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ION-PAIR CONVERSION THERMODYNAMICS IN ALCOHOL SOLUTIONS OF HYDROGEN HALIDES

The calculation of thermodynamic characteristics of dissociation of contact and solvent-separated ion pairs into ions, conversion of contact ion pairs into solvent-separated ion pairs of ionogens HCl, HBr and HI in *n*-alcohols from methyl alcohol to *n*-octyl alcohol by the method described earlier for the systems HCl – *n*-alcohol in the same solvents at the same temperatures was carried out. The following regularities were established in this work: a) positive values of the change in the Gibbs energy of dissociation ($\Delta_{\mathrm{dis}}G^\circ$) of contact and solvent-separated ion pairs increase in the case of increasing temperature and the number of carbon atoms in the *n*-alcohol molecule and decreasing radius of the halide ion, and their sign and magnitude are determined by the entropic component ($-T\Delta_{\mathrm{dis}}S^\circ$). In this case, the values of $\Delta_{\mathrm{dis}}G^\circ$ of contact ion pairs exceed the same values for ion pairs separated by solvent; b) the values of the Gibbs energy change ($\Delta_{\mathrm{conv}}G^\circ$) for the studied ionogens HCl, HBr, and HI are also positive, except for the values of $\Delta_{\mathrm{conv}}G^\circ$ of ionogens in methanol and HBr solutions in ethanol. In these cases, the $\Delta_{\mathrm{dis}}G^\circ$ values for solvent-separated ion pairs exceed the same values for contact ion pairs, and the $\Delta_{\mathrm{conv}}G^\circ$ values are negative. With increasing temperature and radius of the halide ion, $\Delta_{\mathrm{conv}}G^\circ$ become more negative, and vice versa with increasing hydrocarbon radical; c) the concentration of contact ion pairs increases in the methanol – *n*-octanol series for all ionogens, decreases slightly with increasing temperature and radius of the anion, and varies from ~30% (methanol) to ~95% (*n*-octanol). In methanol, solvent-separated ion pairs predominate; in alcohols from *n*-propyl to *n*-octyl, contact ion pairs predominate, i.e., deconversion of ion pairs occurs.

Keywords: ionic pair, proton, conversion, hydrogen halide, *n*-alcohols, acid ionization

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ТЕРМОДИНАМІКА КОНВЕРСІЇ ІОННИХ ПАР У СПИРТОВИХ РОЗЧИНАХ ГІДРОГЕНГАЛОГЕНІВ

Проведено розрахунок термодинамічних характеристик дисоціації контактних і розділених розчинником іонних пар на іони, конверсії контактних іонних пар у розділені розчинником іонні пари іоногенів HCl, HBr і HI у *н*-спиртах від метилового до *н*-октилового за методикою, викладеною нами раніше для систем HCl – *н*-спирт у тих самих розчинниках при тих же температурах. У роботі встановлено такі закономірності: а) позитивні значення зміни енергії Гіббса дисоціації ($\Delta_{\text{дис}}G^\circ$) контактних і розділених розчинником іонних пар зростають у разі збільшення температури, числа атомів карбону в молекулі *н*-спирту, зменшення радіуса галогенід-іону, а їхній знак і величина визначаються ентропійною складовою ($-T\Delta_{\text{дис}}S^\circ$). При цьому значення $\Delta_{\text{дис}}G^\circ$ контактних іонних пар перевищують ті самі величини для розділених розчинником іонних пар; б) значення зміни енергії Гіббса конверсії ($\Delta_{\text{конв}}G^\circ$) для вивчених іоногенів HCl , HBr і HI також позитивні, за винятком величин $\Delta_{\text{конв}}G^\circ$ іоногенів у метанолі і розчинів HBr в етанолі. У цих випадках величини $\Delta_{\text{дис}}G^\circ$ для розділених розчинником іонних пар перевищують ті ж самі значення для контактних іонних пар, а значення $\Delta_{\text{конв}}G^\circ$ – негативні. Зі зростанням температури та радіусу галогенід-іону $\Delta_{\text{конв}}G^\circ$ стають більш від’ємними, а зі зростанням вуглеводневого радикалу – навпаки; в) концентрація контактних іонних пар зростає в ряді метанол – *н*-октанол для всіх іоногенів, незначно зменшується зі збільшенням температури й радіуса аніона та змінюється в межах від ~30 % (метанол) до ~95 % (*н*-октанол). У метанолі переважають розділені розчинником іонні пари, у спиртах від *н*-пропілового до *н*-октилового переважають контактні іонні пари, тобто відбувається деконверсія іонних пар.

Ключові слова: іонні пари, протон, конверсія, гідрогенгалогени, *н*-спирти, іонізація кислот

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ТЕРМОДИНАМИКА КОНВЕРСИИ ИОННЫХ ПАР В СПИРТОВЫХ РАСТВОРАХ ГАЛОГЕНОВОДОРОДОВ

Проведен расчет термодинамических характеристик диссоциации контактных и разделенных растворителем ионных пар на ионы, конверсии контактных ионных пар в разделенные растворителем ионные пары ионогенов HCl, HBr и HI в *н*-спиртах от метилового до *н*-октилового по методике, изложенной нами ранее для систем HCl – *н*-спирт в тех же растворителях при тех же температурах. В работе установлены такие закономерности: а) положительные значения изменения энергии Гиббса диссоциации ($\Delta_{\text{дис}}G^\circ$) контактных и разделенных растворителем ионных пар возрастают в случае увеличения температуры и числа атомов углерода в молекуле н-спирта, уменьшения радиуса галогенид-иона, а их знак и величина определяются энтропийной составляющей ($-T\Delta_{\text{дис}}S^\circ$). При этом значения $\Delta_{\text{дис}}G^\circ$ контактных ионных пар превышают те же величины для разделенных растворителем ионных пар; б) значения изменения энергии Гиббса ($\Delta_{\text{конв}}G^\circ$) для изученных ионогенов HCl , HBr и НИ также положительны, за исключением величин $\Delta_{\text{конв}}G^\circ$ ионогенов в метаноле и растворов HBr в этаноле. В этих случаях величины $\Delta_{\text{дис}}G^\circ$ для разделенных растворителем ионных пар превышают те же значения для контактных ионных пар, а значения $\Delta_{\text{конв}}G^\circ$ – отрицательные. С ростом температуры и радиуса галогенид-иона $\Delta_{\text{конв}}G^\circ$ становятся более отрицательными, а с ростом углеводородного радикала – наоборот; в) концентрация контактных ионных пар возрастает в ряду метанол – *н*-октанол для всех ионогенов, незначительно уменьшается с увеличением температуры и радиуса аниона и изменяется в пределах от ~30% (метанол) до ~95% (*н*-октанол). В метаноле преобладают разделенные растворителем ионные пары, в спиртах от *н*-пропилового до *н*-октилового преобладают контактные ионные пары, то есть происходит деконверсия ионных пар.

Ключевые слова: ионные пары, протон, конверсия, галогеноводороды, *н*-спирты, ионизация кислот

Introduction. One of the fundamental processes of physical chemistry that attract the attention of researchers is the ionization of acids both in water and non-aqueous solvents. It is very important to identify the molecular-level mechanism of acid ionization, proton solvates and ionic pairs (IP) formation. This information gives a key to understanding elementary chemical processes in non-aqueous acid solutions, in biological processes, etc.

Previously [1] we considered the multistep process of hydrogen chloride ionization using the ionization scheme of N.A. Izmailov [2] in *n*-alcohols from methanol to *n*-octanol, including 10 interrelated equilibria. The special place among these equilibria belong to the conversion of contact ion pairs (CIP) into solvent-separated ion pairs (SSIP). However, from our point of view, the equilibrium of CIP to SSIP conversion in the scientific literature is described insufficiently. Practically no experimental data on the conversion constants of CIPs to SSIPs for acids in non-aqueous solvents are available. In our opinion, it is related to the problem of choosing the primary stable particle in which the proton exists in solution and, consequently, the identification of the ion pair by various experimental methods.

In our works [3,4], the calculation of the thermodynamic characteristics of the stages of dissociation of contact ion pairs (CIP) and solvent-separated ion pairs (SSIP) into ions, conversion of CIP into SSIP of the process of ionization of HCl and HBr in *n*-alcohols from methyl to *n*-octanol at 278.15 – 328.15 K. In this work, a systematic study of the process of thermodynamics of the conversion of ion pairs in alcohol solutions of HI is carried out, compatible with the previously considered similar solutions of HCl and HBr.

Despite the same electron configuration, these ionogens differ in physical and chemical properties. Thus, in the series HCl – HBr – HI, the length of the chemical bond increases, the enthalpy of formation decreases (~ by 3 times), solubility in polar solvents increases. The ionization constants of HBr and HI in water exceed the ionization constant of HCl by ~ 800 and ~ 4000 times, respectively: $pK_i(HCl) = -5.9$; $pK_i(HBr) = -8.8$; $pK_i(HI) = -9.5$ [5]). So, these ionogens, HCl, HBr and HI are fully ionized into solvated ions in dilute aqueous solutions.

When passing to non-aqueous solvents, for example to primary alcohols, the pK_i values are positive and the difference between them for HBr and HCl does not exceed 0.3 pK_i units [3, 4, 6]. This indicates that in alcohol solutions they form ion pairs along with solvated ions.

The structure and stability of ion pairs depend on the structural quantities of the solvent and ions. In the case of ionogens, the IP can be considered an intermediate between ions and ionogen molecules.

The most commonly used experimental method for characterizing ionic associates (CIP and SSIP) is vibrational spectroscopy: infrared and Raman spectroscopy [7]. The vibrational frequency of the anion is “shifted” during the formation of ion pairs and other associates, and the degree of shift provides information about the nature of ion pair varieties. However, as noted in [7], the ion pairs of single-atom anions containing halide ions cannot be studied by this method. NMR spectroscopy is also inefficient, since the association/dissociation equilibria are rather fast on the NMR time scale. As a result, time-averaged cation and/or anion signals are obtained [7]. In this connection, the modern scientific literature favors theoretical approaches when studying the properties of ionic associates containing halide ions [8 – 11].

The formation mechanism and structure of IPs in protic solvents with proton participation differ from those for ordinary ions. The ion-ion and ion-molecule interactions of the proton are peculiar due to its small size and specific structure [12]. In contrast to the usual cations, the proton does not contain electrons near the nucleus, but it has a significant charge density. This leads to a strong polarizing effect on the solvent molecules, and as a result, the proton in solution exists exclusively in the form of solvates [12]. The specifics of its behavior in liquid solutions are largely related to the molecular structure of the solvent [12]. Thus, in protolytic solvents, the proton forms charged clusters of the composition $H(M)_n^+$ (M is a solvent molecule). The simplest of these in composition are the products of the primary solvation of the proton at $n = 1, 2$ – lyonium MH^+ and Zundel M_2H^+ cations. As a rule, in model problems of physical chemistry, the simplest in composition lyonium ion (MH^+) has been considered as a specific solvate. However, [13] rather convincingly argues that the most stable cluster is the Zundel cation, and the lyonium ion is formed only in concentrated solutions at an equimolar ratio of H^+ ions and solvent molecules. The lyonium ion is a component of the Zundel ($n = 2$) and Eigen ($n = 4$) cations. This raises many questions regarding the state of the proton and the transformation of its indicated clusters as the temperature increases.

It seems to us that the specific behavior of the proton in protolytic solvents also determines its state in IPs (CIPs and SSIPs). Obviously, the structure of ion pairs and, consequently, the mechanism of their formation should include (take into account) the simplest products of primary proton solvation [1, 3].

The CIP in alcohol solutions of hydrogen halides can be represented as a neutral particle consisting of a lyonium ion (alkoxonium) and a halogenide ion: $ROH_2^+...Hal^-$. Such a representation of the CIP is in agreement with the generally accepted one [14, 15]. In this case, the H-bond in such a formation is asymmetric. The electron cloud density is shifted toward the Hal^- ion [15]. SSIP can be viewed as a formation consisting of a Zundel cation and a H-bonded halide ion: $(ROH)_2H^+...Hal^-$.

Methods. The electrostatic and non-Coulomb interactions act between ions in protolytic solvents [16]. Taking the latter into account is fraught with difficulties in describing the discrete structure of the solvent and with strong ion-molecule interactions at short distances.

In connection with the above, we used the Ebeling equation [17] (1) to calculate the dissociation constants of CIP:

$$K_{\mathrm{dis}}^{\mathrm{CIP}} = \frac{1000}{8\pi N_{\mathrm{A}} a^3} \cdot \left(\sum_{m \geq 2}^{\infty} \frac{b^{2m}}{(2m)!(2m-3)} \right)^{-1} \qquad (1)$$

According to [18], equation (1) implicitly takes into account the short-range repulsive forces between the ions in the IP and the dispersion interactions between the solvent molecules. Among the known equations of this type, it is the most acceptable for describing such systems at different temperatures.

We calculated K_{dis}(SSIP) according to the method described in [19] using equation (2)

$$-\ln K_{\mathrm{dis}}^{\mathrm{SSIP}} = \left[\left(\frac{N_{\mathrm{A}} e^2}{4\pi\varepsilon_0 \varepsilon a R T} \right) \cdot \left(1 + \frac{\partial \ln \varepsilon}{\partial \ln T} \right) + \left(\frac{1}{2} + \frac{\partial \ln V_{\mathrm{f}}}{\partial \ln T} \right) \right] - \left[\left(\frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon a R} \right) \cdot \left(\frac{\partial \ln \varepsilon}{\partial T} \right) \right] \qquad (2)$$

,

where ε_0 is the dielectric constant of vacuum; R is the molar gas constant; for the SSIP $\mathrm{MH}^{+}_{\mathrm{solv}} || \mathrm{I}^{-}_{\mathrm{solv}}$ the three radii of the solvent molecule (r(S)) $a = r(\mathrm{I}^-) + 3r(\mathrm{S})$ were added to the crystallographic radius of the I^- ion. In equation (2), the first term is equal to $\Delta_{\mathrm{dis}}H°$(SSIP)/RT, the second one is $\Delta_{\mathrm{dis}}S°$(SSIP)/R.

The dielectric permittivity of alcohols is taken from [20]. The radius of the alcohol molecules was calculated from the solvent density data given in the monograph [21]. The free volume (V_f) was calculated by the Prigozhin formula [22]:

$$V_f = \frac{R\beta_T}{\alpha_p}$$

where β_T is the isothermal compressibility, α_P is the thermal expansion. These values are also taken from the monograph [21].

The choice of equation (2) to calculate K_{dis}(SSIP) is due to the fact that the ions in the ion pair are bound together predominantly by Coulomb forces. In addition, taking into account the free volume of the solvent and its isothermal compressibility reflects the structural features of n-alcohols under the influence of temperature and dielectric permittivity.

The conversion constants (K_{conv}) [1], the values of which are given in Table 1, were calculated from the data on the dissociation constants of the CIP and SSIP by the relationship (3):

$$K_{\mathrm{conv}} = \frac{K_{\mathrm{dis}}(\mathrm{CIP})}{K_{\mathrm{dis}}(\mathrm{SSIP})} \qquad (3)$$

From the ion pair dissociation constants (IP) data of the CIP and SSIP, their thermodynamic quantities (thermodynamic quantities) ($\Delta\ \mathrm{G}_{\mathrm{dis}}^{\circ}$ (IP), Δ_{dis} H°(IP), Δ_{dis} S°(IP) were determined from equations (4), (5) and (6) (see Tables 2 and 3).

$$\Delta_{\mathrm{dis}}G° (\mathrm{IP}) = -RT \ln K_{\mathrm{dis}}(\mathrm{IP}) \qquad (4)$$

$$\Delta_{\mathrm{dis}}S^{\circ}(\mathrm{IP}) = -\frac{\partial \Delta_{\mathrm{dis}}G^{\circ}(\mathrm{IP})}{\partial T} \qquad (5)$$

$$\Delta_{\mathrm{dis}}H^{\circ}(\mathrm{IP}) = \Delta_{\mathrm{dis}}G^{\circ}(\mathrm{IP}) + T\Delta_{\mathrm{dis}}S^{\circ}(\mathrm{IP}) \qquad (6)$$

The thermodynamic quantities of CIP to SSIP conversion were calculated using expression (7) derived from the thermodynamic cycle

$$\square_{\mathrm{conv}}Y° = \square_{\mathrm{dis}}Y°(\mathrm{CIP}) - \square_{\mathrm{dis}}Y°(\mathrm{SSIP}) \qquad (7)$$

Here $Y = G, H, S$.

The values of $\Delta_{\mathrm{conv}}H°$ and $\Delta_{\mathrm{conv}}S°$ are shown in Table 4.

Results and discussion. From the analysis of the obtained data on the thermodynamic quantities of the stages of CIP dissociation, SSIP dissociation and CIP to SSIP conversion of HCl [3], HBr [4], HI (Tables 1-5) ionization process in n-alcohols from methanol to n-octanol at 278.15 – 328.15 K the following regularities were established:

1. The values of $\Delta_{\mathrm{dis}}G°$(CIP) and $\Delta_{\mathrm{dis}}G°$(SSIP) (Tables 2 and 3) are positive, increasing with increasing temperature and the number of carbon atoms in the n-alcohol molecule. In this case $\Delta_{\mathrm{dis}}G°(\mathrm{CIP}) > \Delta_{\mathrm{dis}}G°(\mathrm{SSIP})$.

2. The values of $\Delta_{\mathrm{conv}}G°$ are also positive, except for the values of $\Delta_{\mathrm{conv}}G°$ in methanol at 278.15 – 328.15 K and HBr solutions at 298.15 – 328.15 K in ethanol. For these cases, $\Delta_{\mathrm{dis}}G°(\mathrm{SSIP}) > \Delta_{\mathrm{dis}}G°(\mathrm{CIP})$ and $\Delta_{\mathrm{conv}}G°$ are negative. As the temperature increases, $\Delta_{\mathrm{conv}}G°$ become more exothermic, and vice versa as the hydrocarbon radical increases.

3. The values of $\Delta_{\mathrm{dis}}H°$(CIP), $\Delta_{\mathrm{dis}}H°$(SSIP), $\Delta_{\mathrm{conv}}H°$, $\Delta_{\mathrm{dis}}S°$(CIP), $\Delta_{\mathrm{dis}}S°$(SSIP), $\Delta_{\mathrm{conv}}S°$ of three ionogens are negative, except the values of $\Delta_{\mathrm{dis}}H°$(SSIP) in methanol. As the length of the alkyl group of n-alcohol increases, the enthalpy quantities of the above processes become more exothermic, while the opposite is true as the radius of Hal^- increases.

4. The values and sign of the change in $G°$ for the dissociation stages of CIP and SSIP into ions and the conversion of CIP into SSIP are determined by the entropic component ($-T\Delta S°$), except for those cases for which $\Delta G°_{\mathrm{conv}} < 0$ (methanol, ethanol). In these cases, the value and sign of $\Delta_{\mathrm{conv}}G°$ are determined by the enthalpic component.

The conversion process of CIP and SSIP for in methanol and partially in ethanol proceeds spontaneously. The differences in the signs of $\Delta_{\mathrm{conv}}G°$ in methanol and ethanol and other n-alcohols are due to the opposite sign contribution from the short-acting

Table 1 – Conversion constants (K_{conv}) CIP to SSIP for HI

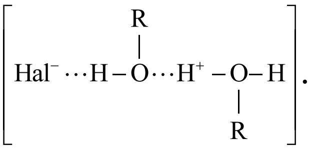
T, K	K_{conv} ,·mol/dm^3							
	methanol	ethanol	n-propanol	n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol
278.15	2.24	0.99	0.48	0.27	0.165	0.105	0.067	0.041
288.15	2.31	1.04	0.52	0.30	0.188	0.119	0.078	0.048
298.15	2.37	1.10	0.56	0.32	0.207	0.133	0.093	0.057
308.15	2.49	1.18	0.59	0.35	0.227	0.160	0.104	0.065
318.15	2.53	1.26	0.66	0.39	0.266	0.197	0.130	0.079
328.15	2.72	1.39	0.72	0.46	0.310	0.215	0.154	0.096

component of the ion-molecule interaction to the non-Coulomb ion-ion potential d_{ij} [23]. In the case of methanol and ethanol $\Delta_{\mathrm{im}}G^* < 0$, and for other *n*-alcohols $\Delta_{\mathrm{im}}G^* > 0$. The contribution of $\Delta_{\mathrm{im}}G^* < 0$ to $\Delta_{\mathrm{ij}}G^*$ seems to prevent the formation of ion pairs, while at $\Delta_{\mathrm{im}}G^* > 0$ it promotes their formation.

The exothermicity of the dissociation of CIP and SSIP into ions ($\Delta_{\mathrm{dis}}H° < 0$) is due to the excess of the exothermic contribution from the solvation of ions formed in solution compared to the energy required for the separation of charges in the ion pairs. In this case, despite the increase in the number of particles due to the formation of two ions from one IP, the entropy of the system decreases due to the decrease in mobility and polarization of the solvent molecules during the formation of the solvation shells of ions.

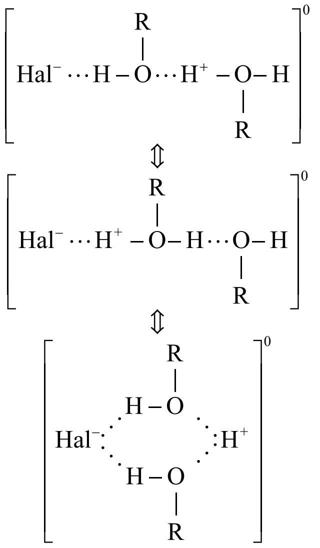
The negative sign of the change $\Delta_{\mathrm{conv}}S°$ indicates, apparently, the ordering of the structure during the conversion of CIP to SSIP, which is due to the strong coordinating effect of ROH_2^+ cations and $(ROH)_2H^+$ cations. The latter is explained by additional solvation with energy release ($\Delta_{\mathrm{conv}}H° < 0$). However, the sign of $\Delta_{\mathrm{conv}}G°$, except for methanol and ethanol, is determined by the entropic component, which indicates a structural rearrangement in the conversion process of CIP to SSIP under the influence of the solvent. Since in the process of structural rearrangement in all alcohols the proton can form no more than two bonds as a coordinating center, $\Delta_{\mathrm{conv}}H°$ will vary depending on the alcohol and the halide-ion. The same electron configuration and slight differences in anion size have little effect on $\Delta_{\mathrm{conv}}H°$. As the radius of the anion increases, the exothermicity of $\Delta_{\mathrm{conv}}H°$ decreases slightly.

The increase in exothermicity $\Delta_{\mathrm{conv}}H°$ and $\Delta_{\mathrm{conv}}S°$ in the series of *n*-alcohols is more significant: $\Delta_{\mathrm{conv}}H° \approx 2$ times, and $\Delta_{\mathrm{conv}}S° \approx 3.5$ times. The latter is associated with an increase in the electron-donating ability of alcohol molecules with the growth of the alkyl group. The enthalpic component ($\Delta_{\mathrm{conv}}H°$) in all alcohols promotes, and the entropic component ($-T\Delta_{\mathrm{conv}}S°$) hinders conversion. The change in the entropic component indicates that the ordering in the system increases as the alkyl group of the alcohol increases and as the temperature increases. This effect of solvent and temperature can be attributed to the stability of both types of IPs. Their dissociation depends on those factors that affect ion-molecule and ion-ion interactions. The drop in relative permittivity contributes to the ion-ion interaction, i.e., the stability of the IP. The increase in the size of the alkyl radical sterically prevents solvation, thus, the above factors as if promote the formation of an IP. It seems that the energy of attraction between oppositely charged ROH_2^+ ions , (ROH) $_2H^+$ and Hal^- is largely influenced by their specific structure and solvation [24]. ROH_2^+ cations and $(ROH)_2H^+$ are solvated negatively, indicating that the solvent molecules easily exchange the primary solvate shell [24]. The dynamic instability of these cations is due to the internal features of their structure and the of a proton presence in their composition as very reactive particle. The presence of "free" solvent molecules in hydroxyl-containing solvents [24, 25] causes negative solvation, which is one of the reasons for the anomalous proton mobility in such solvents. It can be assumed that not only the "free" solvent molecules, but also the anions influence the stability of the above cations. Under certain conditions, the latter can exchange with the molecules of the primary solvate shell of the proton, i.e., participate in the re-solvation of the negatively solvated Zundel cation as the most stable proton particle in the solution [24, 25]. When one solvent (alcohol) molecule is replaced with a Hal^- anion in the primary solvation shell of the proton, a CIP is formed: $ROH_2^+\ldots Hal^-$. The factors listed above will contribute to the stability of such a particle. SSIP formation can be viewed as the addition of Hal^- to the Zundel cation:



$$\left[\mathrm{Hal^-\cdots H-\overset{\overset{\displaystyle R}{|}}{O}\cdots H^+-\underset{\underset{\displaystyle R}{|}}{O}-H}\right].$$

We hypothesize that with an appropriate value of relative permittivity and dynamic mobility of solvent molecules and under the influence of external conditions (thermal motion of molecules, external environment of the solvate) the given structure will undergo a transformation resulting in the formation of a more stable structure:



(8)

For some time it will behave as a kinetically stable formation, the stability of which depends on the factors mentioned above. In addition to the conversion of CIPs to SSIPs, ionic pairs can undergo dissociation into free ions. The concentration of the latter is also determined by many factors and is quantitatively described, like the concentration of IP, by the usual ionogen total ionization process constant [2]. Conducting particles are formed as a result of IP dissociation.

The K_{conv} CIP in SSIP values we calculated were used to estimate the ratio of CIP and SSIP concentrations in alcoholic solutions of halogenated hydrocarbons at 278.15–328.15 K. From the analysis of the data obtained on the concentrations of CIP and SSIP the following regularities were established:

1.The concentration of CIP (SSIP) in alcohol solutions depends on the temperature, the length of the alkyl radical of the alcohol, and the radius of the Hal^- anion.

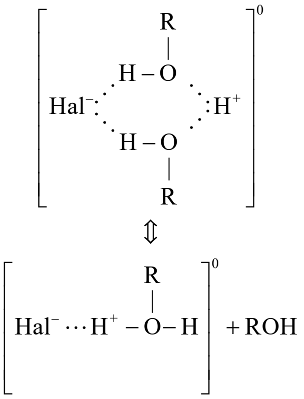
2. In methanol, SSIPs are predominant among IPs, in ethanol the concentration of SSIPs and SSIPs is approximately the same, and in other alcohols, SSIPs predominate (Table 5). The concentration of CIPs increases from methanol to *n*-octanol from 30 to 95 %, respectively, as the alkyl radical of the alcohol increases.

3. The ratio of enthalpic ($\Delta_{\text{conv}}H°$) and entropic ($-T\Delta_{\text{conv}}S°$) factors in methanol and ethanol ensures the spontaneous conversion of the CIP to SSIP, while in other alcohols there is deconversion. The latter is largely due to a decrease in the relative permittivity in the series of alcohols (from 32.6 to 9.7), which increases the attraction between oppositely charged ions and enhances their association.

The formation of IPs and the increase in their stability is also influenced by the solvatability of the ions. ROH_2^+ cations and $(ROH)_2H^+$ are negatively solvated, and their negative solvation increases as the alkyl group of the alcohol increases [3,4]. The latter indicates a weaker proton retention of the solvent molecule. Among Cl^- and Br^- -ions (both solvated positively in alcohols), the most solvated is Cl^- , which contributes to SSIP stabilization and gives a lower K_{conv} value for the smaller anion. As the radius of the anion increases, the translational motion of the alcohol molecules near the ion will increase, which leads to an increase in K_{conv}. The strengthening of the Coulomb interaction between the counterions in the SSIP under the influence of the solvent will certainly lead to the reorganization of the solvent near the IP, i.e., the Hal^- accession product to the Zundel cation. The resulting SSIP can dissociate into Hal^- ions and $(ROH)_2H^+$ (or ROH_2^+).

This process is facilitated by high relative permittivity and solvateability of the ions.

When the dielectric constant of the solvent is low, the SSIP can turn into a CIP:



$$\left[\begin{array}{c} R \\ | \\ H-O \\ Hal^-{:} \qquad {:}H^+ \\ H-O \\ | \\ R \end{array}\right]^0 \Updownarrow \left[Hal^- \cdots H^+ - \overset{\overset{R}{|}}{O} - H \right]^0 + ROH \qquad (9)$$

Thus, as a result of deconversion (conversion of RIPs to CIPs), CIPs predominate in higher *n*-alcohols.

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