Conductivity and association of NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$ and NaSCN in ethanol at 213.15–333.15 K

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Based on Krumgalz conductivity data of dilute (1×10^{-6}–5×10^{-2} mol kg^{-1}) electrolyte solutions of NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$ and NaSCN in ethanol in the temperature range 213.15–333.15 K (at 10 K intervals), the standard Gibbs energy, enthalpy and entropy of ion-pair formation, as well as contributions of the electrostatic and the non-electrostatic interactions to these functions, have been calculated.

Modern physical chemistry of solutions analyses electrolyte association with two types of interaction: electrostatic and short range.[1,2] In pure ethyl alcohol conductivity and association constants of electrolytes are known at 298.15 K only for MSCN (where M = Li, Na, K, Rb or Cs), $MClO_4$ (where M = Li, Na or NH_4) and for $LiNO_3$.[3] Other salts in ref. 3 are NaCl, NaBr, $NaClO_3$, $NaNO_2$ and salts with organic anions such as sodium ethylate, sodium ethylcarbonate, sodium picrate and sodium 3-methyl-2,4,6-trinitrophenolate. Data for NaI and $NaBPh_4$ at –45 to +25 °C in ethanol are available.[4]

Precise experimental data on the temperature dependence of sodium salts in ethanol were determined by Krumgal'z *et al.*,[5] but data analysis yielding the coefficients of Fuoss-Onsager conductivity equation[6,7] has not been executed. Data in a large temperature interval yield the thermodynamic properties of ion solvation and ion association that are the key for the understanding of the properties of these solutions. Therefore, we have used the known experimental data[5] on NaCl, NaBr, NaI, $NaNO_3$, $NaClO_4$ and NaSCN in ethanol in the temperature range 213.15–333.15 K (at 10 K intervals) to determine the coefficients of the Fuoss–Onsager conductivity equation in the framework of the low concentration chemical model (lcCM),[1,8] which takes into account the long-range Coulombic and short range non-electrostatic interactions of ion association.

Data analysis in the framework of the low concentration chemical model[1] based on the Fuoss–Justice conductivity equation yields the values of limiting molar conductivity, Λ_0, association constant, K_A, ion distance parameters, mean ionic activity coefficients and activity coefficients of 'free ions' (dissociated part of electrolyte) as a function of temperature and electrolyte concentration by means of the following set of equations (c^0 = 1 mol dm^{-3}):

$$\Lambda = \alpha[\Lambda_0 - S\sqrt{\frac{\alpha c}{c^0}} + E\frac{\alpha c}{c^0}\ln\frac{\alpha c}{c^0} + J_1(R_1)\frac{\alpha c}{c^0} + J_2(R_2)\left(\frac{\alpha c}{c^0}\right)^{3/2}], \quad (1a)$$

$$K'_A = K_A c^0 = \frac{1-\alpha}{a^2(c/c^0)}\frac{1}{(y'_\pm)^2}, \quad (1b)$$

$$y'_\pm = \exp\left[-\frac{\kappa q}{1+\kappa R}\right], \quad (1c)$$

where Λ and Λ_0 are the molar conductivities at molarity c and infinite dilution, $(1-\alpha)$ is the fraction of ion pairs, and K_A is the association equilibrium constant, $y'_\pm$ is the mean activity coefficient of 'free ions' (*i.e.* the dissociated part of the electrolyte), κ is the Debye parameter, and q is the Bjerrum parameter for oppositely charged ions:

$$\kappa^2 = \frac{N_A e^2}{\varepsilon\varepsilon_0 kT}\sum_j c_j z_j^2;\ q = \frac{e^2|z_+z_-|}{8\pi\varepsilon\varepsilon_0 kT}.$$

The equations for the calculation of the coefficients S, E, J_1, J_2 can be found elsewhere.[9]

$$S = S_1\Lambda_0 + S_2;\ E = E_1\Lambda_0 - 2E_2;\ J_1 = \sigma_1\Lambda_0 + \sigma_2;\ J_2 = \sigma_3\Lambda_0 + \sigma_4.$$

The coefficients S and E are independent of the ionic distance parameter. The coefficients J_1 and J_2 depend on the upper limit R of association defining the distance up to which ions form ion pairs. Distance R is the cut-off distance of the short range forces in the low concentration chemical model (lcCM model[1,8,9]).

The lcCM calculations use the association constant[10]

$$K_A = 4\pi N_A\int_{a'}^{R} r^2\exp\left(\frac{2q}{r} - \frac{W^*_\pm}{kT}\right)dr, \quad (2)$$

where $W^*_\pm$ is a part of the potential of the mean forces between cations and anions, which is due to the non-Coulombic interactions. The upper limit R of association is $R = a' + ns$, where n = 0, 1, 2, 3, ..., s is the length of an oriented solvent molecule and a' is the nearest possible ionic distance, $W^*_\pm$ is defined as:

$W^*_\pm = \infty$ for $r \le a'$,
$W^*_\pm$ = const for $a' \le r \le R$,
$W^*_\pm = 0$ for $r \ge R$.

Then equation (2) yields

$$K_A = 4\pi N_A\exp\left(-\frac{W^*_\pm}{kT}\right)\int_{a'}^{R} r^2\exp\left(\frac{2q}{r}\right)dr. \quad (3)$$

The Gibbs association energy ΔG^0_A may be split into a non-electrostatic and an electrostatic part $\Delta G^0_A = \Delta G^{0,*}_A + \Delta G^{0,el}_A$, where $\Delta G^{0,*}_A = N_A W^*_\pm$. According to equation (3) the electrostatic part of the Gibbs association energy is given by

$$\Delta G^{0,el}_A = -RT\ln\left[4\pi N_A\int_{a'}^{R} r^2\exp\left(\frac{2q}{r}\right)dr\right]. \quad (4)$$

Data analysis was executed as a three parameter fit, *i.e.* parameter R and coefficients S , E and J_1 are calculated by the use of ref. 9 with the help of known ion and solvent data; $R = a' + ns$, $a' = a + d_{solv.\ gr.}$, $a = a_+ + a_-$ and s = 0.28 nm,[11] n = 1 according to refs. 10, 12 and 13. The choice of the temperature-independent parameter $R = a_+ + a_- + s + d_{OH}$ considers solvent-separated ion pairs of the type [Na^+(EtOH)(OH)X^-]. Radius a_+ (ionic radius of Na^+) is used as the Goldschmidt distance parameter. Radii a_- of the anions Cl^-, Br^-, I^-, SCN^-, NO_3^- and ClO_4^- are taken[1,14] as thermochemical radii obtained by the Kapustinskii equation from enthalpies of crystal lattice and the radius of its counterion.[15] Dielectric permittivity and viscosity of ethanol at –60 to 60 °C needed for the coefficients of the conductivity equations [equation (1)] are taken from refs. 16–18. So, the value of J_1 is calculated. Data analysis then yields limiting conductivity, Λ_0, thermodynamic association constant, K_A, and coefficients J_1 and J_2. Standard deviation range is from 2×10^{-5} to 0.5×10^{-4} S m^2 mol^{-1}.

The split of the association integral in Coulombic and non-Coulombic contributions [equations (2)–(4)] yields the temperature dependence of the thermodynamic data ln K_A, and ΔG^0_A:

$$-\ln K_A = \frac{A_1}{T} + A_2 + A_3 T, \quad (5)$$

$$\Delta G^0_A = R(A_1 + A_2 T + A_3 T^2),$$

$$\Delta H^0_A = R(A_1 - A_3 T^2),$$

$$\Delta S^0_A = -R(A_2 + 2A_3 T).$$

The results of data treatment. Distance parameters used in the calculations, dielectric permittivity and viscosity of ethanol at –60 to 60 °C, coefficients *S* and *E* of equation (1), the results of data analysis (Λ_0, K_A, J_1, J_2), as well as the standard thermodynamic functions of ion association (ΔG^0_A, ΔH^0_A, ΔS^0_A), and contributions of the electrostatic interaction to these functions ($\Delta G^{0,el}_A$, $\Delta H^{0,el}_A$, $\Delta S^{0,el}_A$) are presented in Online supplementary materials.† Coefficients of the temperature dependence of electrolyte dissociation constant of ion association and its Coulombic part in ethanol according to equation (5) *cf.* of thermodynamic functions of ion association are presented in Table 1.

Conductivity and association constant. Λ_0 is not sensible to the model and agrees within 2×10^{-5} to 0.5×10^{-4} S m^2 mol^{-1} for classical and developed conductivity equations.[3,5] The *R* parameter calculated from $J_2(R)$ values when compared to the parameter from literature data on radii agrees within the usual limits of lcCM calculations, which is generally considered as the compatibility condition of the method.[4,10,19] Value of Λ_0 increases with increasing temperature for all salts considered. The association constant decreases with increasing temperature for NaBr and passes through a minimum for NaCl, NaI, $NaNO_3$, $NaClO_4$ and NaSCN.

Gibbs energy of association. The association process is thermodynamically favourable ($\Delta G^0_A < 0$, $\Delta S^0_A > 0$). The Gibbs energy of association decreases in most cases with increasing temperature, *e.g.* with decreasing dielectric permeability. This change of ΔG^0_A is expected in classical electrostatic view. For all salts considered the enhancing of associates (ion pairs) at increasing temperature is stipulated by the change of entropy. That is $|T\Delta S^0_A| > |\Delta H^0_A|$ and the decrease of '$-T\Delta S^0_A$' with temperature determines the decrease of ΔG^0_A.

Association Gibbs energy is mainly due to the electrostatic contribution to association: the electrostatic part equals to ~60–90% depending on temperature of the total value ΔG^0_A. It is important to note that both the electrostatic and non-electrostatic part in the same direction stipulate the negative value of Gibbs energy ($\Delta G^{0,*}_A < 0$, $\Delta G^{0,el}_A < 0$). Non-electrostatic parts $\Delta G^{0,*}_A$ increase with increasing temperature for NaBr, NaCl or passes through a maximum for NaI and $NaNO_3$. $\Delta G^{0,*}_A$ values for $NaClO_4$ and NaSCN are practically independent of temperature.

Enthalpy and entropy of association. Enthalpy of association rises with increasing temperature in all cases, except for NaSCN and NaCl. In the case of sodium thiocyanate, $\Delta H^0_A = f(T)$ decreases. In the case of sodium thiocyanate, specific interaction may take place of associate ('molecules' are ion pairs or ion aggregates) and ethanol molecules. This is due to geometric and electronic structure features of thiocyanate. The same change of ΔH^0_A: a decrease of positive values of ΔH^0_A with the temperature is observed for the KSCN and NaSCN in propan-1-ol, propan-2-ol[10,20] that indicate stronger solvation of the ion pair in comparison with the individual ions with temperature increase. This result confirms the conclusion on the specific interaction of SCN^- ions with alcohol molecules from absolute standard Gibbs energy of solvation analysis.[21]

The entropy of association at standard temperature ΔS^{298}_A equals to 50–70 kJ mol^{-1} as for other alkali metal salts in ethanol (KI, CsI and KSCN).[19] Tetraalkylammonium salts (Pr_4NI, Pr_4NBr, Pr_4NClO_4, Am^i_3BuNI and $Am^i_3BuNBPh_4$), as well as NaI, $NaBPh_4$, KI, KSCN and CsI, at –45 to 25 °C in ethanol are available from refs. 4, 12, 19. For tetraalkylammonium salts, ΔS_A values are smaller.[4,12,19] At the same time, unlike ref. 4, $\Delta H^{298}_A > 10$ kJ mol^{-1} for potassium salts in ethanol, our results for sodium salts show $\Delta H^{298}_A < 10$ kJ mol^{-1} and equal approximately –10 to 10 kJ mol^{-1}, which is close to ΔH_A of tetraalkylammonium salts.

Non-electrostatic contribution prevails in entropy and enthalpy of association. $\Delta S^{0,el}_A$ and $\Delta H^{0,el}_A$ values are positive. Ordinary, the stabilization of associate (ion pair) by entropy reveals for thermodynamic functions of ion association as well as for their short-range contribution in alcohol systems:[7,8] $\Delta G^{0,*}_A < 0$, $\Delta S^{0,*}_A > 0$, $\Delta H^{0,*}_A > 0$. For most salts considered also the formation of entropy-stabilised associates in ethanol is observed: for $NaNO_3$, NaI, $NaClO_4$, $\Delta H^{0,*}_A > 0$, $T\Delta S^{0,*}_A > 0$, $|T\Delta S^{0,*}_A| > |\Delta H^{0,*}_A|$. The formation of these associates is due to enthalpy change. The formation of enthalpy-stabilised associates (due to the chemical bonds formation) is observed for NaCl and NaBr: $\Delta H^{0,*}_A < 0$, $T\Delta S^{0,*}_A < 0$, $|T\Delta S^{0,*}_A| < |\Delta H^{0,*}_A|$. In the case of NaSCN we observe the formation of associates due to both effects: enthalpy and entropy.

The dependence of $\Delta G^{0,*}_A$ on solvent properties for the series of aliphatic alcohols and anion parameters (molecular weight *M*, reciprocal radii r_A^{-1}, refraction R_D and softness parameter σ) has been analysed. For halide ions, Gibbs energy of association decreases with radius increase [stability of associates (ion pairs) increases], in the case of polyatomic ions stability of associates (ion pairs) is determined not by distance parameters, but by the polarizability and delocalization of charge on the atoms of the anion. The most stable associate (ion pair) is $NaNO_3$, least of all is $NaClO_4$.

Table 1 Coefficients of the temperature dependence of the electrolyte dissociation constant and its Coulombic part in ethanol according to equation (5).

Electrolyte	A_1 /10^2 K	A_2	A_3/10^{-3} K	Disp.[a]
K_A				
NaCl	7.908	–18.0973	33.115	5.1×10^{-2}
NaBr	–9.712	0.3675	–6.438	6.2×10^{-3}
NaI	–33.328	22.0492	–53.593	2.3×10^{-2}
$NaNO_3$	–133.36	86.7136	–158.440	2.9×10^{-3}
$NaClO_4$	–9.171	3.9483	–18.835	2.3×10^{-3}
NaSCN	9.996	–10.5618	7.813	1.5×10^{-3}
K^{el}_A				
NaCl	–4.829	1.7055	–13.420	9.8×10^{-6}
NaBr	–5.752	2.3233	–14.518	8.6×10^{-6}
NaI	–4.815	1.6035	–13.279	1.1×10^{-5}
$NaNO_3$	–4.794	1.6604	–13.344	1.1×10^{-5}
$NaClO_4$	–5.034	1.6745	–13.399	6.1×10^{-6}
NaSCN	–5.199	1.8582	–13.701	6.8×10^{-6}

[a]Dispersion of the approximation of $-\ln K_A$ with equation (5).

† Online Supplementary Materials are available free *via* http://www.turpion.org/suppl/mc/2349/suppl2349.pdf.

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