. For single, symmetrical electrolyte, γ can be estimated using a few physical constants [15]

$$\gamma = K[ez_-(1+r)]^{-1}[(m_- - \rho V_-) + (z_-/z_+)(m_+ - \rho V_+)r] \tag{8}$$

where K is the electrolyte conductivity, m are atomic (molecular) masses, V are partial molar volumes of the cation and of the anion (subscript $+$ and $-$), and r is the anion to cation mobility ratio. Rowlands et al. [20] used values of physical constants corresponding to dilute solutions and assumed that these values are also valid for concentrated electrolytes. The difference $(m_- - m_+)$, which is much higher in absolute value for CsCl than for NaCl or KCl is the leading term on rhs of Eq. (8), thus the substantial difference in the ESA signal of these salts found experimentally is not surprising. The results presented by Rowlands et al. [20] indicate that the contribution of the background signal to the total dispersion signal in Cs salts is much higher than for Na and K salts, and that the example selected in Ref. [19] is not representative for Na and K salts.

Rowlands et al. [20] discussed also the pH dependence of the ESA signal from concentrated electrolyte solutions. There is no apparent reason for existence of such an effect, because the volume fractions of H$^+$ and OH$^-$ ions (Eq. (7)) are negligibly small. Nevertheless, the pH effect was experimentally observed, and it was interpreted as

"electrode effect" linked to the electrode double layer. Certainly, all ions in the system, not only H^+ and OH^- ions, contribute to the electrode double layer. Thus, if the interpretation of the pH effect proposed by Rowlands et al. [20] is correct, then the calibration based on Eqs. (7) and (8) has an approximate character.

Thus, combining the results from Refs. [19] and [20], we conclude that the numerical values of ζ potentials obtained with factory calibration:

- for an ionic strength of 1 mol dm^{-3} are underestimated by a factor of about 2 for certain salts, and by a factor substantially less than 2 for most salts.
- for an ionic strength of 0.3 mol dm^{-3} are underestimated by about 10% for certain salts and substantially less than 10% for most salts.

Apparently, the factory calibration produces quite reasonable numerical values of ζ potentials for most salts at concentrations up to at least 0.3 mol dm^{-3} (and probably much higher). Moreover, Fig. 1 in Ref. [19] demonstrates the position of the IEP is not affected by the calibration procedure, and the calibration error can be corrected by multiplication of the ζ potentials obtained with factory calibration by a pH-independent factor, which increases as the concentration of given salt increases. In the discussed example, the correction factor was about 1.1 for 0.3 mol dm^{-3} CsNO$_3$ and about 2 for 1 mol dm^{-3} CsNO$_3$. Thus, factory calibration does not induce an error in the IEP, even in results obtained beyond the normal operation range of the instrument (high salt concentration).

To estimate the correction factors for different salts, we analyzed the electrokinetic curves obtained by factory calibration in the acidic range (pH <4). At constant pH, the uncorrected ζ potential decreases when the concentration of salt increases. In our opinion, this trend is qualitatively correct; that is, the corrected ζ potential does not increase with the concentration of given salt. We showed above that correction is not necessary for most salts at concentrations below 0.3 mol dm^{-3}. Then, the correction factor must not be higher than the ratio between the uncorrected ζ potential in 0.3 mol dm^{-3} solution of certain electrolyte and at concentration of interest (>0.3 mol dm^{-3}) of the same electrolyte at the same pH in the acidic range. The above ratio indicates the upper limit of the correction factor. On the other hand, the lower limit can be estimated assuming that the ζ potential in the acidic range at constant pH and ionic strength depends only on the nature of the anion, and it does not depend on the nature of the cation. Indeed, we found many examples when the uncorrected ζ potential at certain pH (about 4) assumed the same cation-independent value for given concentration of salts with common anion. Thus, the lower limit of the correction factor is the ratio of the highest uncorrected ζ potential at certain ionic strength in a series of salts with common anion (which may already need some correction) to the uncorrected ζ potential in equimolar solution of certain salt at the same pH. The above correction factors neglect the difference in the static permittivity between water and solution of interest, which may result in an increase in the ζ potential by further 10% or so in a 1 mol dm^{-3} salt solution (cf., Section 9). The correction factors calculated using the discussed above procedure are summarized in Table 1.

The correction factor found in Ref. [19] for 1 mol dm^{-3} CsNO$_3$ is half-way between the minimum and maximum value reported in Table 1.

Table 1
Correction factors for factory calibration of Acustosizer

Salt	Concentration (mol dm^{-3})	Lower limit	Upper limit
CsNO$_3$	0.4	1.2	
	0.6	1.6	2
	1	1.5	2.5
KBr	0.6		1.4
	1.1		2.9
KCl	0.6	1.2	1.5
	0.8	1.2	2.3
	0.9		2.7
KNO$_3$	0.4		1.1
	0.5		1.2
	0.6		1.3
	0.7		1.4
	0.8		1.7
	0.9		1.7
	1		1.8
	1.3		1.9
	1.4		1.9
LiCl	0.6		1.2
	0.8		1.5
	1.1		2
NaBr	0.4		1.1
	0.5		1.2
	0.6		1.3
	0.7		1.5
	0.8		1.6
	0.9		1.7
	1	1.3	1.8
NaCl	0.5	1.2	
	0.9		2.1
	1.5		3
NaClO$_4$	0.7		1.5
	0.9	1.1	1.7
NaNO$_3$	0.4	1.1	1.2
	0.5		1.3
	0.6		1.4
	0.7		1.5
	0.8		1.6
	0.9		1.7
	1.2		2.2
RbCl	1	2.3	3
	1.2		3.3

8. Choice of model system

Anatase dispersion was the first model system used to demonstrate the usefulness of the electroacoustic method in studies of electrokinetic potentials at high ionic strengths.

Various aspects were taken into account in assessment of anatase and other candidates as the model colloid.

1. Anatase is commercially available as relatively pure material, which can be further purified using an inexpensive and well-documented method targeted at specific impurities. This is important because the electroacoustic method requires a substantial amount of material per one experiment (pH titration at one electrolyte concentration), and the experimental study in Ref. [17] required over 100 titrations. Moreover this material consists of nearly spherical particles with relatively narrow particle size distribution. The theories used in interpretation of the raw signal assume that the particles are spherical and monodipersed. Such a theory applied for a real system far from that assumption would produce unrealistic values of ζ potentials.

2. Anatase is practically insoluble in water. Thus, its surface charging is almost entirely due to adsorption–desorption processes. With materials that show appreciable solubility, interpretation of the surface-charging phenomena is more complicated, and it has to take into account selective leaching of various components of the solid.

3. The adsorption–desorption equilibria are fast. This results in absence of a hysteresis loop which is often observed in pH titrations of materials whose adsorption–desorption equilibria need more time to establish. Probably this property is related to #2 (very low solubility).

4. Anatase has a well-established pristine PZC at pH about 6, which is independent of the specific sample of material or method used to study it. Many other materials show more scattered values of PZC/IEP dependent on specific sample of material and experimental method, thus difficult to control. The PZC of anatase is in the center of the pH scale. This allows us to study positively and negatively charged surfaces at moderate pH values.

5. Anatase has a high specific density. According to Eq. (1), this results in a strong ESA signal even at relatively low ζ potential.

6. Anatase can be easily dispersed in water.

There are a few other model systems, which fit this purpose almost equally well.

9. Physical properties of salt solutions

The necessity to use specific values of physical constants (e.g., viscosity, specific density, and permittivity; cf., Eqs. (7), and (8)), which are different from the physical constants of pure water (in certain systems of interest) is the most trivial, but important and an often overlooked aspect of the work with concentrated electrolyte solutions. The difference becomes significant (>1% for most salts) at concentrations above 0.1 mol dm^{-3}. For lower salt concentrations, the error induced by using physical properties of pure water is rather insignificant. The viscosities and specific densities of solutions of common salts are readily available from the literature (e.g., Ref. [21]). On the other hand permittivities can be only found in original papers and in a few specialized monographs (cf., Refs. [22–25] and references therein). Typically, the permittivity of 1 mol dm^{-3} solution of a 1:1 salt is lower by about 10% than the permittivity of water, but the concentration dependence is not linear and salt-specific (e.g., NaCl depresses the permittivity more effectively than CsCl). Kosmulski and Rosenholm [17] explicitly stated, they did not correct their results for the difference between
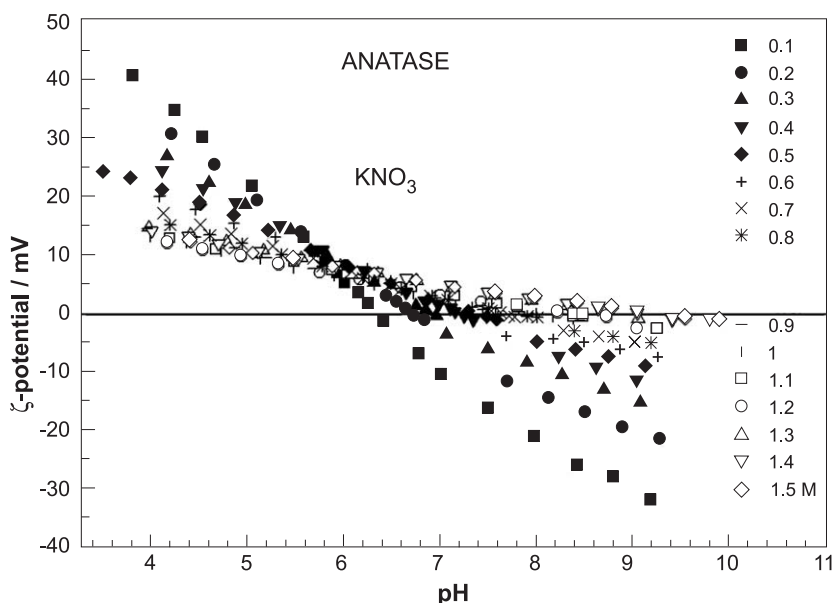

Fig. 1. The electrokinetic potential of anatase in concentrated solutions of KNO$_3$.
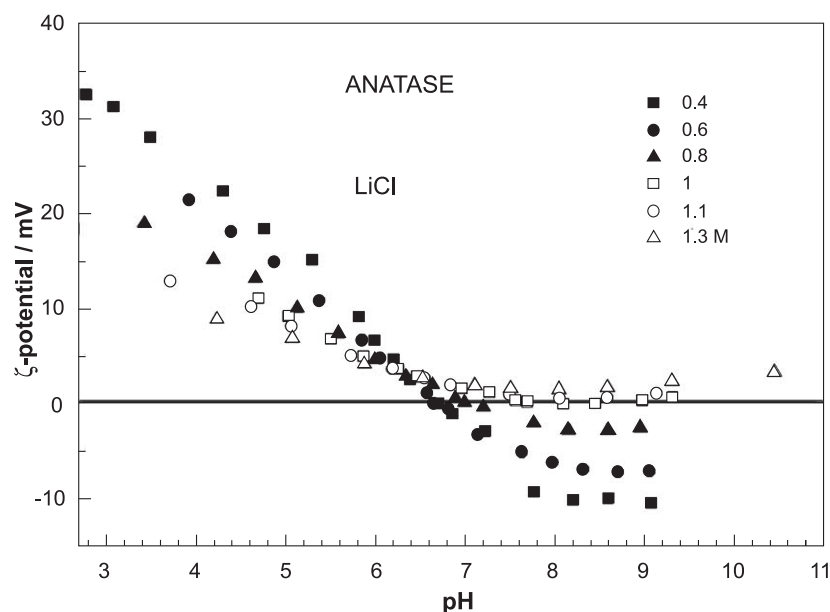
Fig. 2. The electrokinetic potential of anatase in concentrated solutions of LiCl.

the permittivity of water and salt solution. In many other publications, the problem of the difference between the physical constants of water and salt solution was not addressed, and the difference in the permittivity (and in other physical properties) between water and salt solution was probably ignored.

10. Case studies

The electrokinetic behavior of various materials at high ionic strengths is discussed in chronological order.

10.1. Titania

The electrokinetic behavior of anatase (crystalline form of titania) at high ionic strengths was studied more extensively than of any other material. Its advantages as a model system for electroacoustic measurements are summarized in Section 8. The pristine IEP of anatase reported in Ref. [17] is 5.9. Three examples of electrokinetic behavior at high ionic strengths (of 15 salts studied) are presented in Figs. 1–3. The numerical values of the ζ potentials in these figures at high ionic strengths are underestimated due to factory calibration (Section 7).
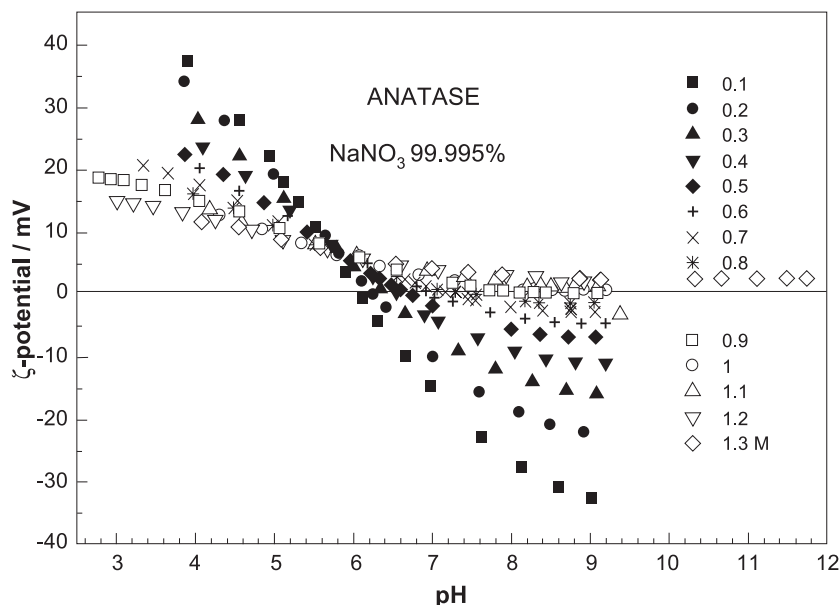

Fig. 3. The electrokinetic potential of anatase in concentrated solutions of NaNO$_3$ (99.995%).

Table 2
The most negative value of ζ potential (in mV) of anatase in 0.4 mol dm^{-3} solutions [17]

	Li	Na	K	Rb	Cs
CH$_3$COO		−10			
Cl	−11	^{a}	−11	−11	
NO$_3$	−2	−11	−12		−16^b
ClO$_4$		−8	^{c}	^{c}	^{c}
Br		−6	−6		
I	−3^d	−2	−7		−15^b

^{a} Error messages.
^{b} Probably underestimated by about 20% due to low-conductivity calibration.
^{c} Low solubility.
^{d} 0.5 mol dm^{-3}.

Figs. 1–3 show individual behavior for each salt, but one trend is common. With one exception of sodium acetate, all studied salts at concentrations in the range of about 0.1–0.5 mol dm^{-3} induced a shift in the IEP of anatase to high pH. The magnitude of this shift was different for different salts. Moreover, the electrokinetic curves became dissymmetrical, i.e., absolute values of the ζ potential above the pristine PZC were lower than the ζ potential below the pristine PZC at the same distance from pristine PZC. This trend can be quantified as the most negative value of ζ potential of anatase observed in 0.4 mol dm^{-3} solution of given salt (ζ_{min}; Table 2). The low-conductivity calibration does not induce a substantial error in the absolute values of the ζ potential for most salts at this concentration (Section 7).

At pH 4 in 0.4 mol dm^{-3} solutions of most salts, the ζ potential of anatase is about +25 mV, then all salts show some degree of dissymmetry in the electrokinetic behavior with respect to the pristine IEP. Negative numbers low in absolute value in Table 2 indicate abnormal behavior (strongly dissymmetrical electrokinetic curves). The high ionic strength behavior depends on the anion and on the cation, but in certain instances the effect of the anion (in a series of salts with common cation) or the effect of the cation (in a series of salts with common anion) is insignificant. This property is termed differentiating effect of small cations and large anions (and absence of differentiating effect for large cations and small anions). For instance, there is a substantial difference in ζ_{min} between NaNO$_3$ and NaI (factor 5.5), but only rather insignificant difference (6%) between CsNO$_3$ and CsI. The ζ_{min} was identical for LiCl, KCl, and RbCl, but very different in a series of iodides (factor up to 7.5).

The differentiating effect is not limited to the behavior at concentration of 0.4 mol dm^{-3} (Table 2). Fig. 4 presents ζ_{min} at various concentrations of Na salts and iodides (strong differentiating effect) and K salts and chlorides (weak differentiating effect). Some absolute values of ζ_{min} in Fig. 4 are underestimated, especially at high concentrations of Cs salts, and introduction of a correction factor (Table 1) would even emphasize the trends shown in Fig. 4.

According to the electrokinetic behavior at high ionic strengths illustrated in Fig. 4, all salts studied can be sorted into two categories. Lithium salts, NaNO$_3$, NaClO$_4$, NaBr, and NaI belong to the first category. Above certain critical
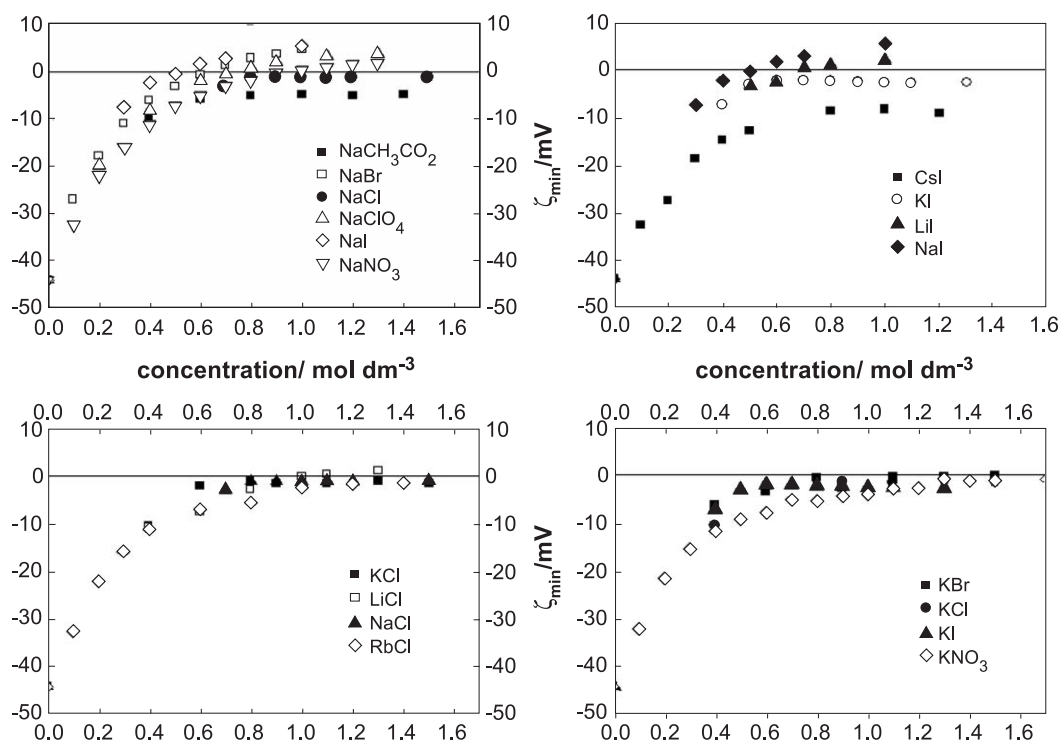

Fig. 4. The minimum values of ζ potentials in concentrated solutions of different salts.

concentration of these salts, the sign of the ζ potential is positive over the entire pH range, and there is no IEP. The critical concentrations (estimated as the zero point in the ζ_{min} plotted as the function of salt concentration) are summarized in Table 3.

NaCl and K, Rb and Cs salts belong to the second category, and for the entire studied concentration range of these salts anatase showed the IEP (no critical concentration). We will show later that the same types of combinations of two ions in the 1–1 salts, namely, small cation (Li or Na) and large anion, induce similar charge reversal phenomena with oxides other than anatase, and other 1–1 salts do not induce such a sign reversal.

A substantial difference between Li and Na salts was observed, although they belong to the same category. At sufficiently high pH and sufficiently high salt concentration, the ζ potential in the presence of most Na salts assumes a constant (pH-independent) positive or negative value (Fig. 3). In contrast, in the presence of concentrated solutions of Li salts (and NaCH$_3$COO), the ζ potential reaches a minimum (positive or negative) value at certain pH and then increases (Fig. 2). This results in two IEP at certain concentrations of Li salts (and probably NaCH$_3$COO). In contrast, the ζ potential in the presence of concentrated solutions of K (Fig. 1), Rb and Cs salts, constantly decreases even at very high pH values, and there is no plateau (as with Na) or minimum (as with Li).

Among the salts which always produce an IEP, three types of behavior can be distinguished. With Cs salts, KI and NaCl, the IEP reaches a maximum at certain salt concentration (about 0.5 mol dm^{-3}), and further increase in the salt concentration ultimately induces a shift in the IEP back to lower values. With RbCl, KBr, and KCl, the IEP reaches a maximum at certain salt concentration (about 0.5 mol dm^{-3}), and further increase in the salt concentration does not affect the position of the IEP. Finally, with KNO$_3$ (Fig. 1), the IEP continuously shifts to high pH as the ionic strength increases.

The absolute values of the ζ potential are low on the both sides of the IEP when the ionic strength is high, and those low ζ potentials are obtained as the result of background subtraction, i.e., as a difference between two large and almost equal numbers. Thus, the exact position of the IEP at high ionic strengths is very uncertain. The shifts in the IEP were confirmed by experiments carried out at different solid to liquid ratios to eliminate errors related to the background subtraction.

Table 3
Critical concentrations (in mol dm^{-3}) of salts [17]

	Li	Na
Cl	1.02	>1.5 if any
NO$_3$	0.56	0.94
ClO$_4$		0.73
Br		0.62
I	0.67	0.53

Experiments with reagent grade NaNO$_3$ on the one hand and very pure reagent (Fig. 3) on the other, did not show substantial difference. Apparently, the purity of salts is not crucial for abnormal behavior observed in the electro-acoustic measurements at high ionic strengths.

Kosmulski et al. [26] studied also another sample of anatase, and the critical concentrations of various salts were consistent.

Gustafsson et al. [27] found a substantial shift in the IEP of anatase (the same material as used in Ref. [17]) to high pH in 0.5 mol dm^{-3} NaCl, and in 1 mol dm^{-3} NaCl, the ζ potential was positive over the entire pH range. Apparently, there is a discrepancy between Ref. [17], which suggests a critical NaCl concentration >1.5 mol dm^{-3} (if any), and Ref. [27], which suggests a critical NaCl concentration between 0.5 and 1 mol dm^{-3}. However, the ζ potentials obtained at high ionic strengths in Ref. [27] were not background-corrected, thus their significance is limited.

The unusual behavior of anatase in concentrated NaI solution found using Acustosizer was qualitatively confirmed using DT-1200 [28]. The zetametric titrations were carried out in 0.1, 0.3, 0.5, and 1 mol dm^{-3} NaI. The measurements were repeated in three laboratories using different pieces of equipment. Only positive ζ potentials were observed over the entire pH range (no IEP) in 1 mol dm^{-3} NaI, which is above the critical concentration found by means of Acustosizer (Table 3). However, the absolute values of the ζ potentials found by means of DT-1200 were substantially lower than for Acustosizer. At lower NaI concentrations, the IEP was higher than the pristine value, and the absolute values of the ζ potentials at pH >8 were almost pH-independent (plateau) and substantially lower than at low pH for the same ionic strength. Also, the IEP found in 0.5 mol dm^{-3} KCl using DT-1200 was consistent with the results obtained by means of Acustosizer.

Rutile is another crystalline form of titania. Kosmulski et al. [29] studied the electrokinetic potentials of rutile at high NaI concentration. The choice of NaI was based on earlier experience with anatase (and other metal oxides), which suggests that NaI shifts the IEP and induces a sign reversal of the ζ potential to positive at lower concentration than any other 1–1 salt. Indeed, NaI induced a substantial shift in the IEP of rutile to high pH at a concentration as low as 0.3 mol dm^{-3}, and with 0.7 mol dm^{-3}, the electrokinetic potential of rutile was positive over the entire pH range. The later concentration is probably beyond the range where low-conductivity calibration produces reliable values of the ζ potential, but the method of calibration affects only the numerical value of the ζ potential but not its sign.

10.2. Zirconia

The experiments with zirconia [17] qualitatively confirmed the trends observed for anatase. The experiments

have been carried out with two salts ($NaNO_3$ and NaBr), for which a shift in the IEP (up to critical concentration of salt) and then positive ζ potentials over the entire pH range were observed (cf., Fig. 3). The critical concentrations observed for zirconia were lower than the corresponding critical concentrations for anatase by about 20%. This result not only confirms the anion specificity found for anatase in a series of sodium salts, but also may suggest similar proportionality for other salts.

10.3. Alumina

Alumina is less suitable as a model system than titania or zirconia, because it shows appreciable pH-dependent solubility, especially at pH >9. The first study of the high ionic strength ζ potentials of alumina was carried out by Rowlands et al. [20] who used gibbsite (hydrous aluminum oxide) as a model adsorbent. The main novelty in Ref. [20] was the introduction of a new calibration method, namely, replacement of the factory calibration based on $K_4SiW_{12}O_{40}$ by CsCl calibration. The difference between the two is in the higher solubility of CsCl, which makes it possible to work at higher conductance. As discussed above, the nonlinearity of the sensor results in underestimated ζ potential at high ionic strength for a factory-calibrated instrument. The concentration of the CsCl solution appropriate as the calibration standard is selected so that the conductivity of CsCl and of the dispersion medium match. Then, each titration at high ionic strength (various salts or various concentrations) needs a separate CsCl calibration.

The effects discussed above for anatase were confirmed in Ref. [20]; 0.5 mol dm^{-3} NaCl induced a shift in the IEP from its pristine value at pH 9.1 to pH 11, and in 3 mol dm^{-3} NaCl, there was no IEP at all (positive, almost pH-independent ζ potentials over the pH range 8–12.8). Concentrations other than 0.5 and 3 mol dm^{-3} or salts other than NaCl were not studied. Thus, Ref. [20] makes it possible to only roughly estimate the critical NaCl concentration and does not give information about salt specificity. However, the results are in line with the general trend reported in Ref. [17], that certain Li and Na salts reverse the sign of the ζ potential to positive even at very high pH.

Johnson et al. [30] studied ζ potentials of α-alumina in the presence of 0.01, 0.1, 0.3, and 1 mol dm^{-3} solutions of alkali nitrates and potassium halides using the high-conductivity calibration procedure designed by Rowlands et al. [20] (vide infra).

Increasing concentrations of potassium salts and of $CsNO_3$ [30] induced a stepwise decrease in the absolute value of the ζ potentials of α-alumina on the both sides of the IEP according to the low-ionic-strength trend (Section 3), and the position of the IEP was almost intact up to 1 mol dm^{-3}. In 1 mol dm^{-3} KNO_3 and $CsNO_3$, the IEP slightly shifted to low pH, and this was interpreted by the authors as an error in the background subtraction procedure. Johnson et al. [30] interpret their results for potassium halides (and

nitrate) as the absence of anion specificity in the electro-kinetic behavior of alumina at high ionic strengths. Thus, they confirmed the absence of differentiating effect for large cations, which was discussed in detail in Ref. [17]. The generalization about absence of anion specificity based on the experimental study with potassium salts is incorrect, because sodium and lithium salts do show anion specificity, as it was discussed above for anatase and (as we will show later) also for alumina.

Also, $NaNO_3$ did not induce a substantial shift in the IEP up to 1 mol dm^{-3}, but the electrokinetic curves were unsymmetrical, namely, the absolute values of negative ζ potentials of α-alumina in the presence of 0.3 and 1 mol dm^{-3} $NaNO_3$ are substantially lower than ζ potentials measured at the same conditions except with potassium salts or cesium nitrate rather than sodium nitrate. The negative ζ potentials of α-alumina in the presence of 0.3 and 1 mol dm^{-3} $NaNO_3$ were also substantially lower than the ζ potentials at the same distance from the IEP on the positive side. This result is substantially different from the study by Rowlands et al. [20], who found a substantial shift in the IEP at NaCl concentration of 0.5 mol dm^{-3}. The difference in the behavior of alumina in the presence of NaCl on the one hand and $NaNO_3$ on the other may be interpreted in terms of the anion specificity (the differentiating effect of Na; cf., Fig. 4), but it may also be due to a difference between gibbsite and α-alumina in their surface properties. The results reported by Johnson et al. [30] for $NaNO_3$ are also substantially different from the behavior of anatase [17], whose IEP was shifted to high pH at relatively low $NaNO_3$ concentration.

Finally, $LiNO_3$ induced a shift in the IEP from pH 9.5 (pristine) to 11 at 0.3 mol dm^{-3}, and at 1 mol dm^{-3}, there was no IEP at all and the ζ potential of α-alumina was positive and almost pH-independent over the range 4–12. This result is very similar to the results obtained for anatase in the presence of Li salts [17].

The differentiating effect of Na in the shift in the IEP of α-alumina was studied in more detail by Kosmulski [31] at salt concentration up to 0.5 mol dm^{-3}. The concentration range was limited because factory calibration was used (Section 7). $NaNO_3$ and $NaClO_4$ induced a rather insignif-icant shift in the IEP over the studied concentration range. This result substantiates the results reported by Johnson et al. [30]. On the other hand, NaBr and NaI induced a substantial shift in the IEP to high pH at concentration as low as 0.3 mol dm^{-3}, and the presence of 0.4 mol dm^{-3} NaI induced a reversal of sign of the ζ potential of α-alumina to positive up to pH 11.4 and probably over the entire pH range. Thus, the differentiating effect of Na in the shift in the IEP found for anatase has been confirmed, and the anion series is the same for the both oxides.

10.4. Silica

The surface charging of silica is very different from the behavior of metal oxides. In many papers, an IEP at pH

about 2 is reported, but the results obtained by different authors are rather scattered. Many other papers suggest that the IEP of silica does not exist, and the ζ potential is negative over the entire pH range. Recent multi-instrument studies [32,33] demonstrated that the same sample of silica (amorphous or quartz) may display IEP at various pH or not at all dependent on the instrument used. Interestingly, the electrokinetic curves at pH >5 obtained using various instruments were rather consistent.

Silica is less suitable for electroacoustic studied than the discussed metal oxides. It has lower specific density and shows higher solubility than alumina, zirconia, or titania, and as discussed above, it does not have a well-established PZC. It is even not certain if the PZC exists at all [34]. On the other hand, anomalous electrokinetic behavior of silica at concentrations of K, Rb, and Cs salts up to 0.1 mol dm^{-3} is well-documented (cf., Section 4). Kosmulski [35] and Franks [36] studied the electrokinetic behavior of silica at ionic strengths >0.1 mol dm^{-3} using the electroacoustic method. The IEP at pH 5.5 found in the presence of 0.1 mol dm^{-3} CsCl was similar to the value found using microelectrophoresis, and the difference between CsCl and CsNO$_3$ was rather insignificant. Thus, the shifts in the IEP of silica at high Cs concentrations are rather insensitive to the nature of the anion, and absence of differentiating effect previously found for K and Cs salts (Fig. 4) was confirmed.

At CsCl concentrations of 0.1–0.5 mol dm^{-3}, an increase in salt concentration did not induce further shift in the IEP to high pH, and with 0.7 mol dm^{-3}, the IEP shifted back to low pH (no positive values of ζ potential were observed). Probably, the absolute values of ζ potential reported in Ref. [35] are substantially underestimated for CsCl concentrations >0.3 mol dm^{-3} (Section 7).

Negative ζ potential of silica at pH 5–8 was found in 0.5 mol dm^{-3} NaI (the salt that induces sign reversal of the ζ potential of metal oxides to positive at a concentration lower than any other 1–1 salt). In this respect, silica behaves differently from titania, zirconia, and alumina, and as we show later from other metal oxides.

10.5. Hematite

In contrast with other metal oxides, 0.3 mol dm^{-3} NaI did not induce substantial shift in the IEP of synthetic hematite, but 0.4 mol dm^{-3} NaI induced a sign reversal of the ζ potential to positive over the entire pH range [29]. The reason for this peculiar difference between 0.3 and 0.4 mol dm^{-3} NaI is not known.

Kirwan and Fawell [37] found shifts in the IEP of hematite at high ionic strengths using ZetaPlus from Brookhaven (based on electrophoresis). The pristine IEP of the hematite was at pH 10, i.e., higher than most results reported in the literature. The critical concentrations of LiNO$_3$ and NaNO$_3$ (which induced a sign reversal of the ζ potential from negative to positive at pH 12 and 13) were

about 0.5 mol dm^{-3}. This result is in good agreement with the critical NaI concentration found in Ref. [29], and comparison of results obtained in these two studies again confirms the anion specificity (differentiating effect of Na) found for anatase and alumina.

10.6. Indium and niobium oxides

In 0.3 mol dm^{-3} NaI, the IEP of indium and niobium oxides was substantially shifted to higher pH with respect to the pristine values, and with 0.4 mol dm^{-3}, the electrokinetic potential of both oxides was positive over the entire pH range [38].

10.7. Goethite

The effect of NaI on the ζ potential of synthetic goethite was studied [39] using two instruments: Acustositzer and DT-1200, and the results were not completely consistent. The measurements with DT-1200 suggest absence of any shift in the IEP at NaI concentrations up to 0.5 mol dm^{-3}. The measurements with Acustosizer suggest a shift in the IEP from the pristine value of 9.4 to 10.8 in 0.5 mol dm^{-3} NaI, but further increase in the NaI concentration caused a shift in the IEP back to its pristine value. The difference in the IEP between the two instruments corresponds to a difference by a few millivolts in the value of ζ potential at pH 9–11. Both instruments indicated that the behavior of goethite at a high concentration of NaI (and probably other Na and Li salts) is different from the behavior of metal oxides. Then, the high ionic strength behavior found for anatase and confirmed for a few other metal oxides must not be uncritically generalized.

10.8. Cerium dioxide

The electrokinetic potential of a sample of cerium dioxide which showed a pristine IEP at pH 6 (lower than most results reported in the literature) was studied at different NaCl concentrations [40]. NaCl (0.1 mol dm^{-3}) induced a shift in the IEP to pH 7, and 0.5 mol dm^{-3} NaCl induced a further shift to pH 8.7. The shift in the IEP was found by means of DT-1200 and confirmed by means of a self-constructed electrophoretic apparatus. The results are in qualitative agreement with the behavior of other metal oxides in the presence of concentrated NaCl.

10.9. Sea water

Sea water can serve as an example of a high ionic strength system of great practical importance. Kosmulski et al. [41] reviewed the ζ potentials of various materials in sea water reported in the literature and obtained using classical electrokinetic methods. Some of these values were relatively high (up to 26 mV in absolute value). In contrast, the ζ potentials of various materials in artificial sea water

measured using the electroacoustic method did not exceed 4 mV in absolute value.

11. Colloid stability

Confirmation of the remarkable shifts in the IEP described in Section 10 by some independent method would be much desired. To this end, correlations of the ζ potential with other physical quantities can be used. Unfortunately, the well-established correlation between the absolute value of ζ potential and colloid stability is not suitable for this purpose.

Interaction curves between two identical particles were calculated using the HHF model [42] for the following model system: spherical particles, radius 10^{-6} m, retarded Hamaker constant $A_{11(3)}$ 10^{-20} J, ζ potential 40 mV, the physical properties of dispersing medium: as water at 25 °C. The Hamaker constant selected for model calculation is somewhat lower than typical values for powders studied in Section 10, and the ζ potential is somewhat higher than the highest value observed in 1 mol dm^{-3} solution of 1–1 electrolyte. The interaction curve in Fig. 5 for ionic strength of 0.1 mol dm^{-3} represents trends observed at low ionic strengths; at certain distance, the repulsive interaction (plus sign) prevails, and the energetic barrier on the order of a few hundred kT prevents fast coagulation.

On the other hand, with the ionic strength of 1 mol dm^{-3}, the repulsive component falls more sharply as the function of the distance, and the energetic barrier ceases. Thus, even at relatively high ζ potential of 40 mV, the HHF theory predicts instant coagulation. For higher values of retarded Hamaker constant, the barrier ceases at even lower electrolyte concentration at otherwise the same conditions. The present model calculations suggest that even relatively high ζ potentials experimentally observed at high ionic strengths

are not sufficient to stabilize a dispersion for typical values of Hamaker constants, and experiments in this direction seem to be pointless. Nevertheless, a few experimental results suggest unusual stability behavior at high salt concentrations. Yoops and Fuerstenau [43] observed a shift in the minimum of the stability of alumina dispersion to high pH at a high ionic strength. Yotsumoto and Yoon [44] reported a shift in the pH of minimum turbidity of titania dispersions when the NaCl concentration increased. This result might indicate a shift in the IEP, although the authors interpreted it differently. Moreover, at high ionic strengths, the region of low turbidity on the basic side became wider, thus apparently indicating a dissymmetry in the electrokinetic curves.

The particle size found in electroacoustic measurements indicates the tendency of particles to aggregate. Kosmulski et al. [26] found a shift in the maximum in mean diameter of titania particles to high pH at high concentrations of NaNO$_3$. The match between the maximum in mean diameter and the IEP was only qualitative.

12. Viscosity and yield stress

The correlation between the IEP on the one hand and the maximum in the viscosity of concentrated dispersions and in their yield stress on the other [45–48] is less well-known than the correlation with colloid stability, but fortunately high ionic strengths do not cause difficulties or limitations in the rheological measurements. Thus, the above correlation provides a possibility to verify the shift in the IEP at high ionic strengths, namely, such shifts should be accompanied with corresponding shifts in the maximum in the viscosity.

Kosmulski et al. [49] studied the shifts in the maximum in the viscosity of anatase dispersions induced by high
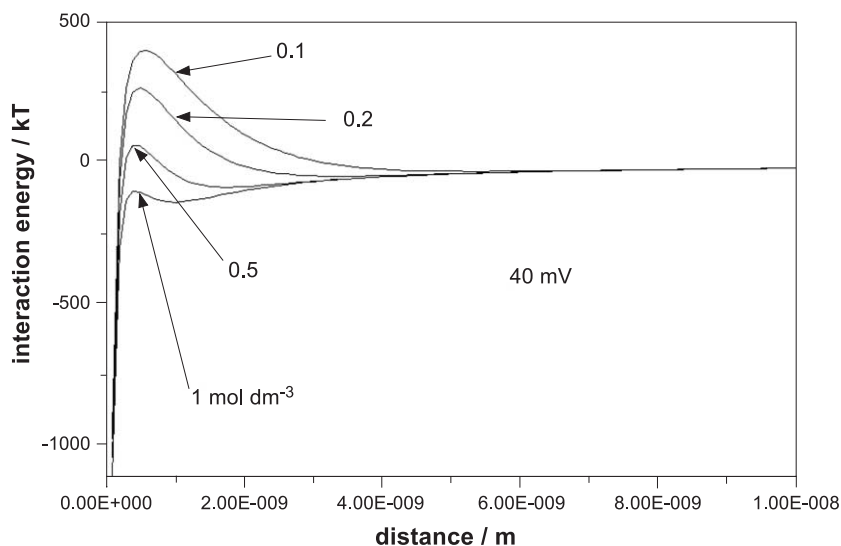

Fig. 5. Calculated interaction curves for two spheres in 0.1–1 mol dm^{-3} solutions of 1–1 electrolyte.

concentrations of NaI and NaNO$_3$. A linear correlation between viscosity at (arbitrarily selected) shear rate of 1.16 s^{-1} and yield stress was found. This type of correlation is well-known [48]. Then, a maximum in the yield stress matches the maximum in the viscosity. The measured viscosities are somewhat scattered, then the maximum in the viscosity could be only roughly estimated. There was a qualitative agreement between the shifts in the IEP on the one hand and in the maximum in the viscosity on the other:

(1) The shifts induced by a concentrated 1–1 electrolyte were always in direction of high pH
(2) The shift at higher concentration of the same electrolyte was more pronounced
(3) The shift induced by NaI was more pronounced than the shift induced by NaNO$_3$ at the same concentration.

However, there was no quantitative agreement: the shift in the IEP was sometimes more pronounced and sometimes less pronounced than the shift of the maximum in the viscosity. Similar shift in the maximum of the viscosity of concentrated dispersion of anatase in concentrated NaCl solution was found in another study from the same laboratory [27].

Johnson et al. [50] studied the yield stress in alumina dispersions in concentrated solutions of alkali nitrates and potassium halides (up to 1 mol dm^{-3}). The maximum in the yield stress of alumina dispersions in the presence of potassium halides and alkali nitrates except for LiNO$_3$ matched the pristine IEP, and this was in agreement with the absence of shift in the IEP. LiNO$_3$, the only studied salt which induced a shift in the IEP, behaved differently; 0.01 and 0.1 mol dm^{-3} solutions induced a shift in the maximum of the yield stress to high pH, and in 0.3 and 1 mol dm^{-3} solutions, there was no clear maximum in the yield stress.

The yield stress increased up to pH about 10 and then assumed a constant, pH-independent value. Then again, the IEP and the maximum in the yield stress are in qualitative agreement.

Franks et al. [51] studied the yield stress in alumina dispersions in 1 mol dm^{-3} solutions of sodium salts, but the ζ potentials for comparison are not available. The maximum in the yield stress shifts to slightly lower pH than at low salt concentration. This result is somewhat surprising in view of the shift in the IEP to high pH induced by sodium salts at concentrations of about 0.5 and 3 mol dm^{-3} reported in two independent publications.

Hsu and Nacu [40] found a shift in the maximum of the viscosity of CeO$_2$ dispersions to high pH when NaCl concentration increased. There was a qualitative agreement between the shift of the maximum of the viscosity and of the IEP. In contrast, the highest yield stress was observed near the pristine IEP, independent of NaCl concentration.

13. Interpretation

First, we will discuss analogies and differences between the results discussed above and adsorption of multivalent cations from their dilute solutions. The results shown in Figs. 1–3 resemble the shift in the IEP induced by specific adsorption of cations (Fig. 6), except the latter is observed at much lower concentrations of metal cations. The shifts in the IEP induced by specific adsorption of multivalent cations are rather insensitive to the nature of the anion, while the shifts in the IEP caused by specific adsorption of alkali metal cations at high ionic strengths substantially depend on the nature of the anion (cf., Section 10.1). The specific adsorption of cations (Fig. 6) is certainly due to metal ion–surface interactions, but at high concentrations of
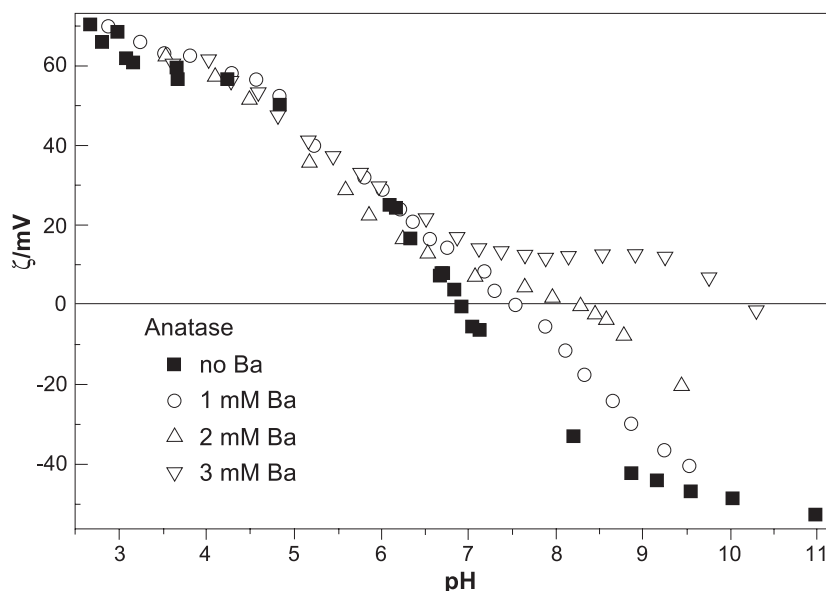

Fig. 6. Specific adsorption of Ba on anatase.

1:1 salts (Figs. 1–3), ion–ion interactions in the solution can substantially contribute to the driving force, and the similarity in electrokinetic behavior of various metal oxides (Section 10) supports this hypothesis. On the other hand, the difference in the cation affinity series between silica on the one hand and metal oxides on the other indicates that some specific interaction between the surface and particular ionic species ions in solution also plays an important role.

The interactions responsible for the shifts in the IEP at high ionic strengths demonstrate only at electrolyte concentrations higher than about 0.1 mol dm^{-3}, thus they are probably related to hydration of the ions and of the surface.

13.1. Hard–soft approach

Hard–soft and structure making–surface breaking scales were invoked to explain unusual electrokinetic behavior of anatase and alumina [17,30] at high ionic strengths. Actually, different wording was used to express the same type of properties. At low ionic strengths, the ions of 1–1 electrolytes are fully hydrated, they interact with other species and with charged surfaces chiefly via electrostatic interaction, and two different alkali metal cations (or two halide anions) behave similarly. Thus, the salt specificity is only observed far from the PZC, at high charge densities, when the concentration of counter-ions in the interfacial region is much higher than in the bulk solution. At high ionic strengths, the hydration is not complete, and the ions reveal their individual nature. Hard cations (Li, Na) have an enhanced affinity to the surfaces of metal oxides, which are also hard even near the pristine PZC when the electrostatic attraction does not exist or is very weak. Cations are usually harder than anions (relatively soft cations are still harder than relatively hard anions).

The result of the competition between the surface on the one hand and the anions in solution on the other for the hard cations depends on the hard–soft character of the anion in the 1–1 salt. Hard anions (Cl) in solution successfully compete with the surface for the hard cations. This prevents excessive adsorption of hard cations. Moreover, hard anions are also present in the interfacial region. This prevents formation of excessive charge (by high adsorption of cations and low adsorption of anions).

When the anion is soft, the situation diametrically changes. Soft anions less successfully compete with the surface for hard cations. Moreover, soft anions are less numerous in the interfacial region. This results in excess of the cations in the interfacial region and formation of positive electrokinetic charge. The above mechanism explains not only the cation specificity but also the differentiating effect of small cations. When the cation is sufficiently hard and the anion is sufficiently soft, substantial excess of cations with respect to anions in the interfacial region can occur even against the electrostatic repulsion.

Unless the surface carries substantial amount of negative charge, soft cations do not adsorb on a hard surface but remain in the solution irrespective of the nature of the anion. This explains absence of the differentiating effect of large cations.

The soft surface of silica has an enhanced affinity to soft anions, and this results in negative ζ potential over the entire pH range when the cation is hard. However, soft cations in the solution (Cs) can successfully compete with silica surface for soft anions and prevent their excessive adsorption. Moreover, soft cations enter easier the interfacial region than the hard cations, and this results in the shift in the IEP of silica to high pH at high concentrations of Cs salts.

13.2. Structure making–breaking approach

Among many structure making and breaking scales published in the literature, the Marcus' ΔG_{HB} scale [52] was found to be the most suitable for quantification of the effects of different salts on the ζ potential of anatase. At 25 °C, an average water molecule participates in 1.55 hydrogen bonds, and the change of this number per mole of the solute (individual ion) is defined as ΔG_{HB}. It was found that at sufficiently high concentrations of all salts for which ΔG_{HB} (cation)$-\Delta G_{HB}$(anion) >0.6, the ζ potential of anatase was reversed to positive over the entire pH range. In contrast, when ΔG_{HB} (cation)$-\Delta G_{HB}$(anion) <0.6, anatase had an IEP even at very high salt concentrations. The substantial difference between ΔG_{HB} and other structure making and breaking scales is in large gap between Na and K, which is also observed in the effect of salts on the electrokinetic behavior of salts. Many other properties (as ionic radii) change more smoothly from Li to Cs.

13.3. Dielectric exclusion approach

Yaroshchuk [53] and Dukhin and Goetz [16] interpret the shifts in the IEP at high ionic strengths in terms of the models published in the 1980s [54–58]. The difference in permittivity between bulk water and the surface layer is emphasized. The difference in solvation energies of particular ionic species between bulk water and the interfacial region results in uneven distribution of anions and cations between bulk water and the interfacial region and thus in excessive charge. The calculated ζ potentials at various ionic strengths as the function of the pH [53] resemble the course of the experimental curves. The same model was used to explain the unusual electrokinetic behavior induced by an admixture of an organic cosolvent (Section 4).

13.4. Activities of single ions

The shifts in the IEP are also qualitatively consistent with the individual activity coefficient of ions in concentrated solutions of alkali halides [59,60]. In concentrated solutions

of lithium and sodium salts, the activity of the cation is substantially greater (by a factor up to 2 in 1 mol dm^{-3} solution) than the activity of the anion. This creates a driving force for cation adsorption. On the other hand, in concentrated solutions of potassium halides, the anion has a higher activity. Although the individual activities of ions alone are not sufficient for quantitative explanation of the shifts in the IEP (Section 10), they must certainly be used in quantitative modeling of high ionic strength systems rather than mean activity coefficients.

14. Summary

The alkali metal cations, especially Li and Na, adsorb specifically from concentrated solutions of their halides, nitrates V and chlorates VII, on metal oxides. This results in a shift in the IEP of these materials to high pH values and in abnormally high positive values of the ζ potential at low pH observed in >0.1 molar solutions of these salts. However, these ζ potentials are not sufficiently high to stabilize the dispersions. The maximum in the viscosity of concentrated dispersions of metal oxides as the function of the pH also shifts to high pH values when the ionic strength increases. Silica behaves differently; its IEP is rather insensitive to Li and Na salts, while in >0.1 molar solutions of Cs, Rb, and K salts, the IEP shifts to high pH. The peculiar electrokinetic behavior of metal oxides at high ionic strengths discussed in the present review was confirmed by means of different instruments based on entirely different principles.

References

[1] Lyklema J. Fundamentals of Interface and Colloid Science, vol. 2. London: Academic Press; 1995.

[2] Kosmulski M. Chemical Properties of Materials Surfaces. Dekker; 2001.

[3] Yates DA, Healy TW. J Chem Soc, Faraday Trans I 1980;76:9–18.

[4] Breeuwsma A, Lyklema J. Discuss Faraday Soc 1972;52:324–33.

[5] Tschapek M, Wasowski C, Torres Sanchez RM. J Electro Anal Chem 1976;74:167–76.

[6] Mpandou A, Siffert B. J Colloid Interface Sci 1984;102:138.

[7] Zhukov AN, Levashova LG, Evstratova AYu. Kolloidn Z 1981; 43:240–5.

[8] Kosmulski M. In: Papirer E, editor. Adsorption on Silica Surfaces. Dekker; 2000. p. 343–68.

[9] Kosmulski M. In: Kallay N, editor. Interfacial Dynamics. Dekker; 1999. p. 273–312.

[10] Kosmulski M. In: Pelizzetti E, editor. Fine Particles Science and Technology. Kluwer; 1996. p. 185–96.

[11] Kosmulski M, Matijevic E. Colloids Surf 1992;64:57–65.

[12] Kosmulski M, Matijevic E. Colloid Polym Sci 1992;270:1046–8.

[13] O'Brien RW. J Fluid Mech 1988;190:71.

[14] O'Brien RW. J Fluid Mech 1990;212:81.

[15] O'Brien RW, Cannon DW, Rowlands WN. J Colloid Interface Sci 1995;173:406.

[16] Dukhin AS, Goetz PJ. Ultrasound for Characterizing Colloids. Elsevier; 2002. [371 pp.].

[17] Kosmulski M, Rosenholm JB. J Phys Chem 1996;100:11681–7.

[18] Dukhin AS. Personal communication.

[19] Johnson SB, Scales PJ, Healy TW. Langmuir 1999;15:8935–6.

[20] Rowlands WN, O'Brien RW, Hunter RJ, Patrick V. J Colloid Interface Sci 1997;188:325–35.

[21] CRC Handbook of Chemistry and Physics. CRC; 1999. p. 8.60–78.

[22] Nortemann K, Hilland J, Kaatze U. J Phys Chem, A 1997;101: 6864–9.

[23] Buchner R, Hefter GT, May PM. J Phys Chem, A 1999;103:1–9. [and supporting information at pubs.acs.com.].

[24] Chen T, Hefter G, Buchner R. J Phys Chem, A 2003;107:4025–31. [and supporting information at pubs.acs.com.].

[25] Lileev AS, Filimonova ZA, Lyashchenko AK. J Mol Liq 2003; 103–104:299–308.

[26] Kosmulski M, Durand-Vidal S, Gustafsson J, Rosenholm JB. Colloids Surf, A Physicochem Eng Asp 1999;157:245–59.

[27] Gustafsson J, Mikkola P, Jokinen M, Rosenholm JB. Colloids Surf, A Physicochem Eng Asp 2000;175:349–59.

[28] Kosmulski M, Dukhin AS, Priester T, Rosenholm JB. J Colloid Interface Sci 2003;263:152–5.

[29] Kosmulski M, Maczka E, Rosenholm JB. J Phys Chem, B 2002;106:2918–21.

[30] Johnson SB, Scales PJ, Healy TW. Langmuir 1999;15:2836–43.

[31] Kosmulski M. Langmuir 2002;18:785–7.

[32] Kosmulski M, Hartikainen J, Maczka E, Janusz W, Rosenholm JB. Anal Chem 2002;74:253.

[33] Kosmulski M, Maczka E, Janusz W, Rosenholm JB. J Colloid Interface Sci 2002;250:99–103.

[34] Koopal LK. Electrochim Acta 1996;41:2293.

[35] Kosmulski M. J Colloid Interface Sci 1998;208:543–5.

[36] Franks GV. J Colloid Interface Sci 2000;249:44–51.

[37] Kirwan LJ, Fawell PD, van Bronswijk W. Langmuir 2004;20: 4093–100.

[38] Kosmulski M, Rosenholm JB. J Colloid Interface Sci 2002;248:30–2.

[39] Kosmulski M, Maczka E, Jartych E, Rosenholm JB. Adv Colloid Interface Sci 2003;103:57–76.

[40] Hsu JP, Nacu A. J Colloid Interface Sci 2004;274:277–84.

[41] Kosmulski M, Maczka E, Marczewska-Boczkowska K, Rosenholm JB. Mar Pollut Bull 2003;46:120–2.

[42] Hogg R, Healy TW, Fuerstenau DW. Trans Faraday Soc 1966; 62:1638.

[43] Yoops JA, Fuerstenau DW. J Colloid Sci 1964;19:61.

[44] Yotsumoto H, Yoon RH. J Colloid Interface Sci 1993;157:426.

[45] Hunter RJ, Nicol SK. J Colloid Interface Sci 1968;28:250–9.

[46] Friend JP, Hunter RJ. J Colloid Interface Sci 1971;37:548–56.

[47] Firth BA. J Colloid Interface Sci 1976;57:257–65.

[48] Leong YK, Scales PJ, Healy TW, Boger DV, Buscall G. J Chem Soc, Faraday Trans 1993;89:2473–8.

[49] Kosmulski M, Gustafsson J, Rosenholm JB. J Colloid Interface Sci 1999;209:200–6.

[50] Johnson SB, Scales PJ, Healy TW. Langmuir 1999;15:2844.

[51] Franks GV, Johnson SB, Scales PJ, Boger DV, Healy TW. Langmuir 1999;15:4411–20.

[52] Marcus Y. J Solution Chem 1994;23:831.

[53] Yaroshchuk AE. J Colloid Interface Sci 2001;238:381–4.

[54] Derjaguin BV, Dukhin SS, Yaroshchuk AE. J Colloid Interface Sci 1987;115:234.

[55] Yaroshchuk AE. Colloid J USSR 1983;45:114.

[56] Yaroshchuk AE. Colloid J USSR 1984;46:82.

[57] Alexeev OL, Boiko YuP, Ovcharenko FD, Shilov VN, Chubirka LA. Colloid J USSR 1988;50:211–6.

[58] Dukhin SS, Churaev NV, Shilov VN, Starov VM. Usp Khim 1988; 57:1010–30.

[59] Lin CL, Lee LS. Fluid Phase Equilib 2003;205:69–88.

[60] Taghikhani V, Modarress H, Vera JH. Fluid Phase Equilib 1999; 166:66–7.