Simple model of surface-induced electrolytic dissociation of weak acids in organic solvents

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Abstract The electric conductivity of solutions of oxalic and phosphoric acid (up to 0.025 M) in ethanol and methanol has been studied in the presence of TiO_2 (1–10% by mass). TiO_2 enhanced the conductivity of solutions of oxalic and phosphoric acid in the both alcohols. The experimentally observed behavior was successfully modeled using a model with two types of surface sites. Sites of the first type bind the acids in molecular form. Sites of the second type bind the acids in form of hydrogen oxalate and dihydrogen phosphate anions, respectively, and protons are released to the solution, and contribute to enhanced conductivity. The adsorption model properly reflects the electrokinetic potential of titania particles in alcoholic solutions of oxalic and phosphoric acid.

Keywords Organic solvents · Non-aqueous solvents · Degree of dissociation · Electrolytic dissociation · Adsorption · Surface heterogeneity · Zeta potential

1 Introduction

Kosmulski et al. (2009, 2010) reported enhancement in the electric conductivity of oxalic and phosphoric acid solutions in lower n-alcohols in the presence of titania. This result is rather surprising, and it differs from usual behavior observed for aqueous solutions, in which the presence of adsorbents (including titania) depresses the conductivity of electrolyte solutions.

The difference between aqueous and alcoholic solutions was qualitatively interpreted in terms of different degrees of dissociation of acids in different solvents. In water, the degree of dissociation is relatively high, and titania adsorbs existing ions. In alcohols, the degree of dissociation and the concentration of pre-existing ions are low, and titania adsorbs acids chiefly in molecular form. The interaction between electroneutral acid molecules and titania surface produces titania-phosphate (or titania-oxalate) surface complexes and protons in solution. This phenomenon, termed "surface-induced electrolytic dissociation" enhances the concentration of ionic species in solution. The surface-induced electrolytic dissociation is probably responsible for high electrokinetic charges in nonaqueous media. Namely, high zeta potentials have been reported in solvents, in which the concentrations of pre-existing ions are low (van der Hoeven and Lyklema 1992; Morrison 1993). The very existence of electric double layer requires presence of sufficient concentration of ions. The concentrations of ions calculated from solution chemistry in solvents of dielectric constants of about 2 are not sufficient to support electric double layers.

The surface-induced electrolytic dissociation must not be confused with surface conduction (Hunter 2003; Lyklema and Minor 1998), which has been invoked in interpretation of electric conductance of dispersions in the presence of 1-1 electrolytes. In certain systems those two phenomena may co-exist, but their nature and significance is completely different. The surface conduction occurs with pre-existing ions, which are adsorbed in Stern layer (non-specific adsorption), and which substantially contribute to the conductance of the dispersion. In contrast the adsorption of oxalate and phosphate anions on titania is a strong specific adsorption. The

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adsorbed oxalate and phosphate ions are rather immobile, but strong interaction between electroneutral acid molecule and the titania surface produces ions, which contribute to the conductance of the dispersion.

In this present study a mechanistic model is derived explaining the concentration-dependence of the conductivity and of the zeta potential in dispersions of titania in alcoholic solutions of weak acids.
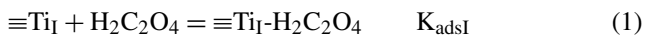
2 Experimental data

TiO_2 was Aeroxide from Evonic-Degussa, anatase, with specific surface area of 50 m^2/g, primary particle diameter 30 nm, and IEP in aqueous solution of 6.5 (Kosmulski 2009). The conductivity and zeta potential in dispersions of anatase in alcoholic solutions of oxalic and phosphoric acid were measured at 25 °C by means of Acoustosizer IIs (Colloidal Dynamics, Warwick, USA). The dispersions were open to atmosphere during the experiments, and vigorously stirred to prevent their sedimentation. The presence of dissolved gases affects the conductivity, so the experimental setup is not suitable for very accurate measurements in solutions. On the other hand, typical equipment used for measurements of conductivity in solutions is not suitable for measurements in unstable dispersions. More experimental details can be found in our previous papers (Kosmulski et al. 2009, 2010).

3 Adsorption model

A few one-site models have been tested, but they failed to properly reflect the experimentally observed trends, and they will not be discussed here. The following two-site model was the simplest successful model (physically acceptable and requiring the lowest number of adjustable parameters) found in this study.
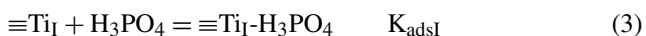
The adsorption of oxalic acid on titania from alcoholic solutions occurs on two types of surface sites. Type I surface sites denoted $\equiv Ti_I$ adsorb the acid in molecular form, that is,

$$\equiv Ti_I + H_2C_2O_4 = \equiv Ti_I\text{-}H_2C_2O_4 \qquad K_{adsI} \qquad (1)$$

Type II surface sites denoted $\equiv Ti_{II}$ adsorb the acid in ionic form, that is,

$$\equiv Ti_{II} + H_2C_2O_4 = \equiv Ti_{II}\text{-}HC_2O_4^- + H^+ \qquad K_{adsII} \qquad (2)$$
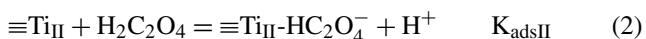
The adsorption of phosphoric acid on titania occurs on two types of surface sites. Type I surface sites denoted $\equiv Ti_I$ adsorb the acid in molecular form, that is,

$$\equiv Ti_I + H_3PO_4 = \equiv Ti_I\text{-}H_3PO_4 \qquad K_{adsI} \qquad (3)$$

Type II surface sites denoted $\equiv Ti_{II}$ adsorb the acid in ionic form, that is,

$$\equiv Ti_{II} + H_3PO_4 = \equiv Ti_{II}\text{-}H_2PO_4^- + H^+ \qquad K_{adsII} \qquad (4)$$

The adsorption of oxalic and phosphoric acid on type II surface sites is responsible for enhanced conductivity of dispersions of titania with respect to solutions of acid, and for the sign reversal of electrokinetic potential of titania from positive to negative. The adsorption of oxalic and phosphoric acid on type I surface sites slightly depresses the conductivity of dispersions of titania (due to decrease in total amount of phosphorus-containing species in solution) and has negligible effect on the electrokinetic potential.

The site densities and K_{adsI} and K_{adsII} are adjustable parameters found by data-fitting procedure described in detail below.

4 Data-fitting procedure

In principle oxalic acid is dibasic and phosphoric acid is tribasic, but in alcoholic solutions of acids, the concentrations of di- and trivalent anions are negligibly low. Therefore di- and trivalent anions are neglected in the present study, and both acids are treated as monobasic. A few physical properties of water, methanol and 94% ethanol (by mass) are summarized in Table 1. The molar conductivity of proton in water is higher by an order of magnitude than molar conductivities of other ionic species relevant to the present study, due to Grotthuss mechanism (Cukierman 2006). Thus, the conductivity of oxalic or phosphoric acid solution can be estimated from the concentration of protons, and negligence of the contribution of the anions to the conductivity results in an error of about 10%. The molar conductivities of aqueous species reported in Table 1 refer to infinite dilution. The molar conductivity of proton in 10^{-3}–10^{-2} M acid solutions (concentration range studied in the present paper) is substantially lower than at infinite dilution.

Also in alcoholic solutions the molar conductivity of proton is substantially higher than the molar conductivities of other ionic species, as indicated by the studies of conductivity of HCl solutions in anhydrous and aqueous alcohols (De Lisi et al. 1976, 1978, 1980). The molar conductivities of proton in alcoholic solutions are lower by an order of magnitude than the molar conductivity of proton in water due to lower degree of hydrogen bonding. In alcohols, the molar conductivity is a function of electrolyte concentration, but this effect was neglected in the present model studies. Namely, one value of molar conductivity of proton (reported in Table 1) was used over the entire concentration range. This value is lower than the molar conductivity reported by De Lisi et al. (1976, 1978, 1980) for infinite dilution by a

Table 1 Physical properties of solvents at 25 °C

Solvent	Water	Methanol	94% ethanol
ε	78.5	32.66	26.5
η(cP)	0.892	0.541	1.317
$\Lambda(H^+)$ 10^{-4} m^2 S mol^{-1}	349.65	49[a]	40.2[a]
$\Lambda(HC_2O_4^-)$ 10^{-4} m^2 S mol^{-1}	40.2		
$\Lambda(H_2PO_4^-)$ 10^{-4} m^2 S mol^{-1}	33		

[a]Assumed in the present study. The other quantities in this table are well-established literature data from CRC Handbook of Chemistry and Physics

factor of about 2, and it is relevant to the concentration range (10^{-3}–10^{-2} M) studied in this paper.

The molar conductivity of proton in alcoholic solutions (Table 1) and the conductivities of acid solutions measured in the present study are consistent with the dissociation constants of oxalic and phosphoric acid in alcoholic solutions reported by Bhattacharyya et al. (1980), Bandyopadhyay and Lahiri (2002), Gumtya et al. (2002), and Tossidis (1976). Apparently the ions located in the diffuse part of electric double layer are expected to have lower mobilities than bulk ions. However, in the systems of interest, the electric double layer is thick due to low ionic strength. Moreover, experiments with porous plugs indicated (Hunter 2003; Lyklema and Minor 1998) that even ions in Stern layer show mobilities similar to those of bulk ions. Therefore, only minor (if any) effect of charged particles on proton mobility is expected in the systems of interest.

The dissociation constants of oxalic and phosphoric acid in alcoholic solutions reported in Table 2, estimated from the conductivities of acid solutions measured in the present study using the molar conductivity of proton in alcoholic solutions from Table 1 are consistent with the literature data. The dissociation constants of oxalic and phosphoric acid in methanol are lower by a factor of 10^3, and in 94% ethanol they are lower by a factor of 10^4 than the corresponding dissociation constants in water. Determination of exact values of dissociation constants of oxalic and phosphoric acid was not the main goal of the present study.

The equilibrium constants of reactions (1–4) and the densities of type I and type II sites were determined by data-fitting using the experimental conductivity data and pre-assumed values of dissociation constants of oxalic and phosphoric acid (derived from parameters from Table 1, and reported in Table 2). It was assumed that the conductance is proportional to the concentration of protons in solution. The following sum (taken over 40 experimental data points obtained for a 10% titania dispersion) was minimized

$$\Sigma\{\log\sigma \text{ (measured)} - \log[[H^+] \text{ (calculated)} \times \Lambda(H^+)]\}^2 \tag{5}$$

by adjustment of [Ti$_I$] (total), [Ti$_{II}$] (total), K$_{adsI}$, and K$_{adsII}$ in the following equations:

$$[Ti_I] \text{ (total)} = [Ti_I] \text{ (free)} + [\equiv Ti_I\text{-}H_2C_2O_4] \tag{6}$$

$$[Ti_{II}] \text{ (total)} = [Ti_{II}] \text{ (free)} + [\equiv Ti_{II}\text{-}HC_2O_4^-] \tag{7}$$

$$[H_2C_2O_4] \text{ (total)} = [H_2C_2O_4] \text{ (free)} + [HC_2O_4^-]$$
$$+ [\equiv Ti_I\text{-}H_2C_2O_4] + [\equiv Ti_{II}\text{-}HC_2O_4^-] \tag{8}$$

$$[H^+] = [\equiv Ti_{II}\text{-}HC_2O_4^-] + [HC_2O_4^-] \tag{9}$$

$$K_a = [H^+] \times [HC_2O_4^-]/[H_2C_2O_4] \text{ (free)} \tag{10}$$

$$K_{adsI} = [\equiv Ti_I\text{-}H_2C_2O_4]/\{[Ti_I] \text{ (free)}$$
$$\times [H_2C_2O_4] \text{ (free)}\} \tag{11}$$

$$K_{adsII} = [\equiv Ti_{II}\text{-}HC_2O_4^-]$$
$$\times [H^+]/\{[Ti_{II}] \text{ (free)} \times [H_2C_2O_4] \text{ (free)}\} \tag{12}$$

or of analogous equations for phosphate. All concentrations (including those of surface sites) are on molar scale.

The presence of electric double layer, that is, the effect of electric potential at solid/liquid interface on the equilibria of reactions (2) and (4), was neglected. A model with electric-double-layer-interactions would be physically more correct, but it would involve additional adjustable parameters. The success of non-electrostatic model in this study does not imply that the double-layer interactions were negligible in the systems of interest. A few successful sets of model parameters are summarized in Table 2.

5 Results and discussion

5.1 Conductivity

The experimental results and the model calculations (see Table 2 for parameters) of the conductivity of dispersions of titania in solutions of oxalic acid in methanol are compared in Fig. 1. The concentrations on x-axis in Figs. 1–3 are total concentrations of acids in the system (not corrected for uptake of acid from solution by titania particles). The

Table 2 Model parameters

| Figure(s)	Solvent	Acid	pK_a	$[Ti_I]$ nm^{-2}	$[Ti_{II}]$ nm^{-2}	$\log K_{adsI}$	$\log K_{adsII}$
1	MeOH	$H_2C_2O_4$	4.5	0.334	0.702	6.09	1.67
2, and 4	94% EtOH	$H_2C_2O_4$	4.5	0.458	0.42	5.19	0.122
3 (solid lines)	94% EtOH	H_3PO_4	6	0.649	0.308	5.8	1
3 (dotted lines)	94% EtOH	H_3PO_4	4.8[a]	0.301	1.3	7.05	2.302

[a] $\Lambda(H^+) = 10.2 \times 10^{-4}$ m^2 S mol^{-1}

Fig. 1 The effect of TiO$_2$ on the conductivity of oxalic acid in methanol. The model parameters are summarized in Table 2
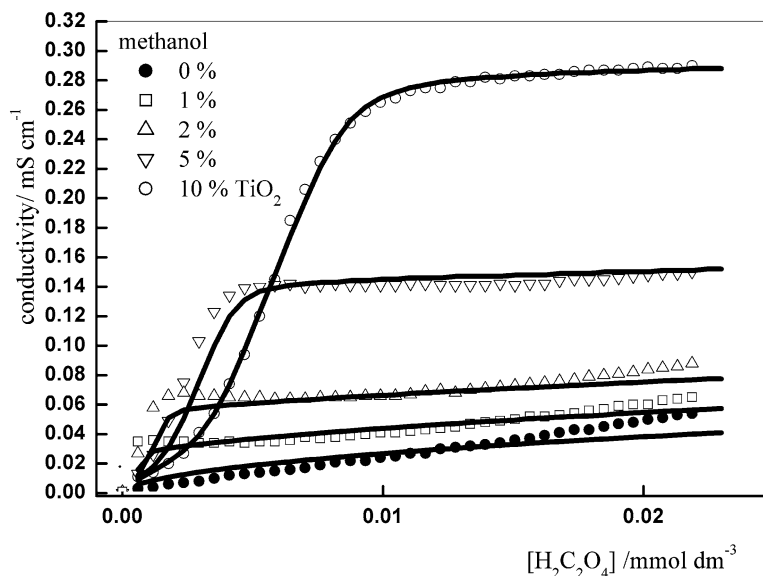
Fig. 2 The effect of TiO$_2$ on the conductivity of oxalic acid in 94% ethanol. The model parameters are summarized in Table 2
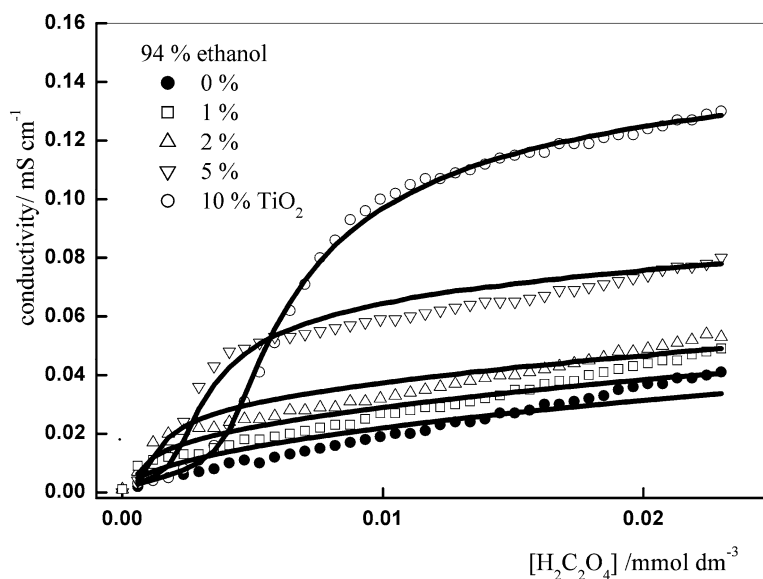
model properly reflects the complex shape of the experimental curves for dispersions. The conductivity of the electrolyte alone (in the absence of titania) was less-well reflected by the model than the conductivity of the dispersions. Similar problem was encountered in all studied systems (Figs. 2, 3).

The experimental curve of the electrolyte alone may suggest that oxalic acid is a relatively strong acid, which is in contradiction with the Born model, which indicates that the degree of dissociation of electrolytes in low-dielectric media is lower than in water, and with specific values of pK$_a$ of

Fig. 3 The effect of TiO$_2$ on the conductivity of phosphoric acid in 94% ethanol. The model parameters are summarized in Table 2
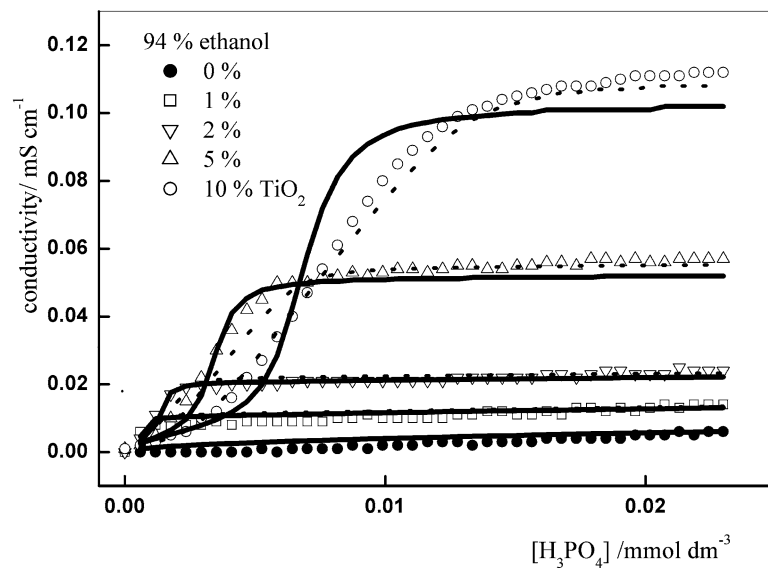
oxalic acid in alcoholic solutions reported by Gumtya et al. (2002). Probably the present model is not suitable for electrolyte solutions. Actually, more complex models have been used to study the conductivity of solutions of weak acids (Tsurko et al. 1999). The discrepancy may also be due to limited quality of experimental results. The model parameters reported in Table 2 (Figs. 1–3) are not unique, and other sets of model parameters produce similar model curves.

The experimental results and the model calculations (see Table 2 for parameters) of the conductivity of dispersions of titania in solutions of oxalic acid in 94% ethanol are compared in Fig. 2. The model properly reflects the complex shape of the experimental curves for dispersions. The conductivity in ethanolic dispersion of titania was less substantially enhanced than in methanolic dispersions, and this is reflected by lower concentration of type II sites and lower log K_{adsII} in ethanol than in methanol.

The experimental results and the model calculations (see Table 2 for parameters) of the conductivity of dispersions of titania in solutions of phosphoric acid in 94% ethanol are compared in Fig. 3. The solid curves roughly reflect the complex shape of the experimental curves, but the match is less spectacular than in Figs. 1 and 2. The match between the model and experiment can be further improved by allowing lower value of molar conductivity of proton in ethanol than the value reported in Table 1. An example is shown in Fig. 3 (dotted lines, parameters in Table 2). However, such an approach has limited significance. The pK$_a$ of phosphoric acid used in model curves (dotted lines in Fig. 3) is substantially lower than the results reported by Bhattacharyya et al. (1980), Bandyopadhyay and Lahiri (2002), and Tossidis (1976), and the molar conductivity of proton in ethanol was lower by an order of magnitude than the molar conductivity of HCl reported by De Lisi et al. (1976, 1978, 1980).

Obviously, in a consistent model, the molar conductivity of proton in ethanol should be identical for oxalic and phosphoric acid.

Also the match demonstrated in Fig. 1 and Fig. 2 can be improved when molar conductivity of proton in ethanol and methanol is treated as a fully adjustable parameter, selected for oxalic and phosphoric acid separately ignoring the existing literature data on the conductivity of acid solutions and the pK$_a$ of acids. The model presented in this study is an example of successful model, and other models or other sets of parameters within the same model can probably reproduce experimental data equally well.

5.2 Zeta potential

The electrokinetic data are seldom used to verify the adsorption models. This is because there is no simple relationship between the zeta potential and concentrations of surface species.

The zeta potential of dispersion of titania in methanol or ethanol (no acid added) was positive, and addition of oxalic or phosphoric acid induced stepwise decrease of the zeta potential, sign reversal, and finally negative zeta potential due to specific adsorption of anions (Kosmulski et al. 2009, 2010). The possible nature of the positively charged groups responsible for positive zeta potential at low acid concentrations was discussed in detail in our previous papers, but they are not included in the model discussed above. It may be assumed for simplicity that the concentration of positively charged groups is independent of acid concentration, and addition of acid enhances the concentration of negatively charged groups according to reaction 2 or 4.

In Fig. 4 the zeta potential is plotted as the function of the calculated surface concentration of Ti$_{II}$-HC$_2$O$_4^-$, which

Fig. 4 The zeta potential of TiO$_2$ in solutions of oxalic acid in 94% ethanol. The model parameters are summarized in Table 2
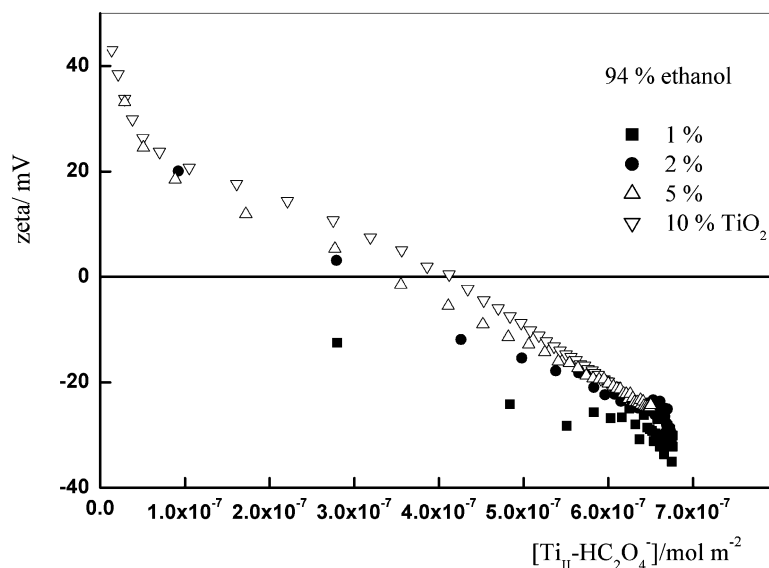
is the only charged surface species in the oxalic acid-TiO$_2$ system, according to the present model (1 and 2). With exception of a few data points obtained for a 1% dispersion, all data points obtained at various solid-to-liquid ratio produce a master curve, which indicates a sign reversal of the zeta potential at about 4×10^{-7} mol m^{-2} of $\equiv$Ti$_{II}$-HC$_2$O$_4^-$. Apparently the concentration of positively charged surface groups responsible for positive charge of the particles in absence of oxalic or phosphoric is about 4×10^{-7} mol m^{-2} (0.24 groups nm^{-2}). The positively charged surface groups contribute to the surface charge, but their contribution to the conductivity of dispersion is negligible. The positively charged surface groups (probably protonated $\equiv$Ti–O or $\equiv$Ti–OH groups) can be incorporated into the present model in different manners. They can be a separate category of surface sites (different from $\equiv$Ti$_I$ or $\equiv$Ti$_{II}$, cf. 1–4), but they can also be a sub-category of $\equiv$Ti$_I$ or $\equiv$Ti$_{II}$ groups). The approach to positively charged surface groups does not affect the model calculations presented in Sect. 5.1 when a "non-electrostatic" model is used.

6 Conclusion

The conductivity and zeta potential measured in titania dispersions in solutions of oxalic and phosphoric acid in methanol and ethanol can be interpreted in terms of a two-site model.

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