

CHEMICAL TECHNOLOGIES

UDC 544.354:544.34(045)

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THE INFLUENCE OF THE SOLVENT ON THE THERMODYNAMICS OF ION ASSOCIATION

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Abstract. *Some approaches which allow to divide thermodynamic functions of the ion association process in two components have been developed. The first component belongs to the process, the second one is caused by the temperature dependence of the dielectric permittivity of the solvent. The theory is confirmed by numerous examples of the ion association process of different electrolytes in the binary mixed solvents.*

Keywords: covalent part of the constant of ionic association, electrostatic part of the constant of ionic association, enthalpy of the chemical equilibria in solution, entropy of the chemical equilibria in solution, ionic association, ionic equilibria, the equilibrium constant.

Introduction

The influence of a solvent on the equilibrium constant of the process of ionic association (K_a) has been a major focus of interest for the general theory of electrolytic solutions during the whole period of its existence. Many investigations have established the correlation between K_a and micro- and macroproperties of the electrolytic system, beginning from the Brensted equation to the most general Izmailov equation [1]. Crystallographic or effective ionic radii, ion-ion and ion-dipole interaction energies belong to the former; crystalline lattice energy and solvent permittivity (ϵ) belong to the latter.

The K_a is a part of all conductivity equations and K_a is one of major parameters beginning from the Debye-Hückel and ending to the mean-sphere approximation (MSA) theories [2] and the Barthel equation [3]. That is why the dependence between the solution conductivity and the temperature and solvent type can not be explained without taking into account the influence of these factors on the magnitude of the association constant.

Analysis of the problem and state of the problem

In accordance with general concepts developed in [4], the thermodynamics of equilibrium which have been established in a solvent, can be described as the equality:



A is all the ionic forms and B is the uncharged forms (irrespective of ionic or ionophoric ones) in this case. The variation of the free energy is described by the equation

$$\Delta G = \Delta G_{A,solv} - \Delta G_{B,solv} - \Delta G^v, \quad (2)$$

where ΔG^v is the variation of the free energy as a result of process (1) in vacuum and $\Delta G_{A,solv}$ and $\Delta G_{B,solv}$ are the variations of the free energy as a result of the solvation of reagents A and products of a reaction B.

The equation of the equilibrium constant in a solution can be presented in a general form

$$\ln K_a = \frac{\Delta G^v + \Delta G_{B,solv} - \Delta G_{A,solv}}{RT}$$

The variation of the free energy consists of covalent and electrostatic components in a result of any equilibrium process:

$$\Delta G = \Delta G^{cov} + \Delta G^{elst}$$

The equation (2) in a more detailed form is derived as

$$\Delta G = -\Delta G^v + (\Delta G_{A,solv}^{cov} - \Delta G_{B,solv}^{cov}) + (\Delta G_{A,solv}^{elst} - \Delta G_{B,solv}^{elst})$$

thus,

$$\ln K_a = \frac{\Delta G^v + (\Delta G_{B,solv}^{cov} - \Delta G_{A,solv}^{cov}) + (\Delta G_{B,solv}^{elst} - \Delta G_{A,solv}^{elst})}{RT}. \quad (3)$$

The decision of the problem and discussing of scientific results

In a first and quite good approximation it is possible to assume that all the types of electrostatic interactions in a solution are inversely proportional to permittivity $1/\epsilon$, i.e.

$$\Delta G^{elst} = \frac{-\beta}{\epsilon},$$

Then (3) can be presented in the form, which already have certain predictability relative to the solvent effect on the position of the chemical equilibrium in the solution

$$\ln K_a = \frac{\Delta G^v + \delta\Delta G_{sol}^{cov} + \delta\beta_{sol} / \epsilon}{RT} \quad (4)$$

In the case when an energy of the specific solvation in a solvent is much lower than the energy of the universal (nonspecific) solvation, i.e. $\Delta G_{sol}^{elst} \gg \Delta G_{sol}^{cov}$, it can be accepted in the well observed approaching, that

$$\ln K_a = \frac{\Delta G^v + \delta\beta_{sol} / \epsilon}{RT} \quad (5)$$

These general thoughts show that the influence of a solvent on the equilibrium of the chemical process in all cases is determined by the difference of the free energies of the solvation of the members of the equilibrium.

The constant of equilibrium of chemical process (when the temperature is constant) changes in such measure in which it takes to the change of $\delta\Delta G_{sol}^{cov}$ and $\delta\beta_{sol}$. It is obvious, that when $\delta\Delta G_{sol}^{cov}$ and $\delta\beta_{sol}$ are constant, the dependence (4) changes to the equation

$$\ln K = a + b/\epsilon. \quad (6)$$

The constancy of both solvation terms of equation (4) can be observed in the homologous series of solvents (with certain approximation, e.g., in series of n-aliphatic alcohols) and also in mixed binary solvents formed by one solvat-active and other solvat-inert solvent.

Such media are proposed to be called conditionally universal [4]; H_2SO_4 in a binary solvent DMSO- CCl_4 can serve an example of fulfilment of equation (6) [5] (fig. 1).

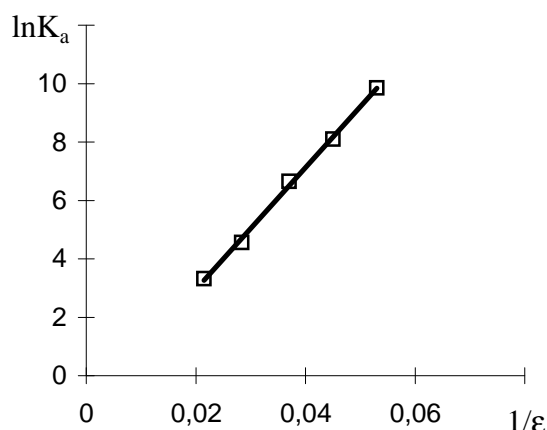


Fig. 1. Dependence $\ln K_a = f(1/\epsilon)$ for H_2SO_4 in binary solvent DMSO- CCl_4 (298.15 K)

In the systems where only universal solvation is realized the dependence of the equilibrium constant and permittivity is reduced to the equation the form of which is identical to that of equation (6). Such case can be illustrated by the variation of the ionic association constant for such salt as $[CH_3(n-C_8H_{17})_3N]^+OSO_3CH_3^-$ in different pure solvents [6] (fig. 2).

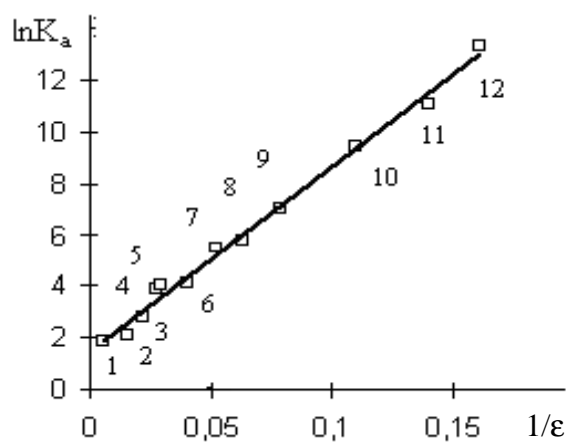


Fig. 2. Dependence $\ln K_a = f(1/\epsilon)$ for $[CH_3(n-C_8H_{17})_3N]^+OSO_3CH_3^-$ in different pure and mixed solvents:

- 1 - N-methylacetamide,
- 2 - propylene carbonate,
- 3 - DMSO,
- 4 - DMFA,
- 5 - nitrobenzene,
- 6 - Py - DMFA,
- 7 - Py - acetonitrile,
- 8, 9 - nitrobenzene - acetic acid,
- 10 - propylene carbonate - acetic acid,
- 11 - Py - hexane,
- 12 - acetic acid

Large ionic radii of a cation and an anion leads to the fact that the energy of specific solvation is negligible in solvents of any nature, from sufficiently acid (e.g. HAC) to strongly basic (e.g. Pyridine). At last, when the terms of equation (5) are changed when other solvent is used, $\ln K_a = f(1/\epsilon)$ relation is non-linear. This case is illustrated by picric acid solutions in a binary solvent $H_2O - i-PrOH$ both components of which are solvation active on a relation to the electrolyte [7] (fig. 3).

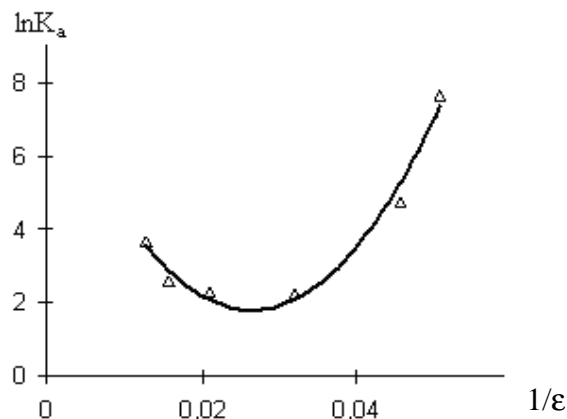


Fig. 3. Dependence $\ln K_a - 1/\epsilon$ for picric acid in binary solvent $H_2O - n-C_3H_7OH$

The analysis of the $\ln K_a = f(1/\epsilon)$ relation geometry can give rather valuable information about the nature of the process proceeding in the system and about the influence of a solvent on this process. The use of binary solvents allow to directionally change both main factors influencing on the ionic association constant and, thus, to control the K_a variation.

The values of ionic association constants derived from polytherms are the source of information about the thermodynamics of ionic association. However, the determination of reliable ΔH_a and ΔS_a values often encounters with several difficulties. The thermal curve $\ln K_a$ often passes through the extreme in rather wide temperature range. A good example can be found in Barthel's works [8; 9] (fig. 4).

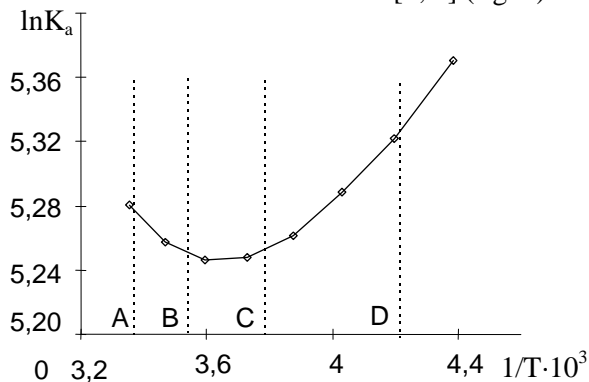


Fig. 4. Dependence $\ln K_a - 1/T$ for $i-Am_3BuNI$ in ethanol

It is evident that the calculation ΔH_a and ΔS_a in A-B, B-C, and C-D temperature ranges will give entirely different results. The reason for extreme behaviour of a $\ln K_a - 1/T$ curve is obvious: in the beginning the temperature increase results in a lower equilibrium constant of an exothermal process of ionic association, then the fall of permittivity of a solvent leads to a stronger ion-ion interaction and, thus, to a higher K_a .

The dependence of ΔG_a from the temperature is linear or it can be considered linear with a minimum error in the temperature range which corresponds to a range of the existence of a solvent in a liquid phase at the normal pressure

$$\Delta G_a = \Delta G_0 + \Delta G_1 T \quad (7)$$

Substituting (7) in (3), we get the equation

$$\ln K = \frac{\Delta G_0^v + \Delta G_1^v T + \Delta G_{0,solv}^{cov} + \Delta G_{1,solv}^{cov} T + \Delta G_{0,solv}^{elst} + \Delta G_{1,solv}^{elst} T}{RT}$$

which describes the thermal dependence for any equilibrium process in a solution, including the process of ionic association.

After similar splitting of coefficients of equation

(6), i.e. if we assume that $a = \frac{a_0 + a_1}{T}$ and

$b = \frac{b_0 + b_1}{T}$, we obtain a convenient approximated

form of the equilibrium constant for universal and conditionally universal media [4, p. 82]

$$\ln K_a = a_0 + a_1/T + b_0/\epsilon + b_1/\epsilon T \quad (8)$$

The coefficients of equation (8) have quite clear physical meaning:

$$a_0 + a_1/T = \ln K_{a,\epsilon=\infty};$$

$$b_0 + b_1/T = \ln K_{a,\epsilon=1} - \ln K_{a,\epsilon=\infty}.$$

The condition of appearance of the extremum on the politerme K_a , which effluent from equalization (8), is:

$$\frac{(a_1 + b_1/\epsilon)}{T_{extr}^2} + \frac{1}{\epsilon} \frac{d \ln \epsilon}{dT} (b_0 + b_1/T) = 0.$$

In a range of 100-150°C the thermal dependence of permittivity is well described with the equation

$$\epsilon = \exp(\beta T + \gamma), \quad (9)$$

and, thus, a relative thermal coefficient of permittivity is $\beta = d(\ln \epsilon)/dT$. With the account of this, the condition of extremum can be presented as an equation, which allows to calculate temperature corresponding to the extremum of the ionic association constant:

$$a_1 \exp(\beta T_{extr} + \gamma) + b_1 + \beta T_{extr} (b_0 T_{extr} + b_1) = 0. \quad (10)$$

To confirm the correctness of such approach, we site the data [10] on the temperature dependence of K_a for picric acid in the binary solvent ethylene glycol - 2 methoxyethanol (ME); in [11] polytherms of permittivity for this solvent are given. The data [10,11] were used to calculate the coefficients of equation (8) equal to

$$a_0 = -6,675; a_1 = 2840; b_0 = 228,1; b_1 = -32710.$$

Table 1 compares experimental and calculated (using equation (10)) temperature values corresponding to the extremum on $K_a=f(T)$ polytherms.

Table 1. Experimental and calculated temperatures corresponding to the extremum on ionic association constant polytherms for picric acid in the binary solvent ethylene glycol 2-metoxyetanol

Solvent composition, mole part of EG	Coefficients of equation (9)		T_{extr} , K	
	$\beta \cdot 10^3$	γ	exp	theor
1	5,115	5,240	325	325
0,9272	5,127	5,179	308-318	318
0,8499	5,132	5,116	303-113	312
0,7676	5,277	5,089	293-303	305
0,6799	5,307	5,023	283-298	298
0,5861	5,259	4,928	278-300	291
0,4856	5,427	4,885	273-298	282
0,3776	5,892	4,919	268-293	274
0,2614	6,079	4,864	263	265

The enthalpy of ionic association is calculated by temperature differentiation of equation (8) using Van't Hoff's equation:

$$\begin{aligned} \Delta H_{a,integr} &= RT^2 (d \ln K_a / dT) = \\ &= -R(a_1 + b_1 / \varepsilon) - RT^2 \frac{d \ln \varepsilon}{dT} (b_0 + b_1 / T) / \varepsilon. \end{aligned} \quad (11)$$

The entropy equation is derived correspondingly:

$$\begin{aligned} \Delta S_{a,integr} &= \frac{\Delta H_{a,integr} + RT \ln K_a}{T} = \\ &= -R(a_0 + b_0 / \varepsilon) - RT (d \ln \varepsilon / dT) \cdot (b_0 + b_1 T) / \varepsilon. \end{aligned}$$

The meaning and contents of the "integr." index will be explained below.

The right parts of the last two equations contain two terms each. The first terms are related to the process of ionic association, the second ones are referred to the solvent. The thermodynamics of ionic association is obviously characterised only by the first terms which we propose to call "temperature

components" as opposed to the second ones which are called "dielectric components" [2, p. 188], i.e.

$$\Delta H_{integr} = \Delta H_T + \Delta H_\varepsilon \quad (12)$$

$$\Delta S_{integr} = \Delta S_T + \Delta S_\varepsilon. \quad (13)$$

Equations (12) and (13) demonstrate that magnitudes of enthalpies and entropies of chemical equilibrium in the solution are integral values including thermodynamic characteristics both of the process itself and those associated with temperature variations of permittivity.

Strictly speaking, temperature changes of solvent's density also influence the calculated values of ΔH and ΔS , and the calculated concentrations of chemical equilibrium members. However, if we take into account the variation of molarity with the change of temperature, the correction for the variation of volume is not required. When the concentration is expressed in terms of molality, the temperature variation of density does not influence the calculated values of ΔH , but influences ΔS quit considerably.

Thus, for the equilibrium $K^+ + A^- = K^+A^-$ the calculated entropies when the concentration is expressed in terms of molarity (ΔS_c) or molality (ΔS_m) can differ quite considerably:

$$\Delta S_c - \Delta S_m = R \ln s,$$

where 's' is the quantity number of moles of a solvent per 1000g of the solvent.

Thus, real thermodynamics characteristics of ionic association as well as any other equilibrium process in a solution should be calculated by the equations:

$$\Delta H_{a,T} = -R(a_1 + b_1 / \varepsilon); \quad (14)$$

$$\Delta S_{a,T} = -R(a_0 + b_0 / \varepsilon). \quad (15)$$

Using these equations, one can find $\Delta H_{a,T}$ and $\Delta S_{a,T}$ for the solvents with corresponding permittivity. This approach is especially convenient in case of mixed (binary) solvents.

The physical meaning of the conception "temperature component of enthalpy" could be understood by taking into account the coinciding of this value with ones measured calorimetrically and extrapolated (by the heat of ionic association) to infinite dilution. This conception is illustrated by fig. 5.

The differentiation of the polyterm $\ln K_a - f(T)$ with respect to T for points 1, 2, 3 results in $\Delta H_{a,integr}$ and $\Delta S_{a,integr}$. The values of $\Delta H_{a,T}$ and $\Delta S_{a,T}$ determined by equations (14) and (15) are related to isoelectric cuts a'-b'; a''-b''; a'''-b'''.

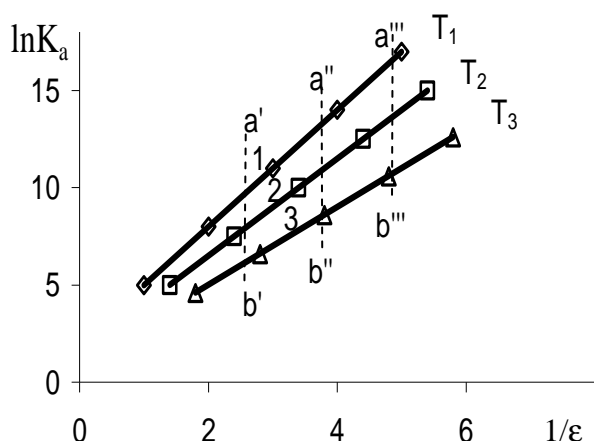


Fig. 5. Isotherm $\ln K_a - f(1/\epsilon)$ for different temperatures ($T_1 < T_2 < T_3$).

It is also seen in fig. 5 that such calculations of the thermodynamics of ionic association are not necessarily referred to linear isotherms $\ln K_a = f(1/\epsilon)$ described by equation (8). In the general case, if the isotherms $\ln K_a = f(1/\epsilon)$ are non-linear, i.e. if $\ln K_a = f(1/\epsilon)$ that is at:

$$\ln K_a = a + b/\epsilon + c/\epsilon^2 + \dots,$$

it is possible to approximate each of these coefficients by $1/T$, arriving at the equation

$$\ln K_a = a_0 + a_1/T + a_2/T^2 + \frac{b_0 + b_1/T + b_2/T + \dots}{\epsilon} + \frac{c_0 + c_1/T + c_2/T + \dots}{\epsilon^2} + \dots \quad (16)$$

By differentiation of equation (16) with respect to T , it is possible to find $\Delta H_{a,T}$ and $\Delta S_{a,T}$ related to definite values of permittivity.

The terms of equations (14) and (15) give grounds to split the thermodynamics of ionic association into covalent and electrostatic members:

$$\Delta H_{a,T} = -Ra_1 - Rb_1/\epsilon = \Delta H_{a,T}^{\text{cov}} + \Delta H_{a,T}^{\text{elst}};$$

$$\Delta S_{a,T} = Ra_0 + Rb_0/\epsilon = \Delta S_{a,T}^{\text{cov}} + \Delta S_{a,T}^{\text{elst}}.$$

Because of this we should note that the splitting of the ionic association constant into covalent and electrostatic parts is one of the main points of the MSAT application [2] to ionic equilibria. The analysis of each part of thermodynamic characteristics permits to obtain more comprehensive information about the effect of specific and universal solvation on ionic association.

Thus, e.g., the independence of $\Delta H_{a,T}^{\text{cov}}$ (12.0 kJ/mol) and $\Delta S_{a,T}^{\text{cov}}$ (43.2 J/mol·K) [12] for ionic association of Et_4NBr in the mixed solvent propylene carbonate (PC) - o-dichlorobenzene demonstrates that in this binary system only one component (PC) is active in the process of the solvation. The effect of universal solvation determined by the variation of solvent permittivity in system on the electrostatic components of ionic association is illustrated by tab. 2.

Table 2. Electrostatic components of ionic association of Et_4NBr in the mixed solvent propylene carbonate - o-dichlorobenzene

Components	0	0,2	0,4	0,6	0,8	1
ϵ	9,9	21,0	32,0	43,0	54,1	65,1
$\Delta H_{a,T}^{\text{elst}}$, kJ/mole	1,2	0,57	0,37	0,27	0,22	0,18
$\Delta S_{a,T}^{\text{elst}}$, kJ/mole	4,3	2,1	1,4	1,0	0,8	0,7

Such separate analysis is especially important as the application of integral characteristics can sometimes lead to inadequate understanding of the nature of solvation in the electrolytic system. It follows from equation (11) that

$$\left[\frac{d\Delta H_{a,\text{integr}}}{d(1/\epsilon)} \right]_T = -R\{b_1(1+T(d\ln\epsilon/dT)) + Tb_0^2(d\ln\epsilon/dT)\}.$$

The analysis of this equation demonstrates that the ratio of absolute values of terms in the right side of equation is such that higher ϵ can lead to any sign of the derivative $\left[\frac{d\Delta H_{a,\text{integr}}}{d(1/\epsilon)} \right]_T$, i.e. cause both higher and lower $\Delta H_{a,\text{integr}}$. At the same time it follows from equation (14) that since

$$\left[\frac{d\Delta H_{a,T}}{d(1/\epsilon)} \right]_T = Rb_1$$

i.e. $\Delta H_{a,T}$ does not depend on the temperature coefficient of permittivity and, thus, higher ϵ in full agreement with the physical model of ionic association should result in lower exothermicity of the process. The analysis of K_a polytherms results in better knowledge of ionic equilibria thermodynamics than that of integral entropies and enthalpies of the process. For example, this can be corroborated by the data on the thermodynamics of ionic association of methylsulfuric acid in n-aliphatic alcohols $\text{C}_1\text{-C}_6$ given in fig. 6.

In fig. 6 integral enthalpies and their components are plotted against $1/\epsilon$. As it is seen in the fig. 6, proceeding from $\Delta H_{a, \text{integ.}}$, one should have come to a conclusion that for all the alcohols ionic association, i.e. the formation of ionic pairs or nondissociated acid molecules, is endothermic.

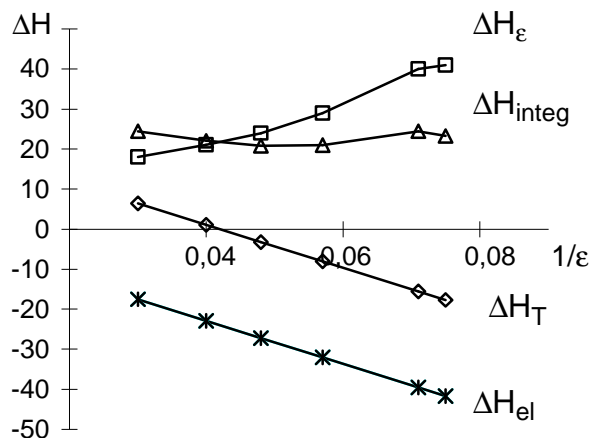


Fig. 6. Dependence ΔH on $1/\epsilon$ for methylsulfuric acid in n-aliphatic alcohols C_1 - C_6

But the endothermicity of the process increases with the permittivity decrease which certainly contradicts the physical model of the process. At the same time the analysis of $\Delta H_{a,T}$ demonstrates that with lower permittivity the exothermicity of ionic association naturally increases. The fig. 6 also confirms a decisive role of electrostatics in determining the enthalpy of this process.

Conclusions

Within the framework of the offered approach appears possibility to explain physical sense of bank of outthermodynamic concepts and conformities. So, for example, compensative effect, which must be observed for the processes of the same nature, in actual fact observes only for temperature constituents, but not for integral. It is possible to think, that nature of process of ionic association of acid in transition of one spirit solvent to other changes substantially. But at the same time the compensative effect here executed strictly.

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Received 11 March 2011.