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Application of Davis Method to Estimation of Ions Activity Coefficients at the Evaluation of Dissociation Constants of Aromatic Dicarboxylic Acids in Organic Solvents

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Abstract—Validity of the Davis method for the estimation of activity coefficients of the ions forming in an acid–base system at the evaluation of thermodynamic dissociation constants of aromatic acids in dimethylformamide medium is evidenced.

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As has been shown in our preceding publications [1–4], calculations concerning ionic components in transport processes [5, 6] (thermal conductivity, electric conductivity, viscosity and diffusion coefficients in solutions of strong and weak electrolytes) considering only the ions formed in the first step of dissociation of multifunctional compounds are not strictly correct. Equilibrium concentrations of all ions in the acid–base system should be taken into consideration. The most complete information on the concentration of all moieties can be obtained from logarithmic diagrams log C–log $a(SH^+)$, where log C means the concentrations of all ions in the solution and log $a(SH^+)$ is the activity of proton solvated in any solvent (activity of lionium ion) [1–4].

For the estimation of activity coefficients the most applicable, as compared with the Debye method, is Davis equation [7]:

$$\log f_i = -\frac{Az_i\sqrt{I}}{1+\sqrt{I}} + 0.1I. \qquad (1)$$

A disadvantage of the Debye method is the necessity of introduction of A value, the tightest distance between particles which is, strictly speaking, is not known and commonly is accepted as 5×10^{-8} cm or less. In solution all the particles (even neutral molecules) are in solvated state (molecular solvates, solvated ions, associated ions, etc.), therefore even simple sum of solvated ions radii (in the first approximation) does not give complete information on the minimal distance between the tightest ions, and its constancy and equality to 5×10^{-8} cm for a pair of the same solvated cation and anion in any solvent seems doubtful.

The A coefficient is defined by the relation

$$A = (2\pi N_A/1000)^{1/2}(e^3/2.303k_B^{3/2})(1/\varepsilon^{3/2}T^{3/2}),$$

where N_A is Avogadro number, k_B is Boltzmann constant, ε is the medium dielectric permeability, T is Kelvin temperature. For DMF this value equals: A = 1.6363.

Thus, the Davis equation removes uncertainty of the distance between the tightest particles and quite applicable to the calculation of activity coefficients of ions in aqueous and, the more so, in non-aqueous solutions where a certain ion is characterized by different radii of solvated shells. With this equation the calculation of dissociation constants of electrolytes is more reliable [8] as compared with the Debye method.

We estimated ionic strenghts, activity coefficients by Davis, and thermodynamic dissociation constants of aromatic dicarboxylic acids at potentiometric titration with a solution of guanidine: diphenic, diphenylphthalide dicarboxylic, *o*-phthalic, isophthalic and terephthalic acids, using Eqs. (1)–(3).

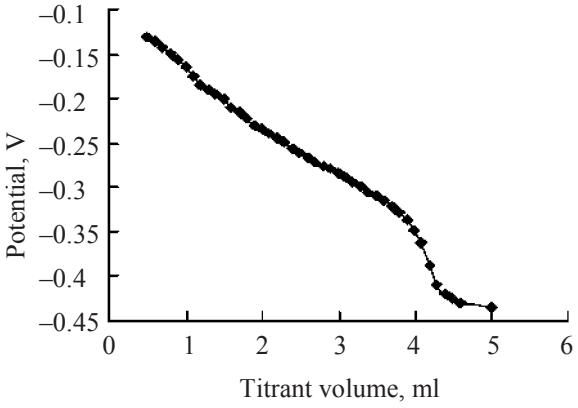

Fig. 1. Potentiometric titration curve of 4.215×10^{-3} M solution of diphenic acid with 5.0178×10^{-2} M solution of guanidine in DMF.

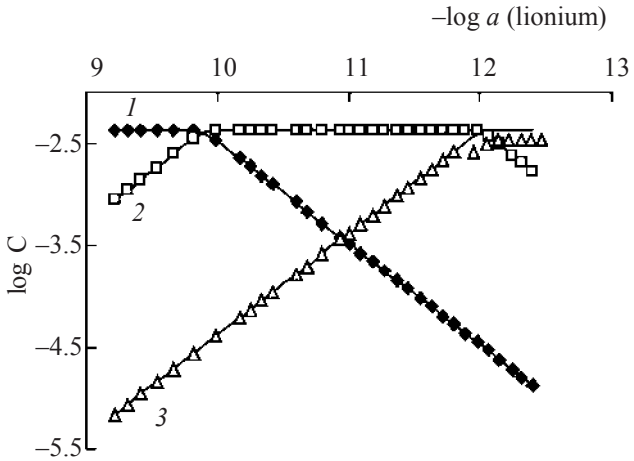

Fig. 2. Logarithmic diagram of estimation of equilibrium concentration at the reaction of diphenic acid with guanidine in DMF: (*1*) acid concentration H_2An, (*2*) concentration of ion HAn^-, and (*3*) concentration of ion An^{2-}.

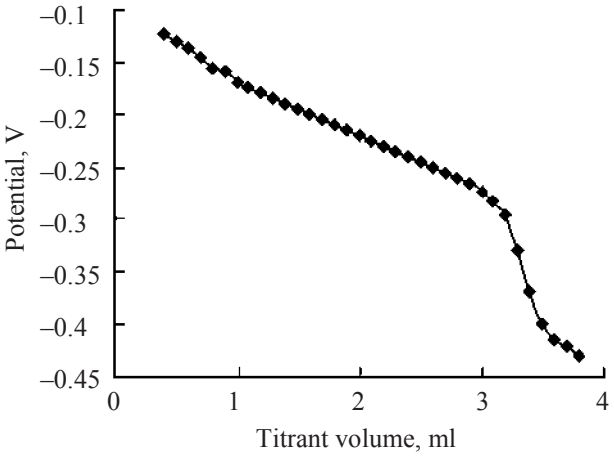

Fig. 3. Potentiometric titration curve of 3.193×10^{-3} M solution of diphenylphthalide dicarboxylic acid with 4.6956×10^{-2} M solution of guanidine in DMF .

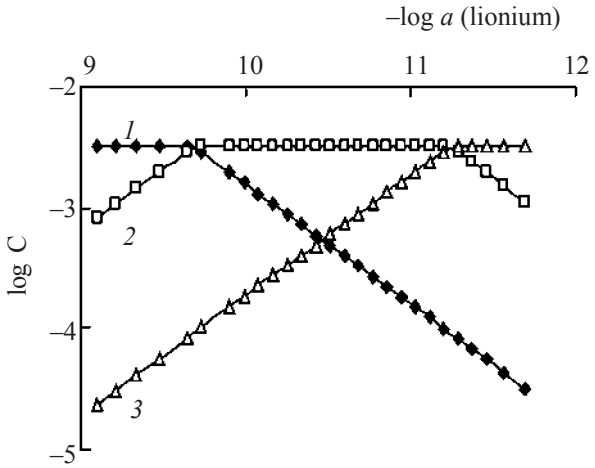

Fig. 4. Logarithmic diagram of estimation of equilibrium concentration at the reaction of diphenylphthalide dicarboxylic acid with guanidine in DMF: (*1*) acid concentration H_2An, (*2*) concentration of ion HAn^-, and (*3*) concentration of ion An^{2-}.

$$H_2A \rightleftarrows HA^- + H^+,\ K_1 = a_{H^+}[HA^-]f_1/[H_2A]f_0, \quad (2)$$

$$HA^- \rightleftarrows A^{2-} + H^+,\ K_2 = a_{H^+}[A^{2-}]f_2/[HA^-]f_1. \quad (3)$$

Figures 1, 3, 5, 7, and 9 depict the curves of potentiometric titration of the explored acids with a solution of guanidine in the medium of DMF. The acids are characterized by unresolved neutralization of both carboxylic groups, except *o*-phthalic and terephthalic acidc that show two titration jumps. Figures 2, 4, 6, 8, and 10 depict the above mentioned logarithmic diagrams log *C*–log $a(SH^+)$ that allow estimation of equilibrium concentrations of all charged and neutral moieties (solvated neutral molecules and ions) formed at the dissociation of an acid at its titration with a strong base.

Statistical treatment of experimentally found thermodynamic dissociation constants of aromatic dicarboxylic acid in DMF medium affords confidence intervals for the experimental pK_1 and pK_2 values with the probability 0.95 (see table).

Thus, we evidenced validity of Davis equation that does not contain the uncertainty inherent in Debye–Hueckel method in the distance of the tightest ions for

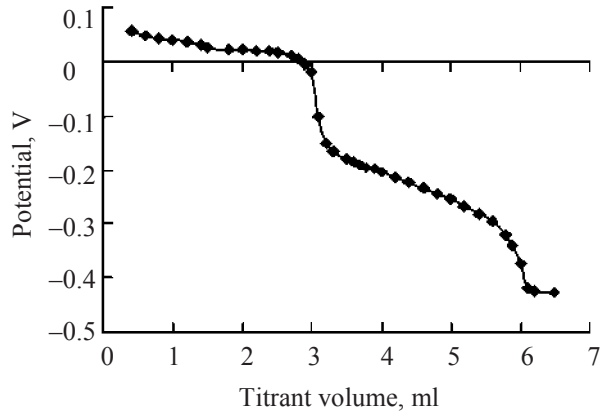

Fig. 5. Potentiometric titration curve of 0.03718 M solution of *o*-phthalic acid with 0.1549 M solution of guanidine in DMF.

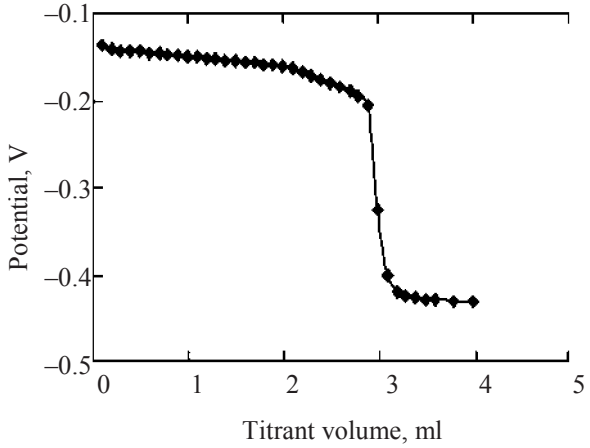

Fig. 7. Potentiometric titration curve of 0.01687 M solution of isophthalic acid with 0.1381 solution of guanidine in DMF.

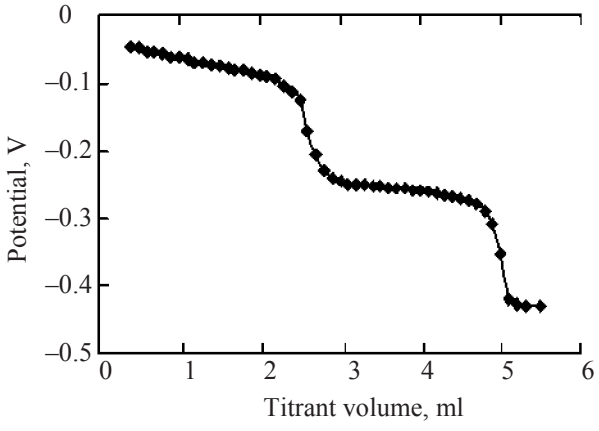

Fig. 9. Potentiometric titration curve of 0.03250 M solution of terephthalic acid with 0.1635 M solution of guanidine in DMF.

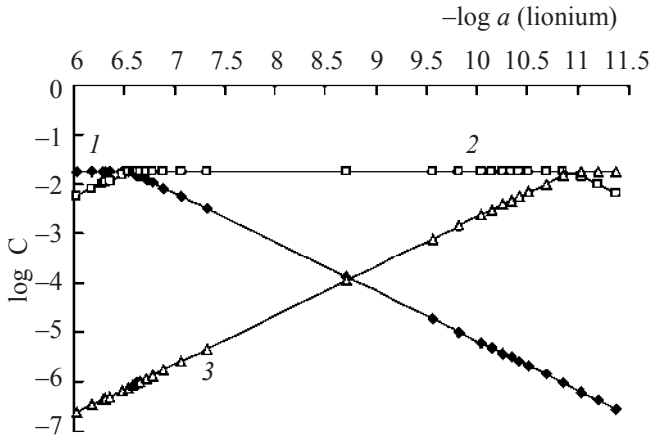

Fig. 6. Logarithmic diagram of estimation of equilibrium concentration at the reaction of *o*-phthalic acid with guanidine in DMF: (*1*) acid concentration H_2An, (*2*) concentration of ion HAn^-, and (*3*) concentration of ion An^{2-}.

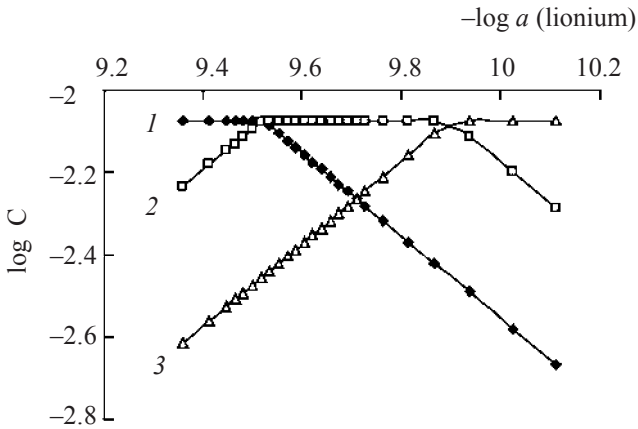

Fig. 8. Logarithmic diagram of estimation of equilibrium concentration at the reaction of isophthalic acid with guanidine in DMF: (*1*) acid concentration H_2An, (*2*) concentration of ion HAn^-, and (*3*) concentration of ion An^{2-}.

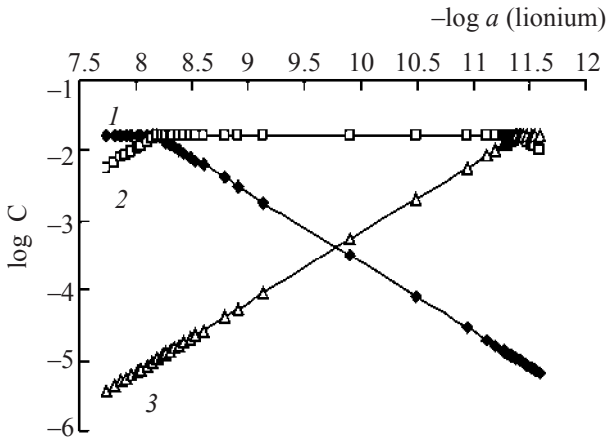

Fig. 10. Logarithmic diagram of estimation of equilibrium concentration at the reaction of terephthalic acid with guanidine in DMF: (*1*) acid concentration H_2An; (*2*) concentration of ion HAn^-, and (*3*) concentration of ion An^{2-}.

Statistical treatment of experimentally found thermodynamic dissociation constants of aromatic dicarboxylic acid in DMF medium

Acid	Number of data points	Confidence interval
Diphenic	30	$pK_1 = 10.03 \pm 0.40$, $pK_2 = 12.22 \pm 0.78$
Diphenyphthalid dicarboxylic	27	$pK_1 = 9.82 \pm 0.45$, $pK_2 = 11.44 \pm 0.69$
o-Phthalic	30	$pK_1 = 6.947 \pm 0.315$, $pK_2 = 11.220 \pm 0.566$
Isophthalic	25	$pK_1 = 9.791 \pm 0.140$, $pK_2 = 10.327 \pm 0.191$
Terephthalic	41	$pK_1 = 8.458 \pm 0.193$, $pK_2 = 11.697 \pm 0.505$

the application to the concept of theoretical estimation and experimental measuring of thermodynamic dissociation constants of aromatic acids in the medium of organic solvents for both the cases of separate and joint neutralization of two acid groups.

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