

The electrokinetic potentials of oxides in mixed water-1-propanol solvent

M. Kosmulski*[§] and J. B. Rosenholm[§]

**Department of Electrochemistry, Technical University of Lublin,
ul. Nadbystrzycka 38A, 20-618 Lublin, Poland*

[§]*Department of Physical Chemistry, Åbo Akademi University,
Porthansgatan 3-5, 20500 Turku, Finland*

The effect of the solvent (water versus mixed solvent 70% water + 30% 1-propanol, mass fraction) on the electrokinetic potential of oxides was studied at NaNO₃ concentrations of 0.1 and 0.01 mol dm⁻³. Only with anatase and indium oxide the IEP was shifted to high pH in the mixed solvent at high ionic strength. The IEP of rutile, and of niobium and tantalum oxides was rather insensitive to the solvent composition. The negative ζ potentials of all oxides were depressed in the presence of 1-propanol, but for silica and tantalum oxide, this effect was substantial only at NaNO₃ concentration of 0.1 mol dm⁻³. The positive branch of electrokinetic curves was less sensitive to the admixture of 1-propanol.

1. INTRODUCTION

Matijevic et al. have shown that replacement of water with water-alcohol mixed solvents leads to decrease in the negative ζ potentials of hematite [1], anatase and yttria [2], and silica [3] at sufficiently high ionic strength and organic component concentration, but the positive branch of the electrokinetic curves is rather unaffected. These results were recently confirmed by other research groups for alumina [4], hematite [5], and anatase [6] by means microelectrophoresis, and for the latter also by means of electroacoustic method [7]. Similar behavior of five oxides may suggest that other oxides behave alike, but such a generalization requires more experimental evidence. The depression in the negative ζ potentials at high ionic strengths caused by addition of organic co-solvents and the shifts in the IEP to higher pH are rather insensitive to the nature of 1-1 salt [8], but again this hypothesis is based on limited experimental data. Similar shifts in the

IEP were observed in purely aqueous systems at much higher ionic strengths [9], but the abilities of particular 1-1 salts to induce such shifts were substantially different.

Systematic studies of the effect of organic co-solvents on the electrokinetic behavior of oxides are scarce. Moser et al. [10] report the ζ potentials of titania in 10% methanol, but without comment as to how could the presence of organic cosolvent affect the results. Several publications report ζ potentials in mixed solvents at unknown pH [11], thus the alleged solvent effects are in fact combinations of solvent and pH effects. Different experimental conditions at which the electrokinetic studies in mixed solvent were carried out (different salts and different organic co-solvents at different concentrations) make it difficult to derive some general principles governing the effect of the organic co-solvents on the ζ potentials of different materials solely on basis of literature survey.

In the present study the electrokinetic behavior of different materials in water and in a mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction) were compared at otherwise the same experimental conditions using the electroacoustic method. In contrast with microelectrophoresis the solid to liquid ratio in the electroacoustic method is high, thus, the surface area involved in the experiment is high, too, and it is rather unlikely that some impurities present in the organic co-solvents substantially affect the results (but this is possible in microelectrophoresis). Moreover, many dispersions in this study were unstable (relatively high ionic strength) and this makes electrophoretic measurements rather difficult while in the electroacoustic method the stability of the dispersions is immaterial.

NaNO_3 was selected for this study as a salt that produces relatively small background signal in the electroacoustic method, i.e., the difference between the non-corrected and background-corrected ζ potential is not dramatic. Therefore small deviations from the initially adjusted ionic strength due to pH adjustment and evaporation of the solvent do not cause significant errors.

Aqueous 1-propanol was selected as the solvent whose physical quantities relevant to the present study (specific density, electric permittivity, viscosity) over the entire concentration range are well established in the literature [12], and the vapor pressure is low, so that no special precautions are necessary to assure constant composition of the solvent during the titration.

2. EXPERIMENTAL

The metal oxides were obtained from commercially available reagent grade materials (Table 1) by means of washing procedure described elsewhere [2]. Quartz (Sikron SF 800 from Quarzwerke Frechen) was washed with 1 molar nitric acid and then with water.

Tab. 1. Experimental conditions and the pristine IEP of oxides

oxide	Manufacturer	Volume fraction, %	Figure	IEP
quartz	Quarzwerte, Frechen	2.5	1	< 2 if any
rutile	Aldrich	1.5	2	6.4
Ta ₂ O ₅	Merck	0.3	3	5.3
Nb ₂ O ₅	Schuchardt	0.6	4	4.3
Anatase	Aldrich	2.5	5	6.1
In ₂ O ₃	Ventron	0.3	6	8.7

The other chemicals were reagent grade, water was MilliQ, and the experiments were carried out at 25 °C. The pH-scale in the Figures reflects the display of the pH-meter standardized using aqueous buffers. The electrokinetic potential was determined using Acustosizer (Colloidal Dynamics) with the 1.13 software version. All measurements at ionic strengths higher than 0.02 mol dm⁻³ were corrected for the electrolyte background. The solid concentration was 0.3 to 2.6 % by volume (Table 1). Details of the titration procedure are described elsewhere [9].

The electrokinetic behavior of indium oxide was studied by means of microelectrophoresis (Delsa 440, Coulter). This is because sufficient amount of material to use electroacoustic method was not available. The mass fraction of the solid was 0.01 %, and the mobility of the particles was calculated from the apparent mobility profile using the parabola method, and then converted to ζ potential using the Smoluchowski equation.

3. RESULTS AND DISCUSSION

The electrokinetic curves of oxides in water and in 30% 1-propanol at NaNO₃ concentrations of 0.1 and 0.01 mol dm⁻³ are shown in Figures 1-6. The pristine IEP (water, 0.01 mol dm⁻³ NaNO₃) are summarized in Table 1. The pristine IEP of rutile, anatase, and the nonexistence of IEP of quartz are in good agreement with the results reported in the literature [13] which are abundant for these materials. The pristine IEP obtained for Ta₂O₅, Nb₂O₅, and In₂O₃ are of special importance because the literature on these materials is rather scarce. The results for Ta₂O₅ and Nb₂O₅ confirm the IEP obtained for similar materials by means of microelectrophoresis [14]. These values are substantially higher than pH 3 often cited even in recent literature and originally published many decades ago. Probably this low value was due to insufficient purity of the oxides. Finally the data points obtained for In₂O₃, shown in Figure 6 are rather scattered and the upper limit of the pH range in which nearly zero ζ potentials were observed matches the IEP obtained for the same sample by electrophoresis but using another instrument [15]. The pristine IEP of In₂O₃ at pH 8.7 was obtained using electroacoustic method (data not shown here), but the solvent effect (Figure 6) was studied using microelectrophoresis.

The effect of mixed solvent on the electrokinetic behavior of particular oxides was very diverse. The negative ζ potential of quartz (Figure 1) was depressed in the mixed solvent (with respect to that in water) over the entire pH range for $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ and only at high pH in $0.01 \text{ mol dm}^{-3} \text{ NaNO}_3$. This result is in perfect agreement with the electrokinetic behavior of Stöber silica in 30% methanol-KCl system [3] except with Stöber silica a shift in the IEP was also observed in $0.1 \text{ mol dm}^{-3} \text{ KCl}$ (but Stöber silica had an IEP also in aqueous system in contrast with quartz).

The ζ potential of rutile (Figure 2) is rather insensitive to the nature of the solvent below the IEP, and is reduced by a factor of about 2 in 30% 1-propanol above the IEP. The position of the IEP is intact. This result suggests that different surface sites are responsible for surface charging in different pH regions, i.e., it favors the MUSIC model [16] over the older 2-pK model in which the positive and negative surface charge are ascribed to reactions of the same surface sites. In contrast with silica the extent of the solvent effect for rutile is rather insensitive to the ionic strength.

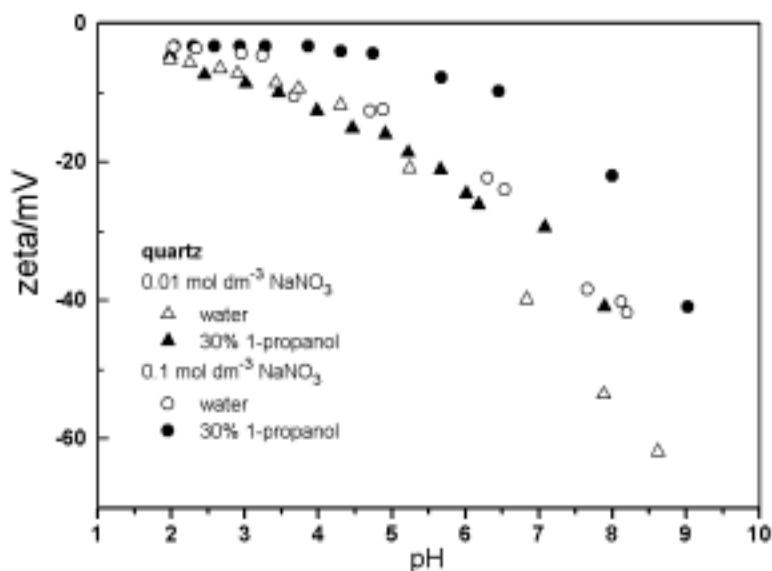


Fig. 1. Electrokinetic potential of quartz in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

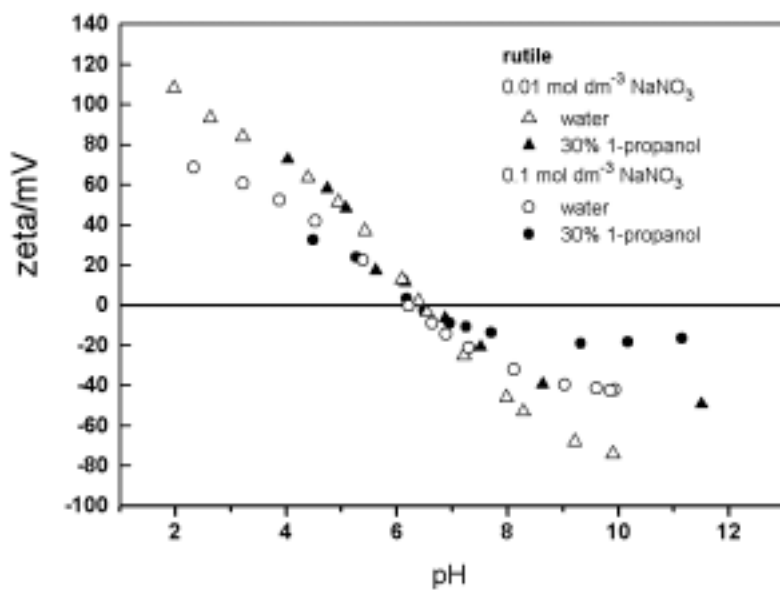


Fig. 2. Electrokinetic potential of rutile in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

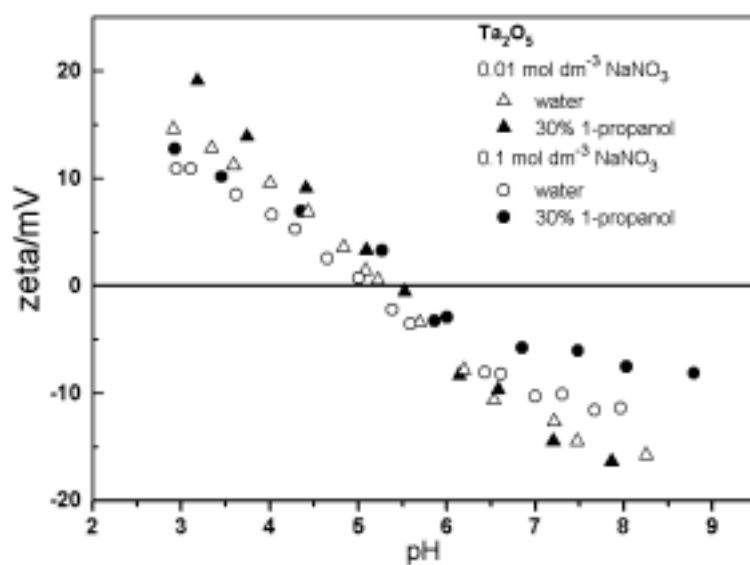


Fig. 3. Electrokinetic potential of Ta₂O₅ in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

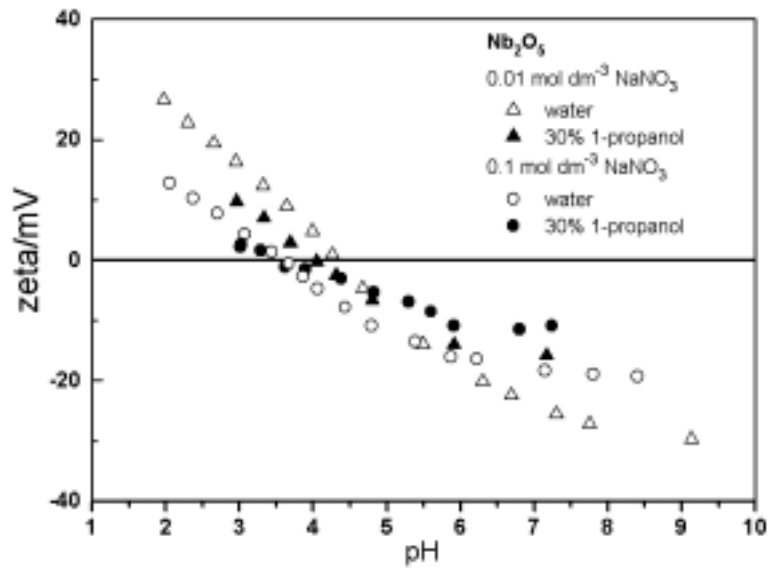


Fig. 4. Electrokinetic potential of Nb_2O_5 in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

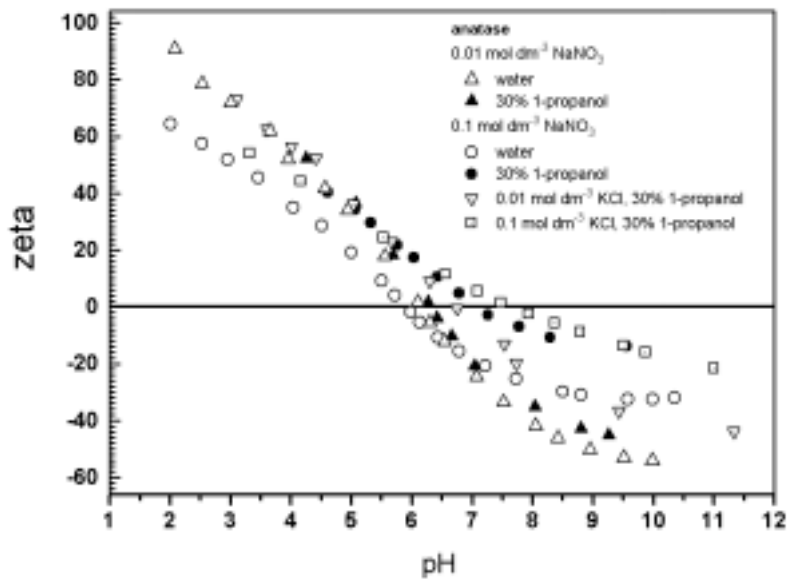


Fig. 5. Electrokinetic potential of anatase in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

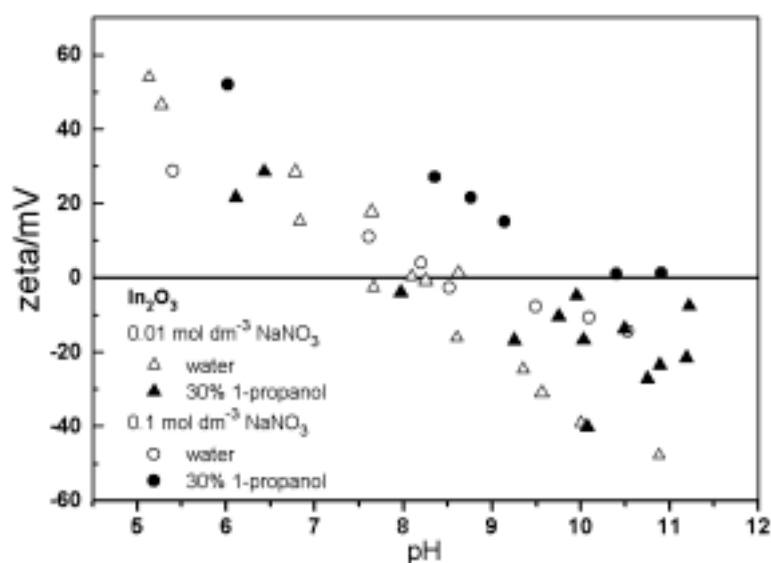


Fig. 6. Electrokinetic potential of In_2O_3 in water and in mixed solvent (water 0.7 mass fraction, 1-propanol 0.3 mass fraction)

The IEP of Ta_2O_5 (Figure 3) is rather insensitive to the nature of the solvent. In $0.01 \text{ mol dm}^{-3} \text{ NaNO}_3$ the ζ potential of Ta_2O_5 is insensitive to the solvent above the IEP and it is enhanced below the IEP. In $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ the ζ potential of Ta_2O_5 is insensitive to the solvent below the IEP and above the IEP the negative ζ potential is depressed. The ζ potentials shown in Figure 3 are of limited significance, namely their absolute values are unusually small (for given ionic strength and $|\text{pH-IEP}|$). This is because the powder was rather coarse (a few μm in diameter with only a small fraction of fine particles) and the instrument software was not able to properly interpret the signal from large particles. The results from Figure 3 should be multiplied by a factor of about 3 to obtain realistic values of the ζ potential.

The increase in the ionic strength from 0.01 to $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ induces a shift in the IEP of Nb_2O_5 to lower pH (Figure 4) in water and in the mixed solvent. The $|\zeta|$ is depressed in the mixed solvent irrespective of the sign of the surface charge and ionic strength. Also here the absolute values of ζ potential are clearly underestimated, and probably the results from Figure 4 multiplied by a factor of about 2 correspond to the actual ζ potentials (for the same reason as discussed above for Ta_2O_5). The concern about the absolute values of ζ potential in Figure 3 and 4 has one more important aspect. Namely particular portions of the oxides (used in consecutive titrations) might have somewhat different particle size distribution and this might result in underestimation of the absolute values of ζ potential by different factor. Thus, the proportions of the ζ potentials

in water on the one hand and in aqueous 1-propanol on the other found in Figs. 3 and 4 have limited significance.

The IEP of anatase in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ is shifted to high pH in the presence of organic solvent (Figure 5) and the ζ potentials in the presence of 1-propanol are more positive than in water over the entire pH range. However, this effect is less significant than previously reported in similar system (KCl in methanol, and KI and alkali chlorides in ethanol) [2]. This difference suggests some degree of salt specificity. Thus, an additional experiment with KCl was carried out, and indeed, KCl (Figure 5) induced more substantial shift in the IEP in the presence of 1-propanol than NaNO_3 at the ionic strength of 0.1 mol dm^{-3} , and in contrast with NaNO_3 , the shift was also substantial with KCl concentration as low as 0.01 mol dm^{-3} . This result gives solid grounds to challenge the alleged absence of salt specificity discussed in the Introduction. One substantial difficulty in systematic studies of the salt specificity by means of electroacoustic method is in gigantic amount of the solid material necessary for such a study. The difference between the present results and the previous study [2] is probably also due to various surface properties of particular samples of anatase. Two samples studied in ref. [2] also behaved differently from one another, namely, the shifts in the IEP of washed commercial powder were less substantial than for the synthetic (home-made) anatase. On the other hand the difference in the solid to liquid ratio between the electroacoustic method and microelectrophoresis is probably not crucial for the observed solvent effects. The shift in the IEP of another sample of anatase in the presence of organic solvents measured using electroacoustic method [7] was comparable with that measured using microelectrophoresis [2].

The electrokinetic potentials of In_2O_3 presented in Figure 6 were obtained by means of microelectrophoresis and they show more scatter than the results presented in Figs. 1-5. In contrast with other oxides studied in this paper the sign of the ζ potential of In_2O_3 is reversed to positive over the entire pH range in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ in 30% 1-propanol (no IEP).

Thus, literally each of six oxides studied in this paper produced somewhat different pattern of electrokinetic behavior in the mixed solvent, and apparently there is no simple general rule governing the solvent effect.

The only common feature (substantiated by the results reported in the literature) is that the absolute value of the negative ζ potential in $0.1 \text{ mol dm}^{-3} \text{ NaNO}_3$ in 30% 1-propanol is lower than in water.

This result corroborates the existence of surface species involving cations of the inert electrolyte, e.g., $\equiv\text{SiONa}$ for all oxides. These species considerably contribute to the surface charging at high ionic strength and/or at high pH. The generic depression in the negative ζ potential in mixed solvents at high ionic strengths can be explained in terms of enhanced activity of sodium in solution and thus the shift in the equilibria like:



to the right. Then the concentration of the $\equiv\text{SiONa}$ surface species which does not contribute to the ζ potential increases on the expense of the $\equiv\text{SiO}^-$ surface species which contributes to the negative ζ potential, when water is replaced by organic co-solvent. Probably the same mechanism applies to the shift in the IEP of oxides at very high ionic strengths in purely aqueous systems.

4. CONCLUSION

Combining the present results with those taken from literature we can distinguish two classes of oxides. The IEP of anatase, alumina, Y_2O_3 and In_2O_3 is shifted to high pH in the presence of lower alcohols (concentration about 30% by weight) at ionic strengths of about 0.1 mol dm^{-3} . At sufficiently high ionic strength and alcohol concentration this shift may result in absence of IEP (positive ζ over the entire pH range). The other oxides, namely, rutile, Nb_2O_5 and Ta_2O_5 do not show such shifts. Interestingly a pair of polymorphs: anatase-rutile does not behave alike in this respect. Thus, existence of some simple correlation (with the position of the pristine IEP and other well-established physical quantities) is rather unlikely. Three of the four materials whose IEP was shifted in mixed solvent and none of the materials whose IEP was not shifted belong to the cubic system, but this can be just fortuitous coincidence. Far more likely the difference between the two groups of oxides is in the stoichiometry of the surface species involving cations of the inert electrolyte. With reaction (1) or analogous reaction with Si replaced by metal atom(s) even at very high activity of the cations in the solution, the negative ζ potential can be only neutralized but not overbalanced by the positively charged cations. However if the cation binding reaction is like



or



as suggested by van Riemsdijk et al.[17] then at very high activity of Na^+ in solution its adsorption can overbalance the negative sign of the ζ potential. Our results suggest that anatase requires much lower sodium activity than rutile to induce such an overbalance.

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CURRICULA VITAE



Marek Kosmulski is a professor at Department of Electrical Engineering of Technical University of Lublin, Poland. His research interest covers electric double layer at solid-liquid interface and low temperature ionic liquids.



Jarl B. Rosenholm is a professor at Department of Physical Chemistry of Åbo Akademi, Turku, Finland. His research interest covers biomaterials, ceramics, corrosion, drug release, ion solvation in aqueous and nonaqueous media, mesoporous materials, modification of the surface of glass fibers, rheology and wood chemistry.