

TRANSFERENCE NUMBER AND CONDUCTANCE STUDIES OF SODIUM CHLORIDE IN AQUEOUS MIXTURES OF ETHANOL AT 298.15 K

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Abstract

Transference numbers of sodium ion constituent were determined at 298.15 K from the potential difference measurements of the cell with liquid junction, at various sodium chloride molalities against fixed molality in aqueous mixtures of ethanol (containing 20 and 40 mass % ethanol) by using literature data for the activity coefficient. Molar conductivities of sodium chloride were determined in both mixtures and treated by the Lee-Wheaton equation to obtain their limiting value. Limiting transference number of the sodium ion, obtained by extrapolation to zero-molarity, serves to derive ionic conductivities.

Key words: *transference numbers, ionic conductivities, sodium chloride, ethanol + water mixtures, potentiometry, conductometry*

1. INTRODUCTION

The solvation behaviour of ions in binary mixtures of water with organic solvent can be studied if the ionic limiting molar conductivities (λ°) are available. The limiting molar conductivities of individual ions can be obtained by the direct or indirect methods. Direct method does not include any assumptions. If the transference numbers can be obtained accurately, this method is the most reliable. Namely, the limiting molar conductivity of an electrolyte (Λ°) and the limiting transference numbers of the ions constituting the electrolyte (t°) are determined experimentally, and Λ° is divided into ionic contributions. For example, for an electrolyte of MA-type ($z_+ = z_- = 1$), Λ° is given by:

$$\Lambda^\circ = \lambda_{M^+}^\circ + \lambda_{A^-}^\circ \quad (1)$$

We have recently reported data for transference numbers of NaCl in aqueous mixtures of formamide at 298.15 K obtained from the potential difference (pd) measurements (Tomaš et al., 2013). In order to determine ionic conductivities, we used our limiting transference number of the sodium ion, obtained by extrapolation to zero-molarity. In a previous paper (Bošković et al., 2013), molar conductivities of dilute solutions of KCl in aqueous mixtures of ethanol at different temperatures were determined. The ionic limiting molar conductivities were obtained using the literature values of the cation limiting transference number from the same temperature range.

Extending our study, in the present paper, transference number of sodium ion constituent at various NaCl molalities in aqueous mixtures of ethanol with 20 (Z_1) and 40 (Z_2) mass % ethanol at 298.15 K are presented. Furthermore, the limiting molar conductivity and association constant (K_A) were determined in both mixtures at the same temperature using the chemical model of conductivity based on the Lee-Wheaton equation. Finally, ionic limiting molar conductivities, λ° , were derived from the Λ° and t° values. All derived quantities were compared with that in similar systems and discussed in terms ion solvation.

2. EXPERIMENTAL

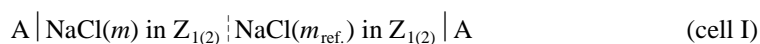
Absolute ethanol (99.8 %) and NaCl (*p.a.*), all from Merck, was used in conductometric and potentiometric experiment. Water was distilled twice. Sodium chloride was heated for three hours at 700 °C to constant mass, and then stored in a desiccator before use. Solvent mixtures (Z_1 and Z_2) and all solutions of NaCl in Z_1 and Z_2 were prepared by direct weighing. Solution molarity (c) was determined from solution molality (m) and solution density (d):

$$c = \frac{1000 d m}{(1000 + m M)} \quad (2)$$

where M denote molar mass of NaCl. The solution density, as well as the densities of solvent mixtures Z_1 and Z_2 (d_0), were determined at 298.15 K by a digital densimeter Anton Paar (model DMA 4500M) with precision of $\pm 1 \times 10^{-5} \text{ g cm}^{-3}$, and accuracy $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$. The instrument is equipped with Peltier-type thermostating unit and temperature is kept constant with accuracy of $\pm 0.01 \text{ K}$. The densimeter was calibrated daily with dry air and double distilled water at atmospheric pressure. The relative error in molarity and solvent compositions was about $\pm 0.1 \%$. The viscosity of solvent mixtures Z_1 and Z_2 (η_0) was measured at 298.15 K using an Ostwald viscometer; the uncertainty in the viscosity measurements was $\pm 1 \text{ mPa s}$.

The conductance measurements were carried with a Wayne-Kerr (model 6430 A) precision component analyzer working at four frequencies ($f = 500, 800, 1000$ and 2000 Hz). A dipping type conductivity cell Orion (model 018001) with two electrodes of bright platinum was used. The cell constant is 0.10402 cm^{-1} . The measured values of conductivity were corrected for the conductivity of solvent mixture. Conductometric procedure was described earlier in detail (Sokol et al., 2012).

An pd cell with transference (concentration cell with a liquid junction; see cell I) similar to that described by Braun and Weingärtner (1985), was manufactured in Šurlan-laboratory glassware (Medulin, Croatia). $\text{AgCl} | \text{Ag}$ electrodes reversible to the Cl^- anion (A) in the cell I:



were prepared as described earlier (Tomaš et al., 2004), also the cell description and the procedure in pd measurements of the cell (Tomaš et al., 2013). Potentiometric measurements were performed using a high input impedance ($>10^{15} \Omega$) Keithley electrometer (model 6514) with sensitivity of 0.01 mV . For cell I, the solution molality, $m_{\text{ref.}}$, is fixed, whereas m is varied within the required molality range in the investigated mixed solvents.

Temperature was maintained constant ($298.15 \pm 0.01 \text{ K}$) using a circulating water bath (Thermo-Haake DC10-V15/B). Traces of dissolved CO_2 were removed from the solution by a short bubbling of high-purity nitrogen.

3. CALCULATIONS, RESULTS AND DISCUSSION

3.1 Solvent properties and solution conductivity

Densities, viscosities, and relative permittivities (ϵ_r) of aqueous mixtures of ethanol (Z_1 and Z_2) are reported in Table 1. The permittivity values were taken from literature (Esteso et al., 1989). Measured molar conductivity for the NaCl solutions of different concentrations for both mixtures is given in Table 2; values in brackets represents the data computed using Eq. (3). As seen in Table 2, the values for Λ continually decrease with increasing NaCl molarity.

Table 1. Density, viscosity and relative permittivity for Z_1 and Z_2 at 298.15 K

Properties:	Z_1	Z_2
$d_0 / \text{g cm}^{-3}$	0.96605	0.93155
$\eta_0 / \text{mPa s}$	1.7802	2.3661
ϵ_r	67.0	55.0

Table 2. Molar conductivity (Λ) as a function of the NaCl molarity (c) for Z_1 and Z_2 at 298.15 K

Z_1		Z_2	
$10^3 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$	$10^3 c / \text{mol dm}^{-3}$	$\Lambda / \text{S cm}^2 \text{mol}^{-1}$
17.705	59.063 (59.058)	17.439	40.929 (40.911)
21.792	58.429 (58.416)	21.563	40.386 (40.368)
25.939	57.840 (57.839)	25.649	39.922 (39.916)
30.006	57.322 (57.331)	29.606	39.519 (39.513)
33.950	56.872 (56.879)	33.483	39.148 (39.153)
37.784	56.459 (56.474)	37.267	38.826 (38.828)
41.695	56.069 (56.088)	41.043	38.522 (38.527)
45.522	55.749 (55.733)	44.702	38.249 (38.252)
49.298	55.410 (55.403)	48.391	37.985 (37.992)
52.970	55.100 (55.099)	51.944	37.751 (37.753)
56.567	54.821 (54.814)	55.425	37.525 (37.530)

3.2 Model of conductivity and data processing

Conductivity data processing was carried out by means of the Lee-Wheaton equation in the Pethybridge and Taba version, LWPT (1980), and the following set of equations was used:

$$\Lambda_{c\alpha} = \Lambda^0 \left[1 + C_1 \beta \kappa + C_2 (\beta \kappa)^2 + C_3 (\beta \kappa)^3 \right] - \frac{\rho \kappa}{1 + \kappa R} \left[1 + C_4 \beta \kappa + C_5 (\beta \kappa)^2 + \frac{\kappa R}{12} \right] \quad (3)$$

$$K_A = (1 - \alpha) / (c \alpha^2 y_{\pm}^2) \quad (4)$$

$$y_{\pm}^2 = \exp[-2\kappa q / (1 + \kappa R)] \quad (5)$$

$$\rho = \frac{Fe}{3\pi\eta} \quad (6)$$

$$q = \frac{e^2}{8\pi\epsilon_0\epsilon_r kT} \quad (7)$$

$$\kappa^2 = 16\pi N_A q \alpha c \quad (8)$$

In these expressions, $\Lambda_{c\alpha}$ is the molar conductivity of the free ions, Λ^0 is the molar conductivity at infinite dilution, coefficients C_1 – C_5 are the functions of t and $\ln t$ ($t = \kappa R$), R is the greatest centre-to-centre distance between the ions in the ion-pair formed, κ is the Debye parameter, $\beta = 2q$, q is the Bjerrum critical distance. K_A is the thermodynamic equilibrium constant for the association reaction



where $c\alpha$ and $c(1-\alpha)$ are the equilibrium concentrations of the fraction of free ions and ion pairs, respectively, α is the degree of dissociation ($\alpha = \Lambda/\Lambda_{c\alpha}$) and represents the ratio of the measured molar conductivity to the molar conductivity of free ions, while γ_{\pm} is the mean molar activity coefficient of free ions. The other symbols have their usual meaning.

For adjusting model of conductivity to experimental data was used optimization procedure according to Beronius (1974). The experimental data were processed by a two-parameter fit, $\Lambda = f(c; \Lambda^{\circ}, K_A)$; in this case R was equated to q , as recommended by Justice (1971). The values so obtained for Λ° and K_A , along with the standard deviation of experimental Λ from the model LWPT (σ), are listed in Table 3.

Table 3. Limiting molar conductivities (Λ°), ion-association constants (K_A), and standard deviations (σ) of experimental Λ from the model LWPT for NaCl in Z_1 and Z_2 at 298.15 K with $R = q$

	$\Lambda^{\circ} / \text{S cm}^2 \text{ mol}^{-1}$	K_A	$\sigma / \text{S cm}^2 \text{ mol}^{-1}$	q / nm
Z_1	65.75 ± 0.02	1.43 ± 0.01	0.01	0.418
Z_2	46.59 ± 0.01	2.41 ± 0.01	0.01	0.510

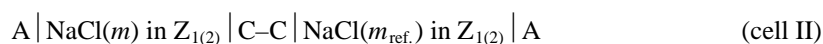
As can be seen from Table 3, $\Lambda^{\circ}(Z_1) > \Lambda^{\circ}(Z_2)$, which is mainly determined by an opposite trend in viscosity (see Table 1). The K_A values indicate no significant ion-association reaction (9); K_A is increasing with the ethanol content as expected – lower mixture permittivity (see Table 1) enhances the attraction of oppositely charged ions.

3.3 Transference numbers measurements

The transference numbers of Na^+ (t_+) in Z_1 and Z_2 were calculated from pd data according to the equation (Augustynski et al., 1967)

$$t_+ = \left(\frac{dE_t}{dE} \right)_m \quad (10)$$

where E_t is the measured pd of the cell I, and E is the pd of the corresponding cell without transference (cell II):



For cell II, C denote electrode reversible to the cation (Na^+); the NaCl molality, $m_{\text{ref.}}$, is fixed, whereas m is varied within the required molality range in the investigated mixed solvents. Values for E were calculated according to the equation

$$E = \frac{2RT}{F} \ln \frac{a_{\pm}}{a_{\pm, \text{ref.}}} \quad (11)$$

by taking interpolated or extrapolated molal activity coefficients (γ_{\pm}) from Estes et al. (1989). In Eq. (11), a_{\pm} is the mean ionic activity at concentration m ; the other symbols have the usual meanings. Corresponding values of E_t and E are given in Table 4, for NaCl solutions in Z_1 and Z_2 at 298.15 K.

Table 4. Experimental results on solutions of NaCl in Z_1 and Z_2 at 298.15 K: cation transference numbers measurements of NaCl (t_+)

$m / \text{mol kg}^{-1}$	$d / \text{g cm}^{-3}$	$c / \text{mol dm}^{-3}$	a_{\pm}	E / V	E_t / V	t_+
Z_1 ($m_{\text{ref.}} = 0.0504 \text{ mol kg}^{-1}$; $d_{\text{ref.}} = 0.96933 \text{ g cm}^{-3}$; $c_{\text{ref.}} = 0.0487 \text{ mol dm}^{-3}$; $a_{\pm, \text{ref.}} = 0.03906$)						
0.0342	0.96779	0.0330	0.02753	-0.01798	-0.00747	0.4207*
0.0746	0.96944	0.0720	0.05558	0.01812	0.00760	0.4144
0.0988	0.97039	0.0953	0.07143	0.03102	0.01294	0.4122
0.1994	0.97430	0.1920	0.13320	0.06304	0.02599	0.4066
0.3425	0.97988	0.3290	0.21715	0.08815	0.03625	0.4022
0.5940	0.98944	0.5680	0.35224	0.11301	0.04622	0.3979
0.8515	0.99886	0.8102	0.49728	0.13073	0.05328	0.3948
0.9868	1.00382	0.9366	0.56445	0.13724	0.05600	0.3936
1.1933	1.01121	1.1280	0.68376	0.14709	0.05954	0.3920
1.4178	1.01909	1.3343	0.79822	0.15504	0.06286	0.3906
1.5889	1.02509	1.4904	0.91044	0.16180	0.06512	0.3894
Z_2 ($m_{\text{ref.}} = 0.0500 \text{ mol kg}^{-1}$; $d_{\text{ref.}} = 0.93361 \text{ g cm}^{-3}$; $c_{\text{ref.}} = 0.0465 \text{ mol dm}^{-3}$; $a_{\pm, \text{ref.}} = 0.03580$)						
0.0092	0.93202	0.0086	0.00782	-0.07817	-0.03362	0.4370*
0.0200	0.93268	0.0186	0.01650	-0.03980	-0.01727	0.4308*
0.0343	0.93302	0.0319	0.02627	-0.01590	-0.00698	0.4273
0.0719	0.93435	0.0669	0.04968	0.01684	0.00700	0.4216
0.0895	0.93502	0.0832	0.05934	0.02597	0.01097	0.4200
0.2023	0.93932	0.1878	0.12138	0.06274	0.02615	0.4141
0.4018	0.94603	0.3714	0.21617	0.09240	0.03855	0.4093
0.6010	0.95249	0.5530	0.30531	0.11014	0.04573	0.4064
0.9037	0.96229	0.8260	0.43468	0.12829	0.05290	0.4034
1.2104	0.97289	1.0998	0.56163	0.14146	0.05855	0.4013
1.4008	0.97879	1.2673	0.65557	0.14941	0.06136	0.4000
1.4945	0.98188	1.3495	0.69494	0.15240	0.06255	0.3995

*Calculations of the limiting transference numbers does not include these values.

Regression analysis showed that dependence of E_t (cell I) on E (cell II) can be adequately fitted by the second-order polynomial

$$E_t / (\text{V}) = a_0 + a_1 E + a_2 E^2 \quad (12)$$

with squared correlation coefficient, $R^2 > 0.9999$. The polynomial coefficients a_j (j is polynomial degree, $j = 0, 1$ and 2) obtained by fitting Eq. (12) to the experimental results are presented in Table 5, together with their standard deviations. From the first derivate of Eq. (12), according to Eq. (10),

$$t_+ = \left(\frac{dE_t}{dE} \right)_m = a_1 + 2a_2E \quad (13)$$

the transference number of Na^+ ion in Z_1 and Z_2 solvent studied were evaluated. The resulting values of the cation transference numbers of NaCl at 298.15 K are given in Table 4. As seen in Table 4, the values for t_+ in Z_1 and Z_2 decrease slightly with increasing NaCl concentration.

The limiting transference numbers (t_+^0) in Z_1 and Z_2 were obtained from extrapolation of the second-order polynomial (see Fig. 1)

$$Y(X) = a_0 + a_1X + a_2X^2 \quad (14)$$

to infinite dilution (no ion-ion interactions); *i.e.*, from Eq. (14) follows: $Y(X = 0) = a_0 \equiv t_+^0$ (coefficient a_0 is equal to the limiting transference number of Na^+ ion). In this expression, Y is the transference number, X is the square-root of molarity, and the coefficients a_0 , a_1 , and a_2 were evaluated by the least-squares method and are also reported in Table 5, together with their standard deviations; standard deviations for the fitting of data (s_f) into Eqs. (12) and (14) are given.

Table 5. Adjustable coefficients of Eqs. (12) and (14) for NaCl in Z_1 and Z_2 at 298.15 K

	a_0	a_1	a_2	s_f
Eq. (12) in Z_1	0.00010 ± 0.00008	0.4176 ± 0.0006	-0.0871 ± 0.0058	0.00010
Eq. (14) in Z_1	0.4262 ± 0.0009	-0.0507 ± 0.0029	0.0172 ± 0.0019	0.0005
Eq. (12) in Z_2	-0.00010 ± 0.00009	0.4243 ± 0.0010	-0.0813 ± 0.0091	0.00010
Eq. (14) in Z_2	0.4324 ± 0.0008	-0.0481 ± 0.0028	0.0173 ± 0.0020	0.0005

The limiting transference numbers of sodium ion, determined in present study, are in good agreement with published data (Mussini et al., 1995: 0.4241 ± 0.0016 in Z_1 and 0.4276 ± 0.0029 in Z_2).

3.4 Ionic conductivities

From the limiting values of the transference number listed in Table 5, and the limiting molar conductivities of NaCl listed in Table 3, the ionic limiting molar conductivities were calculated by applying relation for Na^+ ion:

$$\lambda_+^0 = t_+^0 A^0 \quad (15)$$

and using Eq. (1) for Cl^- ion, respectively. The values obtained for investigated systems are reported in Table 6.

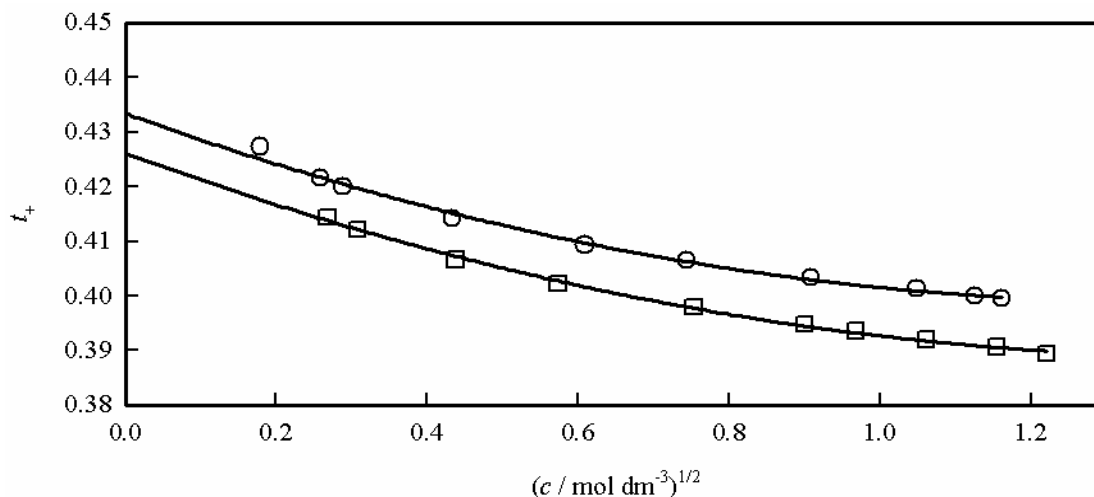


Figure 1. Plots of transference number against (molarity)^{1/2} of NaCl in Z₁ (□) and Z₂ (○) at 298.15 K. The values of t_+^0 are obtained from curve intercept on y-axis (comment given in text)

From Table 6 it is seen that each λ^0 for sodium ion is lower than the corresponding values for chloride ion; stronger solvation of Na⁺ enlarges its hydrodynamic radius. For both ions λ^0 follows the order: $\lambda^0(\text{Z}_1) > \lambda^0(\text{Z}_2)$, which is mainly determined by an opposite trend in viscosity (see Table 1). Earlier study of the same electrolyte in aqueous formamide mixtures (Tomaš et al., 2013) have led to similar observation. Using similar approach, Estes et al. (1991) have determined ionic conductivities ($\lambda^0(\text{Na}^+) = 18.98$ and $\lambda^0(\text{Cl}^-) = 24.53 \text{ S cm}^2 \text{ mol}^{-1}$) in system NaCl – aqueous mixture of ethanol (60 mass % ethanol) at 298.15 K.

Table 6. Derived ionic conductivities (λ^0) in Z₁ and Z₂ at 298.15 K

medium:	$\lambda^0 / \text{S cm}^2 \text{ mol}^{-1}$	
	Na ⁺	Cl ⁻
Z ₁	28.02	37.73
Z ₂	20.15	26.44

From λ^0 values, the Walden products ($\lambda^0 \eta$) for Na⁺ and Cl⁻ in investigated systems were calculated. The lowest values of this product, and accordingly the strongest solvation of both ions, were found for the mixture Z₂.

4. CONCLUSION

The present work has provided information on the solvation behaviour of NaCl in aqueous mixtures of ethanol (containing 20 and 40 mass % ethanol). The K_A values indicate no significant ion-association in the investigated mixtures. The molecular conductivities of NaCl as well as the transference numbers decreased with the increase of the ethanol content of the solvent mixture, indicating that the viscous motion dominates in the solution. From the transference-cell pd data and conductivity data for NaCl in Z₁ and Z₂, the ionic limiting conductivities for Na⁺ and Cl⁻ have been determined at 298.15 K. It was found that the Walden product ($\lambda^0 \eta$) for the investigated ions are less in Z₂, and accordingly the strongest solvation in this mixture.

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