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ION ASSOCIATION OF THE POLYVALENT ELECTROLYTES IN NON-AQUEOUS SYSTEMS

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Abstract. *The work deals with polyvalent electrolytes conductometric investigation of $CuCl_2$, $[Cu(en)_2]Cl_2$, $FeCl_3$ solutions in binary mixed solvent DMSO–CB in a wide range of electrolyte concentrations (10^{-6}–10^{-2} mol/dm^3). Investigations were carried out at the temperature interval 298, 15–323,15 K. Ion association constants (K_{ai}) for given non-symmetrical electrolytes were calculated for two stages of association. Integral thermodynamic characteristics (ΔG_{ai}, ΔH_{ai}, ΔS_{ai}) of stage ion association process were calculated. The comparison of thermodynamic characteristics of equilibrium processes allows to make a conclusion about relative influence of polar and donor properties of medium on the processes of stage ion association in polyvalent electrolyte solutions.*

Keywords: conductometric investigation, ion association constants, polyvalent electrolytes, solution equilibrium processes, thermodynamic characteristics.

Introduction

The problem of the solvent's influence on the ion association constants and the equilibrium ion concentrations of non-symmetric electrolytes in individual and mixed solvents is rather actual for both scientists and engineers. Such type of electrolytes is widely used in a great variety of organic synthesis, galvanic and catalytic processes, etc. The analysis of the thermodynamic characteristic of ion association processes of aprotonic Lewis acids makes possible the evaluation of their relative force and, as a consequence, their catalytic activity. In addition the comparison of thermodynamic characteristics of equilibrium processes allows to make a conclusion about the relative influence of a compound's polar and donor properties on the processes of a stage ionic association in polyvalent electrolyte systems.

The most reliable criteria of acid force is the constant of ion association or free Gibbs' energy as well as enthalpy and entropy of the process. The majority of Lewis' acids are polyvalent electrolytes. So it is necessary to find the constants of the stage association for getting the correct data. A conductometry is one of the best methods of the determination of the thermodynamic characteristics.

The correct conductivity equation must be used for the precise description of the experimental relation $\lambda = f(c)$. It is rater difficult to solve this problem, because there are no equations which can be used for non-symmetric polyvalent electrolytes.

The biggest part of chemical processes passes in a liquid phase. Therefore if possible investigators want to make direct management of the process they should have the reliable information about the medium influence at all stages of equilibria in solutions. Unfortunately, there are no enough bibliographic data about the solvent effect on constants and particularly on thermodynamic characteristics of the ion association processes of polyvalent electrolytes. Hence the mentioned problem is still the central one in the modern theory of electrolyte solutions.

Solvent effect on ionic processes is convenient to investigate in binary mixed solvents. It allows us to trace the influence of universal solvation by means of changing the solvent composition. So dimethylsulfoxide (DMSO) which is characterized by quite high values of permittivity ($\varepsilon = 46,9$) and donor number (29,8), and low value of the autoprotolysis constant ($5 \cdot 10^{-18}$) has been chosen as

the basic solvent. The choice of chlorobenzene (CB, $\varepsilon = 5,6$) as the second component of mixed solvent has been made because it is possible to exclude the adductive interactions among components of the binary solvent. Moreover, CB is an inert component in the specific salvation process and it is well soluble in dimethylsulfoxide. Therefore the role of chlorobenzene is in direct changing of the solvent permittivity values.

Analysis of the problem and state of the problem

Long before the authors have designed the method of the determination of the constants of the stage ion association of polyvalent electrolytes [1]. The mentioned above approach cardinally differes from the known methods. It is based on the solving of the system of nonlinear equations which consists of the ion association constants (K_{ai}), equilibrium ion concentrations and conductivity of the solution. We suggest to check the method on an example of the 2–1 electrolyte. Schematically it is possible to describe the process of ion association as follows:

$$M^{2+} + 2A^- \xleftrightarrow{K_{a1}} MA^+ + A^- \xleftrightarrow{K_{a2}} MA_2$$

where K_{a1} and K_{a2} are the ion association constants at the first and the second stages correspondingly.

So the molar conductometric equation is:

$$\lambda = \left[\lambda_{01} - (A_1\lambda_{01} + B_1)^{1/2}\right]c_1/c_0 +$$
$$+ \left[\lambda_{02} - (A_2\lambda_{02} + B_2)^{1/2}\right]c_2/c_0 \qquad (1)$$

where λ is the molar conductivity;

c_0 is the molar concentration of the electrolyte;

λ_{01} and λ_{02} are limiting molar conductivities at first and second stages of association, correspondingly;

besides $\lambda_{0i} = \lambda_{0+} + \lambda_{0-}$;

λ_{0+} is the limiting molar conductivity of the i-type cation;

λ_{0-} is the limiting molar conductivity of anion;

A_i, B_i are Onzager's coefficients;

c_1, c_2 are molar concentrations of cations MA^+ and M^{2+} correspondingly;

I is the ionic strength of solution.

As it follows from equation (1), the molar conductivity (λ) is the function of the values λ_{0i} and c_i. Values c_i also depend on relationship of the association constants and on the molar concentration of electrolyte (c_0). Therefore for 2–1 electrolyte $\lambda = f(\lambda_{01}, \lambda_{02}, K_{a1}, K_{a2}, c_0)$. It is interesting to note that equation (1) contains Onzager's coefficients which in the case of non-symmetric electrolytes

depend on values of limiting molar conductivity of an anion (λ_{0-}) and on limiting molar conductivity of the electrolyte at i-stage of the association (λ_{0i}).

Equilibrium ion concentrations (c_i) are determined by solving the system of nonlinear equations. This system includes expressions for ion association constants and the mass action law (2, 3), equations of electroneutrality and mass saving:

$$K_{a1} = (c_1 f_1)/(c_2 c_4 f_2 f_4), \qquad (2)$$

$$K_{a2} = \frac{c_5}{(c_1 c_4 f_1 f_4)}, \qquad (3)$$

$$c_4 = c_1 + 2c_2, \qquad (4)$$

$$c_5 = c_0 - c_1 - c_2 \qquad (5)$$

where c_4 is the molar anion concentration;

c_5 is the molar concentration of ionic associate MA_2;

f_i is the activity coefficient of corresponding ion that can be calculated from the Debae-Hiuckel equation:

$$f_i = \exp(-Az_1^2 I^{1/2}),$$

where A is the Debae-Hiuckel's coefficient.

Calculation of unknown values λ_{0i} and K_{ai} executes with the help of nonlinear programming methods by minimization of deviation function:

$$\sigma = \left[\sum_{j=1}^{NT}(\lambda_{\exp.j} - \lambda_{calc/j})^2/(NT-2)\right]^{1/2},$$

where NT is the quantity of experimental points at conductivity isotherm $\lambda = f(c)$;

$\lambda_{\exp.j}$ are experimental molar conductivity values;

$\lambda_{calc.j}$ are values of the molar conductivity calculated with the help of equation (1).

The use of optimization methods requires the initial assumption on the values of association constants that allow us to determine the molar ionic concentrations c_i by solving the system of nonlinear equations (2–5). This gives the possibility to minimize the deviation function $\sigma = \psi(K_{a1}, K_{a2}, \lambda_{01}, \lambda_{02})$. The search of minimum of the deviation function was executed in the range of association constants from 10^{-10} to 10^{+10} using the method of along-coordinate slope [2]. The error of ion association constants determination is about 5 %. The rightness of the given approach was checked on the experimental data of the conductivity of non-symmetrical polyvalent electrolytes in aqueous and non-aqueous solutions, which have been published.

The decision of the problem and discussing of scientific results

The present work deals with polyvalent electrolytes conductometric investigation of $CuCl_2$, $[Cu(en)_2]Cl_2$, $FeCl_3$ solutions in binary mixed solvent DMSO–CB in a wide range of electrolyte concentrations $(10^{-6}–10^{-2}$ mol/dm^3). Investigations were carried out at the temperature interval 298,15–323,15 K. The choice of all electrolytes was due to their good solubility both in individual (DMSO) and binary (DMSO–CB) solvents.

Ion association constants (K_{ai}) for given non-symmetrical electrolytes were calculated for two stages of association according to the schemes: for 2-1 electrolyte $(CuCl_2, [Cu(en)_2]Cl_2)$

$$MCl_2 \xleftrightarrow{K_{a2}} MCl^+ + Cl^- \xleftrightarrow{K_{a1}} M^{2+} + 2Cl^-$$
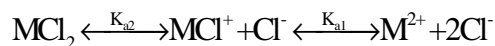
for 3–1 electrolyte $(FeCl_3)$

$$MCl_3 \xleftrightarrow{K_{a2}} MCl_2^+ + Cl^- \xleftrightarrow{K_{a1}} MCl^{2+} + 2Cl^-$$

It is convenient to check the influence of the solvent on ion association constants analyzing dependences of corresponding lnK_{ai} on inverse permittivity. The nature of solvation remains practically unchanged in conventionally– universal solvent DMSO–CB at all range of compositions. The linear dependences $lnK_{ai} = f(1/\varepsilon)$ of binary solvent have been obtained for all investigated electrolytes. Our assumption is about the realization of the solvation in this binary solvent only by one solvatoactive component – dimethylsulfoxide is realized.

The association of the researched electrolytes in the binary mixed solvents grows in the row $CuCl_2 > [Cu(en)_2]Cl_2 > FeCl_3$ on the first and on the second stages. The differentiation of the degree of the Lewis' acid force in the binary solvent increases with the decreasing of permittivity values in comparison with their force differentiation in the individual solvent – DMSO [3; 4].

Integral thermodynamic characteristics $(\Delta G_{ai}, \Delta H_{ai}, \Delta S_{ai})$ are calculated by equations:

$$\Delta G_{ai} = -RT \ln K_{ai},$$

$$\Delta H_{ai} = -Rd \left(\ln K_{ai} \right) / d \left(1/T \right),$$

$$\Delta S_{ai} = \left(\Delta H_{ai} + RT \ln K_{ai} \right) / T$$

superficially describe the process of ionic association. It is so because the stage association constants depend not only on temperature but also on solvent permittivity which in its turn depends on temperature, e.g. $K_{ai} = f(T, \varepsilon(T))$. The thermodynamic characteristics determination exhibited an error no more than 3%.

Conclusions

To sum up it is interesting to note that the given analysis allows to predict the direction of the solvent influence on the ionic association constants and hence the equilibrium ion concentrations of non-symmetric electrolytes in individual and mixed solvents. Besides the comparison of thermodynamic characteristics of equilibrium processes allows to make a conclusion about relative influence of polar and donor properties of medium on the processes of stage ion association in polyvalent electrolyte solutions.

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