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THERMODYNAMICS OF ION PAIR CONVERSION IN ALCOHOL SOLUTIONS OF HYDROGEN CHLORIDE

The thermodynamic quantities of the dissociation stages of contact ion pairs (CIP) and solvent-separated ion pairs (SSIP) into ions, conversion of CIP into SSIP of the ionization process of HCl in *n*-alcohols from methyl to *n*-octyl at 278.15 – 328.15 K, i.e. in non-aqueous solvents that are most frequently used in chemical research and in chemical technology have been calculated. The proton and chloride ion forming HCl are modeled in a comparative study of the solvation process and the molecular mechanism of acid ionization in various solvents, which emphasizes the relevance of this study, in which the influence of the nature of the solvent, hydrogen chloride ions and temperature on the above thermodynamic quantities are considered. The calculation of the dissociation constants of CIP was carried out according to Ebeling's equation, which takes into account the short-range repulsive forces between the ions in the ion pair and the dispersion interactions between the solvent molecules. The dissociation constants and thermodynamic quantities of SSIPs have been calculated by the Schwartz method, which evaluates the physical and chemical parameters of the solvent (besides the dielectric permittivity also the free volume of the solvent molecules, isothermal compressibility, etc.) that significantly affect the properties of ion pairs. The main conclusions drawn from our analysis of the array of thermodynamic data on the ionization stages of HCl in *n*-alcohols from methyl to *n*-octyl: (a) in methanol the predominant among the ion pairs are SSIPs, in ethanol the concentration of CIPs and SSIPs is approximately the same, and in other alcohols, the CIPs predominate; b) the concentration of CIPs increases with increasing alkyl radical of the alcohol when passing from methanol to *n*-octanol respectively from 30% to 95%; c) ratio of enthalpic ($\Delta_{conv}H°$) and entropic ($-T\Delta_{conv}S°$) factors in methanol and ethanol ensures spontaneous conversion of CIP to SSIP; d) in alcohols from *n*-propyl to *n*-octyl values and sign $\Delta G°$ for the stages of dissociation of CIP and SSIP into ions and conversion of CIP to SSIP are determined by the entropic term ($-T\Delta S°$), which leads to deconversion of ion pairs, i.e., the conversion of SSIPs into CIPs.

Keywords: ion pairs; proton; conversion; hydrogen chloride; primary alcohols; acids ionization.

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ТЕРМОДИНАМІКА КОНВЕРСІЇ ІОННИХ ПАР У СПИРТОВИХ РОЗЧИНАХ ХЛОРОВОДНЮ

Проведено розрахунок термодинамічних характеристик стадій дисоціації контактних іонних пар (КІП) та розділених розчинником іонних пар (РІП) на іони, конверсії КІП у РІП процесу іонізації HCl в *н*-спиртах від метилового до *н*-октилового при 278,15 – 328,15 К , тобто у неводних розчинниках, які найчастіше використовуються при хімічних дослідженнях та у хімічній технології. Протон та хлорид-іон, що утворюють HCl, є модельними при порівняльному дослідженні процесу сольватації та молекулярного механізму іонізації кислот у різних розчинниках, що наголошує на актуальності даного дослідження, в якому розглянуто вплив природи розчинника, іонів хлороводню та температури на зазначені вище термодинамічні характеристики. Розрахунок констант дисоціації КІП проводили за рівнянням Ебелінга, що враховує короткодіючі сили відштовхування між іонами в іонній парі та дисперсійні взаємодії між молекулами розчинника. Константи та термодинамічні характеристики дисоціації РІП обчислювали за методикою Шварца, в якій враховуються фізико-хімічні параметри розчинника (крім діелектричної проникності також вільний об'єм молекул розчинника, ізотермічна стисливість та ін.), що істотно впливають на властивості іонних пар. Основні висновки, зроблені на підставі аналізу отриманого нами масиву термодинамічних даних щодо стадій іонізації HCl в *н*-спиртах від метилового до *н*-октилового: а) в метанолі серед іонних пар переважають РІП, в етанолі концентрація КІП і РІП приблизно однакова, а в інших спиртах переважають КІП; б) концентрація КІП зі зростанням алкільного радикала спирту збільшується при переході від метанолу до *н*-октанолу відповідно від 30 до 95%; в) співвідношення ентальпійного ($\Delta_{конв}H°$) та ентропійного ($-T\Delta_{конв}S°$) факторів у метанолі та етанолі сприяє самочинній конверсії КІП у РІП; г) у спиртах від *н*-пропілового до *н*-октилового значення та знак ΔG° для стадій дисоціації КІП і РІП на іони та конверсії КІП у РІП визначаються ентропійною складовою ($-T\Delta S°$), що призводить до деконверсії іонних пар, тобто перетворення РІП на КІП.

Ключові слова: іонні пари; протон; конверсія; хлороводень; *н*-спирти; іонізація кислот.

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ТЕРМОДИНАМИКА КОНВЕРСИИ ИОННЫХ ПАР В СПИРТОВЫХ РАСТВОРАХ ХЛОРОВОДОРОДА

Проведен расчет термодинамических характеристик стадий диссоциации контактных ионных пар (КИП) и разделенных растворителем ионных пар (РИП) на ионы, конверсии КИП в РИП процесса ионизации HCl в *н*-спиртах от метилового до *н*-октилового при 278,15 – 328,15 K, т.е. в неводных растворителях, которые наиболее часто используются при химических исследованиях и в химической технологии. Протон и хлорид-ион, образующие HCl, являются модельными при сравнительном исследовании процесса сольватации и молекулярного механизма ионизации кислот в различных растворителях, что подчеркивает актуальность данного исследования, в котором рассмотрено влияние природы растворителя, ионов хлороводорода и температуры на указанные выше термодинамические характеристики. Расчет констант диссоциации КИП проводили по уравнению Эбелинга, учитывающее короткодействующие силы отталкивания между ионами в ионной паре и дисперсионные взаимодействия между молекулами растворителя. Константы и термодинамические характеристики диссоциации РИП вычисляли по методике Шварца, в которой учитываются физико-химические параметры растворителя (кроме диэлектрической проницаемости также свободный объем молекул растворителя, изотермическая сжимаемость и др.), существенно влияющих на свойства ионных пар. Основные выводы, сделанные на основании анализа полученного нами массива термодинамических данных по стадиям ионизации HCl в *н*-спиртах от метилового до *н*-октилового: а) в метаноле преобладающими среди ионных пар являются РИП, в этаноле концентрация КИП и РИП примерно одинакова, а в остальных спиртах преобладают КИП; б) концентрация КИП с ростом алкильного радикала спирта увеличивается при переходе от метанола к *н*-октанолу соответственно от 30 до 95 % ; в) соотношение энтальпийного ($\Delta_{конв}H°$) и энтропийного ($-T\Delta_{конв}S°$) факторов в метаноле и этаноле способствует самопроизвольной конверсии КИП в РИП; г) в спиртах от *н*-пропилового до *н*-октилового значения и знак $\Delta G°$ для стадий диссоциации КИП и РИП на ионы и конверсии КИП в РИП определяются энтропийной составляющей ($-T\Delta S°$), что приводит к деконверсии ионных пар, т.е. превращению РИП в КИП.

Ключевые слова: ионные пары; протон; конверсия; хлороводород; *н*-спирты; ионизация кислот.

Introduction. Ionization of acids in various solvents, in particular in protic ones, belongs to the fundamental processes of physical chemistry that have been attracting the attention of researchers for many decades. The molecular mechanism of acid ionization, the formation of stable proton and ionic pair (IP) states is particularly interesting in this respect, which is very important for understanding elementary chemical processes in non-aqueous acid solutions, in biological processes, etc.

Izmaylov [1] proposed the general scheme of the acids ionization process. Earlier [2] we considered a multi-step process of HCl ionization in *n*-alcohols from methyl to *n*-octyl. Using experimental and calculated equilibrium constants we calculated [2] equilibrium constants for unknown stages of this multistage process. Quantitative quantities of some equilibrium processes were discussed by us earlier [3 – 5]. However, the equilibrium conversion of CIP to SSIP in scientific literature is insufficiently described from our point of view. Practically there are no experimental data on the conversion constants of CIP to SSIP for acids in non-aqueous solvents, which, in our opinion, is related to the problem of choosing the primary simplest stable particle characterizing the proton state in solution and, consequently, the identification of the ion pair containing the proton by various experimental methods.

As is known, an electrolyte solution is an equilibrium mixture of free ions and ionic pairs. In contrast to molecules, ion pairs are stabilized due to weaker interactions and, as a consequence, the distance between the particles in them is larger compared to molecules [6]. Using various experimental and theoretical methods [6], the existence of two different types of ion pairs, CIP and SSIP has been proved.

Contact ion pairs have a single primary solvate shell and represent an electric dipole [7] (Fig. 1a).

In solvent-separated ion pairs, both ions have their own primary solvate shells, but these shells partially overlap [7] (Fig. 1b).

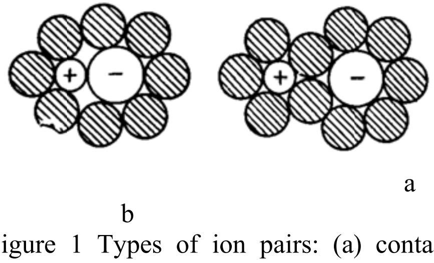


Figure 1 Types of ion pairs: (a) contact ion pair (CIP); (b) solvent-separated ion pair (SSIP)

The most commonly used experimental method to characterise ionic associates is infrared and Raman spectroscopy [6]. The anion vibrational frequency is “shifted” during the formation of ion pairs and other associates and the degree of shift gives information about the nature of the ion pair varieties. However, the study of ion pairs involving halide ions is difficult by these methods. NMR spectroscopy is also inefficient because the association/dissociation equilibria are rather fast on the NMR time scale. As a result, time-averaged cation and/or anion signals are obtained.

On the other hand, the proton and chloride ion are among the ions used to test model theories of solvation. Thus, in [8 – 10] we analyzed and established the type of solvation of the Cl^--ion (positive or negative) in formamide, N-methylformamide, N,N-dimethylformamide, water, and ethylene glycol at different temperatures and pressures. Therefore, in view of the lack of effective experimental methods, rigorous theoretical approaches should be used to describe the physicochemical properties of ion pairs involving them, in our opinion.

The choice of *n*-alcohols from methanol to *n*-octanol as solvents, which have the same chemical nature and different physicochemical quantities due to different contributions from H-bonding and dispersion interactions, allows us to predict that as the alcohol alkyl group length increases, more and more ions in solution will be in the form of IP. The structure and stability of ion pairs is a function of the structural quantities of the solvent and the ions. In the case of ionogens, the IP can be considered an intermediate between ions and ionogen molecules.

The first attempt to calculate the thermodynamic quantities of conversion stage of CIP to SSIP was performed by us [8] for HCl in *n*-alcohols from methanol to *n*-octanol at 278.15 – 328.15 K using data on the equilibrium constants of the dissociation stages of CIP in SSIP to ions. The dissociation constants of CIP and SSIP into ions in [11] were calculated according to Fuoss's equation [12]. However, inter-ion interactions in electrolyte solutions cannot be reduced to electrostatic interactions alone [13]. Non-Coulomb interactions between ions in protic solvents are also active, and their consideration is fraught with difficulties in taking into account the discrete structure of the solvent and the strong ion-molecular interactions at short distances. In addition, in the Fuoss model [12], the solvent is characterized only by the dielectric permittivity.

The mechanism of formation and structure of IPs in protic solvents with proton participation undoubtedly differs from that for ordinary ions. The inter-ion and ion-molecular interactions of the proton are due to its small size and specific behavior [14]. In contrast to the usual cations the proton has no electrons near the nucleus but has a significant charge density. As a result of its strong polarizing effect on the solvent molecules in solution, the proton exists exclusively in the form of solvates [14]. The specificity of the proton behavior in liquid is largely related to the molecular structure of the solvent of the solvent [13]. The state of the proton in protic solvents has remained debatable to date. It is known that in protic solvents the proton forms charged clusters of the composition HM_n^+ (M is a molecule of the solvent). The simplest of them are the products of primary proton solvation at $n = 1{,}2$ – the well-known lionium MH^+ and Zundel M_2H^+ cations. For many decades, in model problems of physical chemistry the simplest in composition lionium ion (MH^+) has been considered as a specific solvate. However, a number of works by Yukhnevich et al. [15] rather convincingly argue that the most stable cluster is the Zundel cation, and lionium ion is formed only in concentrated solutions at an equimolar ratio of H^+ ions and solvent molecules. The lionium ion is a component of the Zundel ($n = 2$) and Eigen ($n = 4$)

cations. This situation raises many questions regarding the state of the proton and the transformation of its indicated clusters with increasing temperature. There is no unanimity of opinion concerning the composition of clusters also among the authors [16, 17] who are engaged in molecular dynamic modeling of proton-containing solutions on the basis of protic solvents.

The CIP in alcoholic solutions of hydrogen halides can be represented as a neutral particle consisting of a lionium ion (alkoxonium) and a halide ion: $(ROH)_2H^+\ldots Hal^-$. Such representation of CIP is in agreement with the generally accepted one [18, 19]. The H-bond in such formation is asymmetrical. The electron cloud density is shifted towards halide-ion [19]. SSIP can be considered as a formation consisting of a Zundel cation and a H-bonded halide ion: $(ROH)_2H^+\ldots Hal^-$.

In connection with the above we used Ebeling equation [20] (1) to calculate the dissociation constants of SSIP:

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

In equation (1) N_{A} is Avogadro's constant; For $MH^+_{\text{solv}}Cl^-_{\text{solv}}$ CIP the parameter a was taken equal to the sum of the crystallographic radius of the Cl^- ion and the radius of the solvent molecule; e is the electron charge in the parameter $b = e^2 / a\varepsilon kT$; ε is the dielectric permittivity (DP) of the solvent; is the Boltzmann constant; T is temperature, K. For SSIP $MH^+_{\text{solv}}||Cl^-_{\text{solv}}$, three radii of solvent molecule $a = r_{Cl^-} + 3r_M$ were added to the crystallographic radius of Cl^--ion.

According to [21], 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.

The thermodynamic quantities (TDQ) ($\Delta_{\text{dis}}G°$, $\Delta_{\text{dis}}H°$, $\Delta_{\text{dis}}S°$) of contact ion pairs were determined from data on dissociation constants of CIPs by equations (2) – (5):

$$\Delta_{\text{dis}}G^{\circ} = -RT \ln K_{\text{dis}} \qquad (2)$$

$$\Delta_{\text{dis}}G^{\circ} = \Delta_{\text{dis}}H^{\circ} - T\Delta_{\text{dis}}S^{\circ} \qquad (3)$$

$$\Delta_{\text{dis}}S^{\circ}_{\text{CIP}} = -\left(\frac{\partial \Delta_{\text{dis}}G^{\circ}_{\text{CIP}}}{\partial T} \right) = -A_1 - 2A_2T \qquad (4)$$

$$\Delta_{\text{dis}}H^{\circ}_{\text{CIP}} = \Delta_{\text{dis}}G^{\circ}_{\text{CIP}} + T\Delta_{\text{dis}}S^{\circ}_{\text{CIP}} \qquad (5)$$

Calculation of $K_{\text{dis}}^{\text{SSIP}}$ was performed according to the Schwartz method [22] using equation (6):

$$-\ln K_{\text{dis}}^{\text{SSIP}} = \left[\left(\frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon a R T} \right) \cdot \left(1 + \frac{\partial \ln \varepsilon}{\partial \ln T} \right) + \left(\frac{1}{2} + \frac{\partial \ln V_f}{\partial \ln T} \right) \right] - \left[\left(\frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon a R} \right) \cdot \left(\frac{\partial \ln \varepsilon}{\partial T} \right) \right] \qquad (6)$$

where ε is the dielectric constant of vacuum; R is the molar gas constant; for the SSIP $MH^+_{\text{solv}}||Cl^-_{\text{solv}}$ the three radii of the solvent molecule $a = r_{Cl^-} + 3r_M$ were added to the crystallographic radius of the Cl^- ion.

In equation (6), the first term is equal to $\Delta_{\text{dis}}H^{\circ}_{\text{SSIP}} / RT$, the second one is $\Delta_{\text{dis}}S^{\circ}_{\text{SSIP}} / R$.

The dielectric permittivity of alcohols is taken from [23]. The radius of the alcohol molecules was calculated from the solvent density data given in the monograph [24]. The free volume (V_f) was calculated by the Prigozhin formula [25]:

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

where β_T is the isothermal compressibility, α_p is the thermal expansion.

Results

The results of calculations using equations (1-6) of the TDQ dissociation of CIP and SSIP are given in Table 1 and Table 2.

Table 1 - Thermodynamic characteristics of the HCl CIP dissociation process in *n*-alcohols

T, K	$\Delta_{\text{dis}}G$, kJ/mol							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	5.82	8.54	8.34	12.1	13.6	15.4	16.6	18.4
288.15	6.28	9.14	9.10	12.9	14.6	16.5	17.8	19.9
298.15	6.77	9.77	10.1	13.7	15.6	17.7	19.3	21.6
308.15	7.29	10.5	11.0	14.9	16.8	19.2	20.9	23.5
318.15	7.96	11.2	12.0	16.1	18.1	20.2	22.8	25.5
328.15	8.40	11.9	13.2	17.0	19.5	22.5	24.8	27.7
T, K	$\Delta_{\text{dis}}H$, kJ/mol							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	-7.31	-8.36	-7.57	-10.7	-11.2	-9.91	-15.3	-21.7
288.15	-7.96	-9.17	-9.57	-12.9	-14.6	-15.17	-21.0	-26.5
298.15	-8.62	-10.0	-12.1	-15.3	-18.1	-20.5	-26.8	-31.4
308.15	-9.30	-10.8	-13.6	-17.3	-21.6	-26.0	-32.9	-36.5
318.15	-9.87	-11.7	-15.7	-19.6	-25.2	-32.4	-39.1	-41.8
328.15	-10.7	-12.6	-17.9	-22.2	-29.1	-37.8	-45.6	-47.2

Continued Table 1

T, K	$\Delta_{dis}S$, J/(K·mol)							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	-47.2	-60.8	-63.9	-82.1	-89.1	-91.0	-114.6	-144.3
288.15	-49.4	-63.6	-70.7	-89.6	-100.9	-109.6	-134.6	-161.1
298.15	-51.6	-66.4	-77.5	-97.1	-112.7	-128.1	-154.6	-177.9
308.15	-53.9	-69.1	-84.3	-104.6	-124.5	-146.7	-174.6	-194.7
318.15	-56.1	-71.9	-91.0	-112.1	-136.3	-165.3	-194.6	-211.5
328.15	-58.3	-74.7	-97.8	-119.6	-148.0	-183.9	-214.6	-228.3

Table 2 -Thermodynamic characteristics of the CIP HCl dissociation process in *n*-alcohols

T, K	$\Delta_{dis}G$, kJ/mol							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	7.57	8.37	8.34	8.82	9.17	9.84	10.0	10.5
288.15	8.17	9.10	9.10	9.74	10.3	11.1	11.4	12.1
298.15	8.81	9.90	10.1	10.7	11.4	12.5	13.1	13.9
308.15	9.51	10.8	11.0	12.0	12.8	14.1	14.9	15.9
318.15	10.3	11.7	12.0	13.4	14.3	15.5	16.9	18.2
328.15	11.0	12.6	13.2	14.7	16.0	17.9	19.3	20.7

Continue Table 2

T, K	$\Delta_{dis}H$, kJ/mol							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	0.78	-0.14	-1.73	-3.61	-5.21	-6.65	-9.18	-10.7
288.15	0.73	-0.26	-1.95	-3.98	-5.68	-7.28	-10.1	-11.9
298.15	0.67	-0.39	-2.20	-4.29	-6.25	-8.03	-11.1	-13.1
308.15	0.60	-0.54	-2.48	-4.93	-6.91	-8.91	-12.3	-14.5
318.15	0.48	-0.71	-2.80	-5.52	-7.67	-9.49	-13.7	-16.0
328.15	0.44	-0.90	-3.15	-5.94	-8.53	-11.0	-15.2	-17.7

Continued Table 2

T, K	$\Delta_{dis}S$, J/(K·mol)							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	-24.4	-30.6	-36.2	-44.7	-51.7	-59.3	-69.1	-76.6
288.15	-25.8	-32.5	-38.5	-47.7	-55.3	-63.7	-74.6	-83.3
298.15	-27.3	-34.5	-41.1	-50.4	-59.3	-68.7	-81.0	-90.6
308.15	-28.9	-36.6	-43.8	-55.1	-64.0	-74.5	-88.2	-98.7
318.15	-30.9	-38.9	-46.7	-59.5	-69.2	-78.6	-96.2	-107.5
328.15	-32.3	-41.2	-49.9	-62.9	-74.9	-87.9	-105.1	-117.0

From the data on the dissociation constants of CIP and SSIP, the conversion constants (K_{conv}) [1] of CIP to SSIP were found by relation (8):

$$K_{conv} = \frac{K_{dis}(\text{CIP})}{K_{dis}(\text{SSIP})}. \tag{8}$$

Here Y = *G, H, S*. The values of $\Delta_{conv}G°$, $\Delta_{conv}H°$ and $\Delta_{conv}S°$ are shown in Table 3.

The TDQ conversion of CIP to SSIP was calculated using expression (9) derived from the thermodynamic cycle:

(8)

$$\Delta_{conv}Y° = \Delta_{dis}Y°\ (\text{CIP}) - \Delta_{dis}Y°\ (\text{SSIP}) \tag{9}$$

From the analysis of the data obtained on the TDQs of the stages of CIP dissociation, SSIP dissociation and conversion of CIP to SSIP of the multistage process of HCl ionization in *n*-alcohols from methanol to *n*-

octanol at 278.15 – 328.15 K [1] the following regularities were established:

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

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

3. Values of $\Delta_{dis}H°$(CIP), $\Delta_{dis}H°$(SSIP), $\Delta_{conv}H°$, $\Delta_{dis}S°$(CIP), $\Delta_{dis}S°$(SSIP), $\Delta_{conv}S°$ are negative except values of $\Delta_{dis}H°$(SSIP) in methanol. As the alkyl group length of *n*-alcohol increases, the enthalpy characteristics of the above processes become more exothermic

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 $\Delta G° < 0$ (methanol, ethanol). For these cases, the magnitude and sign of $\Delta_{conv}G°$ are determined by the enthalpic component.

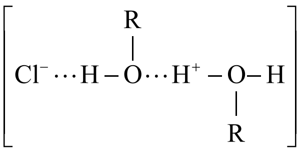
Discussion

The conversion process in methanol and partially in ethanol proceeds spontaneously. The differences in the signs of $\Delta_{conv}G°$ in methanol and ethanol and other *n*-alcohols are due to the opposite sign contribution from the short-acting component of the io*n*-molecule interaction to the non-Coulomb inter-ion potential d_{ij} [26]. In the case of methanol and ethanol $\Delta_{im}G^* < 0$, and for other *n*-alcohols $\Delta_{im}G^* > 0$. The contribution of $\Delta_{im}G^* < 0$ to $\Delta_{ij}G^*$ seems to prevent the formation of ion pairs, while at $\Delta_{im}G^* > 0$ it promotes their formation.

The exothermicity of the dissociation of CIP and SSIP into ions ($\Delta_{dis}H° < 0$) 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.

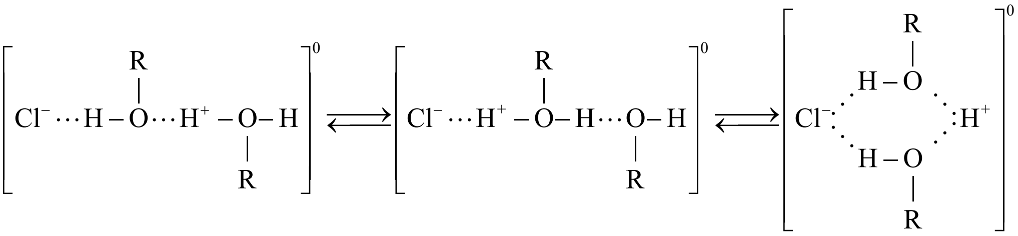
The negative sign of the change $\Delta_{conv}S°$ indicates, apparently, the ordering of the structure during the conversion of CIP to SSIP, which is due to the strong coordinating effect of ROH_2^+ cations and $(ROH)_2H^+$ cations. The latter is explained by additional solvation with energy release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

The increase in exothermicity $\Delta_{conv}H°$ and $\Delta_{conv}S°$ in the *n*-alcohols series will be more significant: $\Delta_{conv}H° \approx 2$ times, and $\Delta_{conv}S° \approx 3.5$ 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 ($\Delta_{conv}H°$) in all alcohols promotes, and the entropic component ($-T\Delta_{conv}S°$) prevents 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-molecular and inter-ion interactions. The drop in DP contributes to the inter-ion interaction lead to the stability of the IP. The increase in the size of the alkyl radical sterically prevents solvation, thus, the above factors as if contribute to the formation of IP. It seems that the energy of attraction between oppositely charged ROH_2^+ ions, $(ROH)_2H^+$ and Cl^- is largely influenced by their specificity of structure and solvation [14]. ROH_2^+ cations and $(ROH)_2H^+$ are solvated negatively, indicating that the solvent molecules easily exchange the primary solvate shell [14]. The dynamic instability of these cations is due to the internal features of their structure, the presence in their composition of a reactive particle – the proton. The presence of "free" solvent molecules in hydroxyl-containing solvents [14, 27] 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 [27]. When one solvent (alcohol) molecule is replaced in the primary solvation shell of a proton by a Cl^- anion, a CIP is formed: $ROH_2^+\cdots Cl^-$. The above factors will contribute to the stability of such a particle. SSIP formation can be viewed as an addition of Cl^- to the Zundel cation:



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

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



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, ion 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 [1]. Conducting particles are formed as a result of IP dissociation.

The values of K_{conv} CIP into SSIP calculated by equation (8) and presented in Table 3 were used to estimate the ratio of CIP and SSIP concentration in alcoholic solutions of HCl at 278.15 – 328.15 K (Table 5). From the analysis of the data obtained in Table 3 and Table 5, the following regularities were established:

1. The concentration of CIP (SSIP) in alcohol solutions depends on the temperature and the length of the alkyl radical of the alcohol.

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 4). 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 ($-T_{\text{conv}}\Delta S°$) 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 dielectric permittivity in the series of alcohols (from 32.6 to 9.7), which increases the attraction between oppositely charged ions and enhances their association.

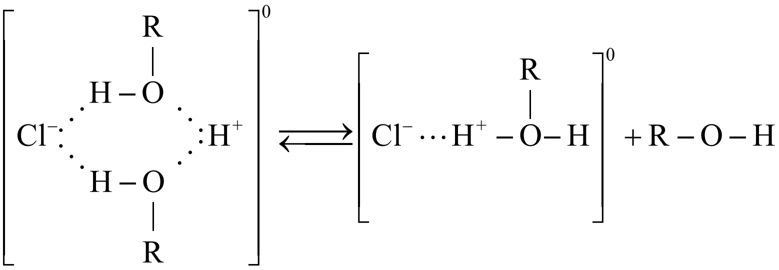
The formation of IPs and the increase in their stability is also influenced by the solvatability of the ions. ROH_2^+ and $(ROH)_2H^+$ cations are negatively solvated, and their negative solvation increases as the alkyl group of the alcohol increases [14]. The latter indicates a weaker proton retention of the solvent molecule. 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 product of the addition of Cl^- to the Zundel cation. The resulting SSIP can dissociate into Cl^--ions and $(ROH)_2H^+$ (or ROH_2^+).

Table 3 - Conversion constants (K_{conv}) CIP HCl to RIP

T, K	K_{conv} ,·mol/dm^3							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	2.13	0.93	0.45	0.24	0.147	0.090	0.058	0.034
288.15	2.20	0.98	0.50	0.27	0.173	0.105	0.069	0.039
298.15	2.28	1.05	0.54	0.30	0.184	0.123	0.082	0.045
308.15	2.38	1.08	0.57	0.32	0.210	0.131	0.096	0.052
318.15	2.42	1.21	0.64	0.36	0.238	0.169	0.108	0.063
328.15	2.59	1.29	0.69	0.43	0.277	0.179	0.133	0.077

This process will be facilitated by high DP and solvatability of the ions.

At low values of the dielectric constant of the solvent, the SSIP can turn into a CIP:



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

Table 4 - Mole fraction of CIP (f) HCl in n-alcohols; $f = 1/(1+K_{\text{conv}})$ [22]

T, K	f(CIP)							
	methanol	ethanol	n-propanol	n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol
278.15	0.3195	0.5181	0.6897	0.8065	0.8718	0.9174	0.9452	0.9671
288.15	0.3125	0.5051	0.6667	0.7874	0.8525	0.9050	0.9355	0.9625
298.15	0.3049	0.4878	0.6494	0.7692	0.8446	0.8905	0.9242	0.9569
308.15	0.2959	0.4808	0.6369	0.7576	0.8264	0.8842	0.9124	0.9506
318.15	0.2924	0.4525	0.6098	0.7353	0.8078	0.8554	0.9025	0.9407
328.15	0.2786	0.4367	0.5917	0.6993	0.7831	0.8482	0.8826	0.9285

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