

# Differentiation of the strength of organic acids in true and organized solutions

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With 36 Figures, 21 Tables, 1530 references.

In this book, various aspects of differentiating of organic acids strength in true and organized solutions are regarded, using mainly a group of acid-base indicator dyes as an example.

The first part of the book is devoted to protolytic equilibria in true solutions.

In **Chapter 1**, the general scheme of dissociation of electrolytes in solutions, proposed by N. A. Izmailov, is considered. The development of Izmailov's ideas about electrolytic solutions in the works of further authors is briefly reviewed. The alterations in the  $pK_a$  values of acids on transferring from water to non-aqueous solvents (the values  $\Delta pK_a = pK_a - pK_a^w$ , or 'medium effects') are treated in terms of activity coefficients and Gibbs energies of transfer. Especial consideration is given to the problem of activity coefficients of transfer of single ions.

Different approaches for the classification of solvents, based on their influence upon the state of electrolytes, are discussed in **Chapter 2**. The peculiarities of acids behavior in so-called dipolar aprotic solvents, i.e. non-hydrogen-bond-donors, and in solvents with low polarity, where the association of oppositely charged ions is of significance, are elucidated. Theoretical approaches to the problem of solvation and acidity are briefly considered. An aspect of acid-base equilibrium in melts is discussed.

Some features of differentiating action of non-aqueous solvents are illustrated in **Chapter 3**. Simplified explanations of several typical cases are proposed, namely, for variations of the  $\Delta pK_a$  values of acids both

with the same and with different dissociating groups, as well as for variations of the ratio of stepwise dissociation constants of some polyprotic acids. Successively are described the systems, where the decisive part is played by: (1) the degree of charge delocalization in anions, (2) the type of charge of acid-base couples and the nature of dissociating functional group, (3) the shift of the tautomeric equilibrium state at going from water to organic solvents, and (4) the selective solvation in mixed solvents. A set of systems with the inversion of the stepwise dissociation constants ( $pK_{a1} > pK_{a2}$ ) are revealed and adequate explanations are proposed. The analysis of the plots of  $pK_a$  vs.  $pK_a^w$  demonstrated that any distribution of reactants with complicated structure among various groups is conventional. Within each group a further subdivision is possible; in some cases a given substance can simultaneously be partially placed into two or more groups, with good reason. Such situation becomes understandable if we use the term 'fuzzy sets'. Finally, the salt effect on the dissociation of organic acids in aqueous solutions is briefly discussed.

**Chapter 4** is devoted to protolytic equilibria of xanthene and triphenylmethane compounds in solutions. The dissociation constants of the dyes in some widely used non-aqueous solvents, obtained Vis-spectroscopically, are tabulated. The presentation of detailed schemes of protolytic equilibria of hydroxyxanthenes, rhodamines, rhodols, phthal-eins, and sulfonephthaleins is accompanied by comparison between the results obtained by various experimental methods and critical analysis of up-to-date literature. Some principal regularities of the influence of the solvents nature on the state of tautomeric equilibrium are revealed; the role of the tautomeric equilibria shifts appears to be sometimes of principal significance in the formation of medium effects ( $\Delta pK_a$  values). The  $pK_a$  values of xanthene, aminoxanthene, phthalein, and sulfonephthalein dyes in numerous organic solvents are explained in terms of prototropic tautomerism and microscopic dissociation constants. The developed conceptions allow to explain the ratios of stepwise dissociation constants of the reagents, to predict these values in different systems yet unstudied, and to govern the behavior of the aforementioned widely used organic reagents and luminophores by rationally chosen solvents. The differentiating action of organic solvents in electroreduction of dyes is demonstrated.

The behavior of acids in organized solutions is considered in the second part of the book.

In **Chapter 5**, some peculiarities of reactivity, first of all of protolytic equilibria and interfacial acidity in lyophilic colloidal systems, are elucidated; the properties of micellar solutions of colloidal surfactants and of other organized solutions as media for chemical reactions are considered. The problem of apparent dissociation constants,  $K_a^a$ , of indicator dyes in micellar surfactant solutions, microemulsions, and liposome dispersions is reviewed. The regularities of protolytic equilibrium in micellar solutions and related systems are discussed in terms of pseudophase concept and electrostatic model.

Specific features of lyophilic dispersions of various types (micelles of cationic and anionic surfactants, of nonionic surfactants with polyoxyethylene chains, zwitterionic surfactants and liposomes of phospholipids) are described in **Chapter 6** from the stand-point of their influence on the state of protolytic equilibria. Various types of differentiating action of micellar pseudophases are revealed. The role of charge type and nature of dissociating functional group in the formation of  $\Delta pK_a^a$  values ( $\Delta pK_a^a = pK_a^a - pK_a^w$ ) are treated in terms of Brönsted–Izmailov theory; such approach allows to interpret the extremely strong differentiating action of micelles and to explain several paradoxical exceptions from the well-known Hartley rules.

**Chapter 7** is devoted to the problem of electrical potential,  $\Psi$ , of micellar surfaces as well as to the methods of its measure, to reasons of its changeability, and to the shielding of interfacial charge by supporting electrolytes. The validity of common methods of  $\Psi$  estimations with the help of acid-base indicators is discussed.

Alterations in the micellar regime and their impact on acid-base properties of species bound to pseudophase are considered in **Chapter 8**. The following sides of the problem are described: (1) specific salt effects of hydrophobic counter ions; (2) mixtures of counterions, (3) non-ionic additives to ionic micelles, (4) mixed micelles of ionic and nonionic surfactants, (5) peculiar of microemulsions. The utility and limitations of the pseudophase model in reference to interpretation and prediction of salt

effects are demonstrated.

In **Chapter 9**, a number of typical cases of incomplete binding of ions and molecules by the pseudophases of different nature are selected. Among them are interactions of dyes with surfactants within the concentration range below c.m.c. of homomicelles as well as partition of various species between surfactant micelles and the bulk (aqueous) phase. The approaches to 'binding constants' estimation using the  $pK_a^a$  dependences vs. surfactants concentration are analyzed, and chemical consequences of selective binding of different species to the pseudophase in equilibrium systems are reviewed. Some examples of dyes binding by cyclodextrins and calixarenes are presented.

A classification of the types of differentiating action of organized solutions is proposed in **Chapter 10**. The differentiating influence of surfactant micelles and other pseudophases is demonstrated to be the main reason for limitation of the common electrostatic model of acid-base interactions and the principal hindrance to exact evaluations of the interfacial electrical potentials by means of acid-base indicators.