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ION PAIR CONVERSION THERMODYNAMICS IN HYDROGEN BROMIDE ALCOHOL SOLUTIONS

The thermodynamic quantities of dissociation of contact and solvent-separated ion pairs into ions, conversion of contact ion pairs into solvent-separated ion pairs of HBr ionogen in *n*-alcohols from methyl to *n*-octyl have been calculated by the procedure we set forth earlier for the HCl – *n*-alcohol systems in the same solvents at 278.15–328.15 K. The following regularities were established in this work: a) positive values of $\Delta_{dis}G^o$ of contact and solvent-separated ion pairs increase with increasing temperature, the number of carbon atoms in the n-alcohol molecule, and decreasing radius of halide ion, and their sign and magnitude are determined by the entropic component ($-T\Delta_{dis}S^o$). In this case, the values of $\Delta_{dis}G^o$ of contact ion pairs exceed the same values for solvent-separated ion pairs; b) $\Delta_{conv}G^o$ values for HCl and HBr are also positive, except for $\Delta_{conv}G^o$ values in methanol at 278.15–328.15 K and HBr solutions at the same temperatures in ethanol. For these cases, by contrast, $\Delta_{dis}G^o(RIP) > \Delta_{dis}G^o(CIP)$ and $\Delta_{conv}G^o$ are negative. As the temperature and radius of the halide ion increase, $\Delta_{conv}G^o$ become more negative, and vice versa as the hydrocarbon radical increases; c) the concentration of contact ion pairs increases in the methanol-n-octanol series, decreases slightly with increasing temperature and anion radius, and changes within ~30 % (methanol) to 95 % (*n*-octanol) at 278.15 K. In methanol, solvent-separated ion pairs predominate; in ethanol, the concentration of both types of ion pairs is approximately the same; in other *n*-octanols, contact ion pairs predominate.

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

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ТЕРМОДИНАМІКА КОНВЕРСІЇ ІОННИХ ПАР У СПИРТОВИХ РОЗЧИНАХ БРОМОРОВОДНЮ

Проведено розрахунок термодинамічних характеристик дисоціації контактних і розділених розчинником іонних пар на іони, конверсії контактних іонних пар у розділені розчинником іонні пари іоногену HBr у *н*-спиртах від метилового до *н*-октилового за методикою, викладеною нами раніше для систем HCl – н-спирт у тих самих розчинниках за 278.15–328.15 К. У роботі встановлено закономірності: а) позитивні значення $\Delta_{дис}G^o$ 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 ($-T\Delta_{дис}S^o$). При цьому значення $\Delta_{дис}G^o$ контактних іонних пар перевищують ті самі величини для розділених розчинником іонних пар; б) значення $\Delta_{конв}G^o$ для HCl і HBr також позитивні, за винятком величин $\Delta_{конв}G^o$ у метанолі за 278.15–328.15 К і розчинів HBr за тих самих температур в етанолі. Для цих випадків, навпаки, $\Delta_{дис}G^o(РІП) > \Delta_{дис}G^o(КІП)$, а $\Delta_{конв}G^o$ – негативні. Зі зростанням температури та радіусу галогенід-іону $\Delta_{конв}G^o$ стають більш від'ємними, а зі зростанням вуглеводневого радикалу – навпаки; в) концентрація контактних іонних пар зростає в ряді метанол – *н*-октанол, незначно зменшується зі збільшенням температури й радіуса аніона та змінюється в межах від ~30 % (метанол) до 95 % (*н*-октанол) при 278.15 К. У метанолі переважають розділені розчинником іонні пари, в етанолі концентрація обох типів іонних пар приблизно однакова, в інших н-спиртах переважають контактні іонні пари.

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

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ТЕРМОДИНАМИКА КОНВЕРСИИ ИОННЫХ ПАР В СПИРТОВЫХ РАСТВОРАХ БРОМОРОВОДОРОДА

Проведен расчет термодинамических характеристик диссоциации контактных и разделенных растворителем ионных пар на ионы, конверсии контактных ионных пар в разделенные растворителем ионные пары ионогена HBr в *н*-спиртах от метилового до *н*-октилового при по методике, изложенной нами ранее для систем HCl – *н*-спирт в тех же растворителях при 278,15–328,15 К. В работе установлены закономерности: а) положительные значения $\Delta_{дис}G^o$ контактных и разделенных растворителем ионных пар возрастают при увеличении температуры, числа атомов углерода в молекуле н-спирта, уменьшении радиуса галогенид-иона, а их знак и величина определяются энтропийной составляющей ($-T\Delta_{дис}S^o$). При этом значения $\Delta_{дис}G^o$ контактных ионных пар превышают те же величины для разделенных растворителем ионных пар; б) значения $\Delta_{конв}G^o$ для HCl и HBr также положительны, за исключением величин $\Delta_{конв}G^o$ в метаноле при 278,15–328,15 К и растворов HBr при тех же температурах в этаноле. Для этих случаев, наоборот, $\Delta_{дис}G^o(РИП) > \Delta_{дис}G^o(КИП)$, а $\Delta_{конв}G^o$ – отрицательны. С ростом температуры и радиуса галогенид-иона $\Delta_{конв}G^o$ становятся более отрицательными, а с ростом углеводородного радикала – наоборот; в) концентрация контактных ионных пар возрастает в ряду метанол – *н*-октанол, незначительно уменьшается с увеличением температуры и радиуса аниона и изменяется в пределах от ~30 % (метанол) до 95 % (*н*-октанол) при 278,15 К. В метаноле преобладают разделенные растворителем ионные пары, в этаноле концентрация обоих типов ионных пар примерно одинакова, в остальных *н*-спиртах преобладают контактные ионные пары.

Ключевые слова: ионные пары, протон, конверсия, бромоводород, *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, and established a number of regularities [3–5]. Further in [6] 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, and of the HCl ionization process in *n*-alcohols from methyl to *n*-octyl at 278.15–328.15 K were calculated. 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.

This work is a continuation of systematic studies of the thermodynamics of ion-pair conversion in alcohol solutions of hydrogen halides.

Despite the same electron configuration, HBr differs from HCl, in particular, it has a longer bonding length, a lower (~ 2.5 times) enthalpy of formation, and better solubility in polar solvents. According to modern studies [7], the ionization constant of HBr in water is ~ 800 times greater than the ionization constant of HCl (pK_i(HBr) = - 8.8; pK_i(HCl) = - 5.9), so HCl and HBr are fully ionized into solvated ions in dilute aqueous solutions.

When passing to non-aqueous solvents, for example to n-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]. 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 [8]. 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 [8], 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 [8]. In this connection, the modern scientific literature favors theoretical approaches when studying the properties of ionic associates containing halide ions [9-12].

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 [13]. 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 [13]. The specifics of its behavior in liquid solutions are largely related to the molecular structure of the solvent [13]. 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, [14] 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 [6, 13].

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 [15, 16]. In this case, the H-bond in such a formation is asymmetric. The electron cloud density is shifted toward the Hal^- ion [16]. SSIP can be viewed as a formation consisting of a Zundel cation and a H-bonded halide ion: $(ROH)_2 H^+...Hal^-$.

Methods. The electrostatic and non-Coulomb interactions act between ions in protolytic solvents [17]. 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 [18] (1) to calculate CIP dissociation constants:

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

According to [19], 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 have calculated K_{dis}(SSIP) according to [20]:

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

where ε_0 is the dielectric constant of vacuum; R is the molar gas constant; for the SSIP $MH^+_{solv} || Br^-_{solv}$ the three radii of the solvent molecule ($a = r(Br^-) + 3r(S)$) were added to the crystallographic radius of the Br^- ion. In equation (6), the first term is equal to $\Delta_{dis}H°$(SSIP) / RT, the second one is $\Delta_{dis}S°$(SSIP) / R.

The dielectric permittivity of alcohols is taken from [21]. The radius of the alcohol molecules was calculated from the solvent density data given in the monograph [22]. The free volume (V_f) was calculated by the Prigozhin formula [23]:

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

where β_T is the isothermal compressibility, α_P is the thermal expansion. These values are also taken from the monograph [22].

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 relationship (3):

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

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

$$\Delta_{dis}G^{\circ}(IP) = -RT\ln K_{dis}(IP) \quad (4)$$

$$\Delta_{dis}S^{\circ}(IP) = -\left(\frac{\partial \Delta_{dis}G^{\circ}(IP)}{\partial T}\right) \quad (5)$$

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

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

$$_{conv}Y^o = {}_{dis}Y^o(CIP) - {}_{dis}Y^o(SSIP) \quad (7)$$

Here $Y = G, H, S$.

The values of $\Delta_{conv}H^o$ and $\Delta_{conv}S^o$ 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 HBr 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 $\Delta_{dis}G^o$(CIP) and $\Delta_{dis}G^o$(SSIP) (Tables 2 and 3) are positive for both HBr and HCl [8], increasing with increasing temperature and the number of carbon atoms in the n-alcohol molecule. In this case $\Delta_{dis}G^o$(CIP) > $\Delta_{dis}G^o$(SSIP).

2. The values of $\Delta_{conv}G^o$ for HCl [8] and HBr (Table 4) are also positive, except for the values of $\Delta_{conv}G^o$ in methanol at 278.15–328.15 K and HBr solutions at 298.15–328.15 K in ethanol. For these cases, $\Delta_{dis}G^o$(SSIP) > $\Delta_{dis}G^o$(CIP) and $\Delta_{conv}G^o$ are negative. As the temperature increases, $\Delta_{conv}G^o$ become more

exothermic, and vice versa as the hydrocarbon radical increases.

3. The values of $\Delta_{dis}H^o$(CIP), $\Delta_{dis}H^o$(SSIP), $\Delta_{conv}H^o$, $\Delta_{dis}S^o$(CIP), $\Delta_{dis}S^o$(SSIP), $\Delta_{conv}S^o$ of both ionogens are negative, except the values of $\Delta_{dis}H^o$(SSIP) in methanol ([8] and Table 4). 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^o for the dissociation stages of CIP and SSIP into ions and the conversion of CIP into SSIP are determined by the entropic component ($-T\Delta S^o$), except for those cases for which $\Delta G^o_{conv} < 0$ (methanol, ethanol) ([8] and Table 4). In these cases, the value and sign of $\Delta_{conv}G^o$ 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 $\Delta_{conv}G^o$ in methanol and ethanol and other n-alcohols are due to the opposite sign contribution from the short-acting component of the ion-molecule interaction to the non-Coulomb ion-ion potential d_{ij} [24]. 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 ($\Delta_{dis}H^o < 0$) 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 $\Delta_{conv}S^o$ 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 ($\Delta_{conv}H^o < 0$). However, the sign of $\Delta_{conv}G^o$, 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, $\Delta_{conv}H^o$ will vary depending on the alcohol and the halide-ion.

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

T, K	K_{conv}·mol/dm^3							
	methanol	ethanol	n-propanol	n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol
278.15	2.18	0.96	0.46	0.26	0.150	0.096	0.062	0.037
288.15	2.25	1.00	0.51	0.28	0.183	0.109	0.075	0.042
298.15	2.32	1.07	0.55	0.31	0.199	0.128	0.087	0.049
308.15	2.43	1.16	0.58	0.34	0.218	0.142	0.100	0.058
318.15	2.45	1.24	0.65	0.37	0.247	0.183	0.120	0.071
328.15	2.62	1.34	0.70	0.45	0.288	0.192	0.143	0.089

Table 2 – Thermodynamic quantities of the CIP dissociation process for HBr 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	5.71	8.42	10.0	11.9	13.5	15.2	16.4	18.1
288.15	6.17	9.02	10.7	12.8	14.4	16.3	17.6	19.6
298.15	6.66	9.65	11.5	13.5	15.4	17.5	19.1	21.3
308.15	7.17	10.3	12.3	14.7	16.6	18.9	20.6	23.1
318.15	7.83	11.0	13.1	15.9	17.9	19.9	22.4	25.1
328.15	8.27	11.8	14.1	16.8	19.3	22.2	24.4	27.2
T, K	$\Delta_{dis}H$, kJ/mol							
278.15	− 7.27	− 7.95	− 8.72	− 10.7	− 9.56	− 9.20	− 14.9	− 21.9
288.15	− 7.88	− 8.52	− 10.3	− 12.8	− 13.3	− 14.3	− 20.2	− 26.1
298.15	− 8.40	− 9.70	− 11.9	− 14.7	− 17.1	− 19.7	− 25.6	− 30.5
308.15	− 9.13	− 10.9	− 13.5	− 17.0	− 21.1	− 25.2	− 31.2	− 35.0
318.15	− 9.65	− 12.3	− 15.2	− 19.1	− 25.2	− 31.6	− 36.9	− 39.7
328.15	− 10.4	− 13.9	− 16.9	− 21.7	− 29.5	− 37.0	− 42.8	− 44.4
	$-T\Delta_{dis}S$, kJ/mol							
278.15	12.98	16.37	18.72	22.60	23.06	24.40	31.30	40.00
288.15	14.05	17.54	21.00	25.60	27.70	30.60	37.80	45.70
298.15	15.06	19.35	23.40	28.20	32.50	37.20	44.70	51.80
308.15	16.30	21.20	25.80	31.70	37.70	44.10	51.80	58.10
318.15	17.48	23.30	28.30	35.00	43.10	51.50	59.30	64.80
328.15	18.67	25.70	31.00	38.50	48.80	59.20	67.20	71.60

Table 3 – Thermodynamic quantities of the SSIP dissociation process for HBr 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	7.51	8.32	8.23	8.76	9.11	9.77	9.96	10.4
288.15	8.11	9.03	9.06	9.70	10.2	11.0	11.4	12.0
298.15	8.75	9.82	9.96	10.6	11.3	12.4	12.9	13.8
308.15	9.44	10.7	10.9	11.9	12.7	14.0	14.7	15.8
318.15	10.2	11.6	11.9	13.3	14.2	15.4	16.8	18.1
328.15	10.9	12.6	13.1	14.6	15.9	17.7	19.1	20.6
T, K	$\Delta_{dis}H$, kJ/mol							
278.15	0.81	− 0.08	− 1.65	− 3.51	− 5.10	− 6.53	− 9.04	− 10.6
288.15	0.79	− 0.19	− 1.87	− 3.88	− 5.56	− 7.15	− 9.93	− 11.7
298.15	0.73	− 0.32	− 2.12	− 4.18	− 6.12	− 7.89	− 11.0	− 12.9
308.15	0.66	− 0.46	− 2.39	− 4.81	− 6.78	− 8.75	− 12.2	− 14.3
318.15	0.55	− 0.63	− 2.70	− 5.40	− 7.53	− 9.34	− 13.5	− 15.8
328.15	0.50	− 0.81	− 3.05	− 5.81	− 8.38	− 10.8	− 15.0	− 17.4
	$-T\Delta_{dis}S$, kJ/mol							
278.15	6.70	8.40	9.88	12.27	14.21	16.30	19.00	21.00
288.15	7.32	9.22	10.93	13.58	15.76	18.15	21.33	23.70
298.15	8.02	10.14	12.08	14.78	17.42	20.29	23.90	26.70
308.15	8.78	11.16	13.29	16.71	19.48	22.75	26.90	30.10
318.15	9.65	12.23	14.60	18.70	21.73	24.74	30.30	33.90
328.15	10.40	13.41	16.15	20.41	24.28	28.50	34.10	38.00

The same electron configuration and slight differences in anion size have little effect on $\Delta_{conv}H^o$. As the radius of the anion increases, the exothermicity of $\Delta_{conv}H^o$ decreases slightly.

The increase in exothermicity $\Delta_{conv}H^o$ and $\Delta_{conv}S^o$ in the series of *n*-alcohols is more significant: $\Delta_{conv}H^o \approx 2$ times, and $\Delta_{conv}S^o \approx 3.5$ 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 ($\Delta_{conv}H^o$) in all alcohols promotes, and the entropic component ($-T\Delta_{conv}S^o$) hinders conversion. The change in the entropic component indicates that the ordering in the system increases as the alkyl gro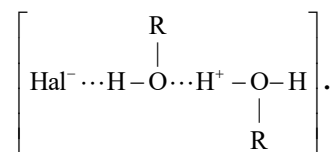up of the alcohol increases and as the temperature increases. This effect of solvent and temperature can be attributed to the stability of both types of IPs. Their dissociation depends on those factors that affect ion-molecule and ion-ion interactions. The drop in relative permittivity contributes to 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 [10]. ROH_2^+ cations and $(ROH)_2H^+$ are solvated negatively, indicating that the solvent molecules easily exchange the primary solvate shell [10]. The dynamic instability of these cations is due

Table 4 – Thermodynamic quantities of the process conversion CIP into SSIP for HBr in *n*-alcohols
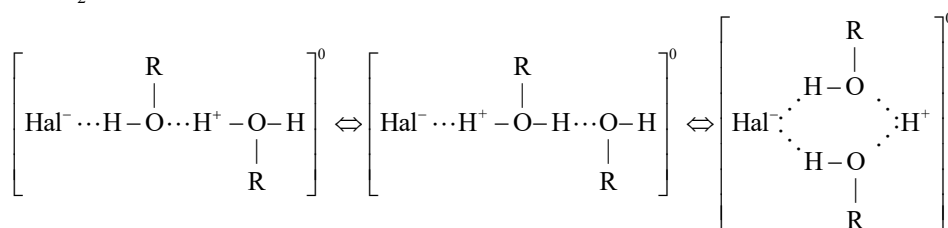
T, K	$\Delta_{conv}G$, kJ/mol							
	methanol	ethanol	*n*-propanol	*n*-butanol	*n*-pentanol	*n*-hexanol	*n*-heptanol	*n*-octanol
278.15	− 1.80	0.10	1.77	3.14	4.39	5.43	6.44	7.70
288.15	− 1.94	− 0.01	1.64	3.10	4.20	5.30	6.20	7.60
298.15	− 2.09	− 0.17	1.54	2.90	4.10	5.10	6.00	7.50
308.15	− 2.27	− 0.40	1.40	2.80	3.90	4.90	5.90	7.30
318.15	− 2.37	− 0.60	1.20	2.60	3.70	4.50	5.60	7.00
328.15	− 2.63	− 0.80	1.00	2.20	3.40	4.40	5.30	6.60
T, K	$\Delta_{conv}H$, kJ/mol							
278.15	− 8.08	− 7.87	− 7.07	− 7.19	− 4.46	− 2.67	− 5.86	− 11.3
288.15	− 8.67	− 8.33	− 8.43	− 8.92	− 7.74	− 7.15	− 10.3	− 14.4
298.15	− 9.13	− 9.38	− 9.78	− 10.5	− 11.0	− 11.8	− 14.6	− 17.6
308.15	− 9.79	− 10.2	− 11.1	− 12.2	− 14.3	− 16.5	− 19.0	− 20.7
318.15	− 10.2	− 11.7	− 12.5	− 13.7	− 17.7	− 22.3	− 23.4	− 23.9
328.15	− 10.9	− 13.1	− 13.9	− 15.9	− 21.1	− 26.2	− 27.8	− 27.0
	$-T\Delta_{conv}S$, kJ/mol							
278.15	6.28	7.97	8.84	10.33	8.85	8.10	12.30	19.00
288.15	6.73	8.32	10.07	12.02	11.94	12.45	16.50	22.00
298.15	7.04	9.21	11.32	13.40	15.10	16.90	20.60	25.10
308.15	7.52	9.80	12.50	15.00	18.20	21.40	24.90	28.00
318.15	7.83	11.10	13.70	16.30	21.40	26.80	29.00	30.90
328.15	8.27	12.30	14.90	18.10	24.50	30.60	33.10	33.60

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 [13, 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 [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:

$$\left[\begin{array}{c} R \\ | \\ Hal^- \cdots H - O \cdots H^+ - O - H \\ | \\ R \end{array}\right].$$

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:

$$\left[\begin{array}{c} R \\ | \\ Hal^- \cdots H - O \cdots H^+ - O - H \\ | \\ R \end{array}\right]^0 \Leftrightarrow \left[\begin{array}{c} R \\ | \\ Hal^- \cdots H^+ - O - H \cdots O - H \\ | \\ R \end{array}\right]^0 \Leftrightarrow \left[\begin{array}{c} R \\ | \\ H-O \\ Hal^- \qquad :H^+ \\ H-O \\ | \\ R \end{array}\right]^0$$

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 Kconv 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:

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.

1. 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.

2. The ratio of enthalpic ($\Delta_{conv}H^o$) and entropic ($-T\Delta_{conv}S^o$) factors in methanol and ethanol ensures the spontaneous conversion of the CIP to SSIP, while in other

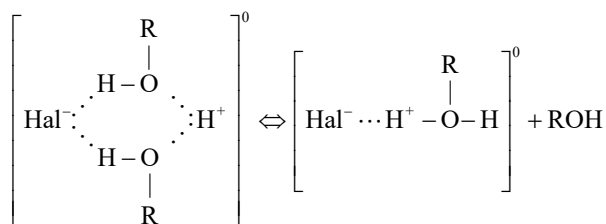Table 5 – Mole fraction of CIP (f) HBr in n-alcohols; $f = 1/(1 + K_{conv})$ [20]

T, K	f(CIP)							
	methanol	ethanol	n-propanol	n-butanol	n-pentanol	n-hexanol	n-heptanol	n-octanol
278.15	0.3145	0.5102	0.6849	0.7937	0.8696	0.9124	0.9416	0.9643
288.15	0.3077	0.5000	0.6623	0.7813	0.8453	0.9017	0.9302	0.9597
298.15	0.3012	0.4831	0.6452	0.7634	0.8340	0.8865	0.9200	0.9533
308.15	0.2915	0.4630	0.6329	0.7463	0.8210	0.8757	0.9091	0.9452
318.15	0.2899	0.4464	0.6061	0.7299	0.8019	0.8453	0.8929	0.9337
328.15	0.2762	0.4274	0.5882	0.6897	0.7764	0.8389	0.8749	0.9183

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.

3. 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 [13]. 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:

$$\left[\begin{array}{c} R \\ | \\ H-O \\ Hal^- \qquad :H^+ \\ H-O \\ | \\ R \end{array} \right]^0 \Leftrightarrow \left[Hal^- \cdots H^+ - O - H \atop \qquad\qquad | \atop \qquad\qquad R \right]^0 + ROH$$

Thus, as a result of deconversion (conversion of SSIPs to CIPs), CIPs prevail in higher n-alcohols (Table 5).

References

1. Булавин В. И., Вьюнник И. Н. Равновесия ионизации HCl в разбавленных спиртовых растворах. Укр. хим. журн. 2005. Том 71. № 2. С. 84–89.
2. Измайлов Н. А. Электрохимия растворов. Изд. 3-е, испр., М.: Химия. 1976. 488 с.
3. Булавін В. І., В'юник І. М., Берегова Н. П. Електрична провідність і асоціація хлороводню в ряді н-спиртів. Вісн. Львівськ. ун-ту. Сер. хім. 2002. Вип. 42. Ч. 1. С. 52–55.
4. Булавин В. И., Вьюнник И. Н., Береговая Н. П., Крамаренко А. В. Электрическая проводимость и ионизация бромоводорода в ряду н-спиртов. Вісн. Харьк. нац. ун-ту. 2006. № 731. Хімія. Вип. 14(37). С. 201–205.
5. Булавин В. И., Вьюнник И. Н., Береговая Н. П., Крамаренко А. В. Термодинамика ионизации галогеноводородов в н-спиртах. Вопр. химии и хим. технологии. 2007. № 3. с. 22–26.
6. Bulavin V. I., Vyunnik I. N., Kramarenko A. V. Rusinov A. I. Thermodynamics of ion pair conversion in alcohol solutions of hydrogen chloride. Bull. Nation. Technical Un-ty "KhPI". Series: Chemistry, Chem. Technology and Ecology. 2022. № 2(8)'2022. P. 3–10.
7. Trummal A., Lipping L., Kaljurand I, Koppel I. A., Leito I. Acidity of strong acids in water and dimethyl sulfoxide. J. Phys. Chem. A, 2016. V. 120. № 20. P. 3663–3669.
8. Шварц М. Ионы и ионные пары в органической химии. М.: Мир, 1975. 424 с.
9. Wick C.D. A comparison of sodium and hydrogen halides at the air-water interface. J. Chem. Phys. 2017. V. 147. № 16. P. 161703–8
10. Feng G., Chen M., Bi S., Goodwin Z. H. N., Postnikov E. B., Brilliantov N., Urbakh M., Kornyshev A. A. Free and bound states of ions in ionic liquids, conductivity, and underscreening paradox// Phys. Rev. X. 2019. № 2. P. 021024–22
11. Sin J-S. Effect of Bjerrum pairs on the electrostatic properties of an electrolyte solution near charged surfaces: a mean-field approach. Phys. Chem. Chem. Phys., 2021. V. 23. № 21. P. 12296–12308.
12. Artemov V., Ryzhov A., Ouerdane H., Stevenson K. J. Ionization difference between weak and strong electrolytes as perturbed by conductivity spectra analysis. J. Phys. Chem. B, 2023. V. 127. № 1. P. 261–268.
13. Булавин В. И., Вьюнник И. Н. Ближняя сольватация и подвижность ионов в предельно разбавленных спиртовых и водных растворах галогеноводородов. Укр. хим. журн., 2012. Том 78. № 8. С.82–91.
14. Юхневич Г. В., Тараканова Е. Г., Майоров В. Д., Либрович Н. Б. Структура сольватов протона и их колебательные спектры. Успехи химии, 1995. Том 64(10). С. 963–974
15. Walewski L., Forbert H., Marx D. Aggregation-induced chemical reactions: acid dissociation in growing water clusters. J. Phys. Chem. Lett., 2011. V. 2. P. 3069–3074
16. Fulton J. L., Balasubramanian M. Structure of hydronium (H_3O^+)/Chloride (Cl^-) contact ion pairs in aqueous hydrochloric acid solutions: a Zundel-like local configuration. J. Am. Chem. Soc. 2010. V. 132. P. 12597–12604.
17. Юхновский И. Р., Курыляк И. И. Электролиты. К.: Наукова думка, 1988. 168 с.
18. Ebeling W., Grigo M. An analytical calculation of the equation of state and the critical point in a dense classical fluid of charged hard spheres. Ann. Phys. 1980. B. 37, H. 1. S. 21–30.
19. Krienke H., Barthel J., Holovko M. et al. Osmotic and activity coefficients associated electrolytes over large concentration ranges from chemical model calculations. J. Mol. Liq., 2000. V. 87. P. 191–216.
20. Шварц М. Анионная полимеризация. Карбанионы, живущие полимеры и процессы с переносом электрона. М.: Мир, 1971. 642 с.
21. Булавин В. И. Физико-химические свойства предельных одноатомных спиртов нормального строения. Вестн. Харьк. гос. политехн. ун-та. Сб. научн. трудов. Вып. 26. с. 37–44. Харьков ХГПУ, 1999
22. Хасаншин Т. С.: Теплофизические свойства предельных одноатомных спиртов при атмосферном давлении. Минск.: Наука і тэхніка, 1992. 256 с.
23. Пригожин И., Дефей Р. Химическая термодинамика. М. , Наука, 1966. 501 с.
24. Булавин В. И., Вьюнник И. Н. Межионные взаимодействия в спиртовых растворах электролитов. Ж. физ. химии, 2008. Т. 82, № 9. С. 1681–1684.

25. Hills G. J., Ovenden P. J., Whitehouse D. R. Proton migration in aqueous solutions. Disc. Faraday Soc., 1965. V. 39. P. 207–215.

References (transliterated)

1. Bulavin V. I., V'yunnik I. N. Ravnovesiya ionizatsii HCl v razbavlennykh spirtovykh rastvorakh. Ukr. khim. zhurn. 2005. Vol. 71. no. 2. S. 84–89.
2. Izmaylov N. A. Elektrokhimiya rastvorov. Izd. 3-e, ispr., M.: Khimiya. 1976. 488 s.
3. Bulavin V. I., V'yunik I. M., Beregova N. pp. Elektrichna providnist' i asotsiatsiya khlorovodnyu v ryadi n-spirtiv. Visn. L'vivs'k. un-tu. Ser. khim. 2002. Vip. 42. Ch. 1. S. 52–55.
4. Bulavin V. I., V'yunnik I. N., Beregovaya N. pp., Kramarenko A. V. Elektricheskaya provodimost' i ionizatsiya bromovodoroda v ryadu n-spirtov. Visn. Khar'k. nats. un-tu. 2006. no. 731. Khimiya. Vip. 14(37). S. 201–205.
5. Bulavin V. I., V'yunnik I. N., Beregovaya N. pp., Kramarenko A. V. Termodinamika ionizatsii galogenovodorodov v *n*-spirtakh. Vopr. khimii i khim. tekhnologii. 2007. no. 3. s. 22–26.
6. Bulavin V. I., Vyunnik I. N., Kramarenko A. V. Rusinov A. I. Thermodynamics of ion pair conversion in alcohol solutions of hydrogen chloride. Bull. Nation. Technical Un-ty "KhPI". Series: Chemistry, Chem. Technology and Ecology. 2022. no. 2(8)'2022. pp. 3–10.
7. Trummal A., Lipping L., Kaljurand I, Koppel I. A., Leito I. Acidity of strong acids in water and dimethyl sulfoxide. J. Phys. Chem. A, 2016. V. 120. no. 20. pp. 3663–3669.
8. Shvarts M. Iony i ionnye pary v organicheskoy khimii. M.: Mir, 1975. 424 c.
9. Wick C.D. A comparison of sodium and hydrogen halides at the air-water interface. J. Chem. Phys. 2017. V. 147. no. 16. pp. 161703–8
10. Feng G., Chen M., Bi S., Goodwin Z. H. N., Postnikov E. B., Brilliantov N., Urbakh M., Kornyshev A. A. Free and bound states of ions in ionic liquids, conductivity, and underscreening paradox// Phys. Rev. X. 2019. no. 2. pp. 021024–22
11. Sin J-S. Effect of Bjerrum pairs on the electrostatic properties of an electrolyte solution near charged surfaces: a mean-field approach. Phys. Chem. Chem. Phys., 2021. V. 23. no. 21. pp. 12296–12308.
12. Artemov V., Ryzhov A., Ouerdane H., Stevenson K. J. Ionization difference between weak and strong electrolytes as perturbed by conductivity spectra analysis. J. Phys. Chem. B, 2023. V. 127. no. 1. pp. 261–268.
13. Bulavin V. I., V'yunnik I. N. Blizhnyaya sol'vatatsiya i podvizhnost' ionov v predel'no razbavlennykh spirtovykh i vodnykh rastvorakh galogenovodorodov. Ukr. khim. zhurn., 2012. Vol. 78. no. 8. S.82–91.
14. Yukhnevich G. V., Tarakanova E. G., Mayorov V. D., Librovich N. B. Struktura sol'vatov protona i ikh kolebatel'nye spektry. Uspekhi khimii, 1995. Vol. 64(10). S. 963–974
15. Walewski L., Forbert H., Marx D. Aggregation-induced chemical reactions: acid dissociation in growing water clusters. J. Phys. Chem. Lett., 2011. V. 2. pp. 3069–3074
16. Fulton J. L., Balasubramanian M. Structure of hydronium (H3O+)/Chloride (Cl–) contact ion pairs in aqueous hydrochloric acid solutions: a Zundel-like local configuration. J. Am. Chem. Soc. 2010. V. 132. pp. 12597–12604.
17. Yukhnovskiy I. R., Kurylyak I. I. Elektrolity. K.: Naukova dumka, 1988. 168 s.
18. Ebeling W., Grigo M. An analytical calculation of the equation of state and the critical point in a dense classical fluid of charged hard spheres. Ann. Phys. 1980. B. 37, H. 1. S. 21–30.
19. Krienke H., Barthel J., Holovko M. et al. Osmotic and activity coefficients associated electrolytes over large concentration ranges from chemical model calculations. J. Mol. Liq., 2000. V. 87. pp. 191–216.
20. Shvarts M. Anionnaya polimerizatsiya. Karbaniony, zhivushchie polimery i protsessy s perenosom elektrona. M.: Mir, 1971. 642 s.
21. Bulavin V. I. Fiziko-khimicheskie svoystva predel'nykh odnoatomnykh spirtov normal'nogo stroeniya. Vestn. Khar'k. gos. politekhn. un-ta. Sb. nauchn. trudov. Vyp. 26. s. 37–44. Khar'kov KhGPU, 1999
22. Khasanshin V. S.: Teplofizicheskie svoystva predel'nykh odnoatomnykh spirtov pri atmosfernom davlenii. Minsk.: Nauka i tekhnika, 1992. 256 s.
23. Prigozhin I., Defey R. Khimicheskaya termodinamika. M. , Nauka, 1966. 501 s.
24. Bulavin V. I., V'yunnik I. N. Mezhionnye vzaimodeystviya v spirtovykh rastvorakh elektrolitov. Zh. fiz. khimii, 2008. V. 82, no. 9. S. 1681–1684.
25. Hills G. J., Ovenden pp. J., Whitehouse D. R. Proton migration in aqueous solutions. Disc. Faraday Soc., 1965. V. 39. pp. 207–215.

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