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Transference Numbers of Sodium Chloride in Formamide + Water Mixtures at 298.15 K from Potential Difference Measurements[#]

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Transference numbers of sodium ion constituent were determined at 298.15 K from the potential difference (pd) measurements of the cell with liquid junction:

$$\mathrm{Ag(s)}\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{NaCl}\ (m)\ \vdots\ \mathrm{NaCl}\ (m_{\mathrm{ref.}})\,|\,\mathrm{AgCl(s)}\,|\,\mathrm{Ag(s)},$$

at various sodium chloride molalities (m) against fixed molality ($m_{\mathrm{ref.}}$) in aqueous mixtures with different mass fraction of formamide (w_F = 0.20, 0.40, 0.60, and 0.80) by using literature data for the activity coefficient. Limiting transference number of the sodium ion, obtained by extrapolation to zero-molarity, serves to derive ionic conductivities. Results are compared with that in similar systems and discussed in terms ion solvation.

Keywords: transference numbers, sodium chloride, formamide + water mixtures, potentiometry

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1. INTRODUCTION

Mixed solvents made up of water and non-aqueous solvent represent an important medium for the study of thermodynamic, kinetic, and transport properties of dissolved electrolytes. The use of mixed solvents enables the variation of the relative permittivity (ε_r) or viscosity (η), and therefore the ion-solvent interactions can be better studied. For obtaining information on ion solvation knowledge of transport properties of electrolytes (conductance, viscosity, and transference numbers) are of particular importance. Unfortunately, measurement of transference numbers are very rare compared to the measurements of viscosity and conductivity of electrolyte solutions.

Transference number measurement is a matter of considerable importance in the study of electrolyte solutions by the conductivity method since the limiting molar conductivity of individual ions (λ_i^o) can be determined without any assumptions by combining limiting transference numbers of the ions (t_i^o) constituting the electrolyte with limiting molar conductivity of electrolyte (Λ^o) [1]. In the case of a (1,1)-type electrolyte at infinite dilution, the transference number of individual ions is given by:

$$t_i^o = \frac{\lambda_i^o}{\Lambda^o} \qquad (1)$$

There are several methods available for measuring the transference numbers: the Hittorf method, the moving boundary method, and the potentiometric method [2].

In this study, the results relating to the transference number measurements for sodium chloride (NaCl) solutions of different molalities (m) in aqueous mixtures with formamide (Z = W + F) at 298.15 K using the potentiometric method have been reported. The transference number data has not yet been reported in the literature for the system of the present study, NaCl in Z, exhibiting high permittivity. A newer literature survey shows that the transference number of NaCl solutions have been determined potentiometrically in water [3-5], and in aqueous mixtures with non-aqueous solvents of low or moderate permittivities (methanol [5], ethanol [6], 1,4-dioxane [7,8], ethylene glycol [8], and acetonitrile [8]).

In this work we have measured the potential difference (pd) in a concentration cell with transference (E_t)

$$\mathrm{A}\,|\,\mathrm{NaCl}(m)\text{ in Z} \;\vdots\; \mathrm{NaCl}(m_{\mathrm{ref.}})\text{ in Z}\,|\,\mathrm{A} \qquad \text{(Cell I)}$$

as a function of the formamide mass fraction in Z (w_F = 0.20, 0.40, 0.60, and 0.80), and NaCl molality at 298.15 K. Furthermore, using data of mean molal activity coefficients ($\gamma_\pm$) available in the literature [9], we have calculated pd (E) of the corresponding cell without transference (electrolytic type)

$$\mathrm{A}\,|\,\mathrm{NaCl}(m)\text{ in Z}\,|\,\mathrm{C–C}\,|\,\mathrm{NaCl}(m_{\mathrm{ref.}})\text{ in Z}\,|\,\mathrm{A} \qquad \text{(Cell II)}$$

according to equation

$$E = \frac{2RT}{F}\ln\frac{a_\pm}{a_{\pm,\mathrm{ref.}}} \qquad (2)$$

where $a_{\pm}$ is the mean ionic activity at concentration *m*, all other symbols have their usual meaning. For cells I and II, A denote electrode reversible to the anion (Cl^-), while C denote electrode reversible to the cation (Na^+); the NaCl molality, $m_{\mathrm{ref.}}$, is fixed, whereas *m* is varied within the required molality range in the investigated mixed solvents Z.

The transference number of Na^+, ($t_{\mathrm{Na^+}}$) can be determined correspond to the definition [7,8,10-13]

$$t_{\mathrm{Na^+}} = \left(\frac{\mathrm{d}E_{\mathrm{t}}}{\mathrm{d}E}\right)_m \qquad (3)$$

where subscript *m* designates the molality to which $t_{\mathrm{Na^+}}$ refers ($m_{\mathrm{ref.}}$ is held fixed). The limiting transference numbers of Na^+ ($t^{\mathrm{o}}_{\mathrm{Na^+}}$) for the series of systems under investigation were estimated and compared with the relevant values in water and other mixed solvents. Finally, we report the ionic conductivities ($\lambda_{\mathrm{i}}^{\mathrm{o}}$) for investigated systems by combining Λ^{o} of NaCl [14] with the present $t^{\mathrm{o}}_{\mathrm{Na^+}}$ values. The results are interpreted in terms of ion-solvent interaction.

2. EXPERIMENTAL

2.1. Materials and equipments

All chemicals were obtained from Merck and are analytical grade. Formamide was further purified by treating it with molecular sieves (0.3 nm) and then with a mixed bed ion-exchanger (Amberlite MB-3). Water was distilled twice. The purity of both solvents was checked by measuring their conductivity using a precision component analyzer Wayne-Kerr (model 6430A). The specific conductance was less than 5×10^{-6} S cm^{-1} for formamide, and less than 2×10^{-6} S cm^{-1}. Sodium chloride was heated for three hours at 700 °C to constant mass, and then stored in a desiccator before use.

All solutions of NaCl in Z were made by weight and the molality, *m*, was converted into amount concentration, *c*, by means of the relation

$$c = \frac{1000\,\rho\, m}{(1000 + m\,M)} \qquad (4)$$

where ρ is solution density, and *M* the molar mass of NaCl; *c* was obtained from Eq. (4) with an uncertainty of ±0.0001 mol dm^{-3}. The densities were obtained with an Anton Paar (model DMA 4500 M) oscillating U-tube densimeter with precision of $\pm 1 \times 10^{-5}$ g cm^{-3}, and accuracy $\pm 5 \times 10^{-5}$ g cm^{-3}. The instrument is equipped with Peltier-type thermostating unit and temperature is kept constant with accuracy of ±0.01 K. The densimeter was calibrated daily with dry air and double distilled water at atmospheric pressure.

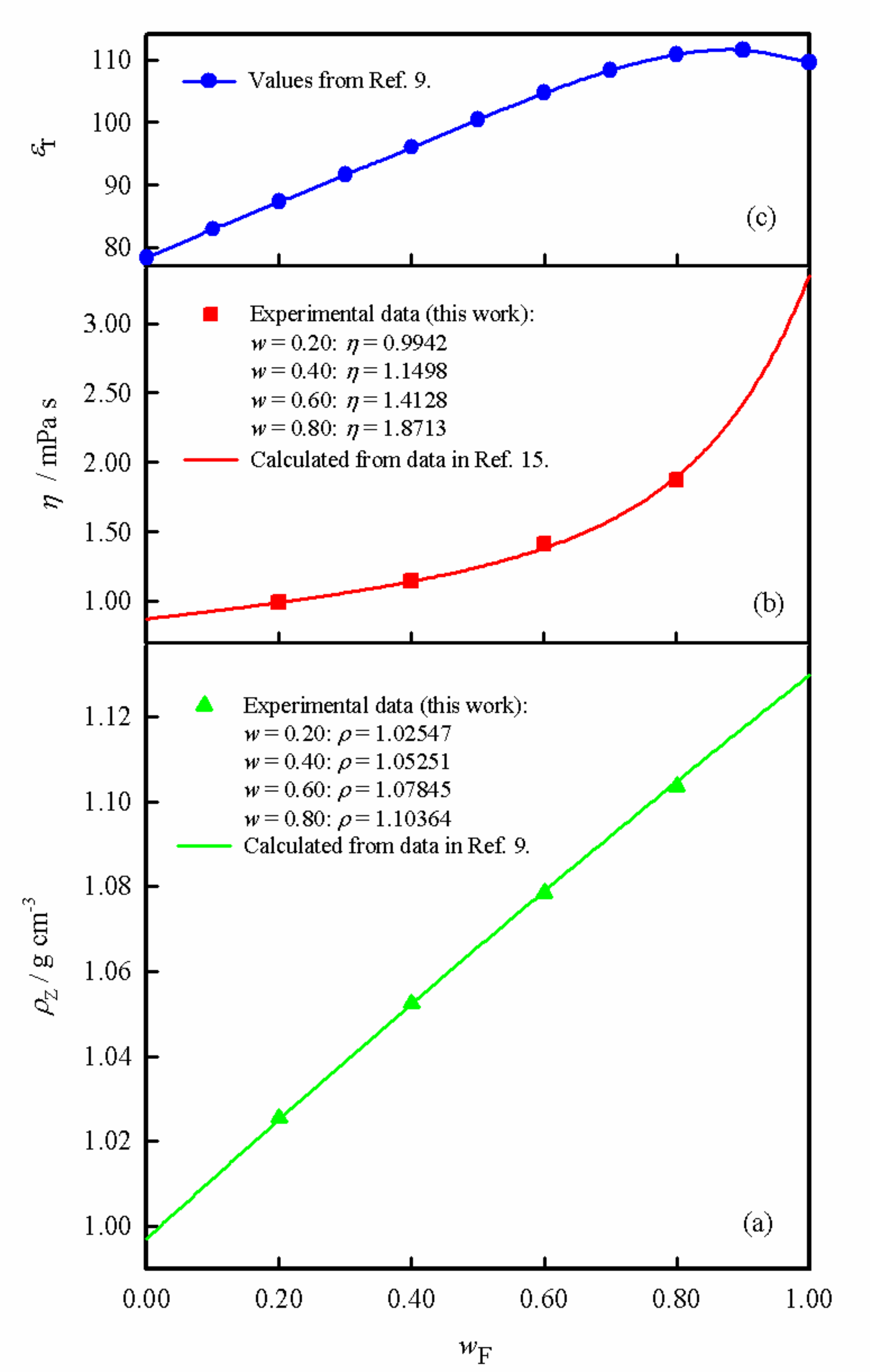

Figure 1. The density (a), the viscosity (b), and the relative permittivity (c) of the formamide + water mixtures (Z) at 298.15 K against formamide mass fraction

Density (ρ_Z) of aqueous mixtures of formamide (Z) was also checked using the above mentioned instrument. The flow times of the mixtures Z were measured at constant working temperature using an Ostwald viscometer previously calibrated with water; the uncertainty in the viscosity measurements was ±1 × 10^{-3} mPa s. Experimental densities and viscosities in the present study are compared with literature data [9,15]. Our results are in good agreement with literature data as can be seen in Fig. 1(a) and (b). The ε_r values of Z at 298.15 K taken from Ref. [9] are also plotted in Fig. 1 as an ilustration (c).

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

Potentiometric measurements were performed using a high input impedance ($>10^{15}$ Ω) Keithley electrometer (model 6514) with sensitivity of ±0.01 mV. A glass electrochemical cell with a liquid junction (see transference cell I), similar to that described by Braun and Weingärtner [3], was manufactured in Šurlan-laboratory glassware (Medulin, Croatia) and set up with two AgCl│Ag electrodes (A) reversible to the Cl^- anion. These electrodes were prepared by the bielectrolytic method [16] in our laboratory. Using a number of AgCl│Ag electrodes of the same material, a maximum bias potential observed in the cell, did not exceed 0.05 mV.

2.2. Potentiometric procedure

The reference and working electrode compartments of the cell I were filled with NaCl solutions. Each set of measurements was performed at a fixed reference molality ($m_{ref.}$ was about 0.05 mol kg^{-1}), with working molalities (m) changing from about 0.005 to 2 mol·kg^{-1}. The glass cell was clamped into a thermostat bath and kept at 298.15 K for about a half of an hour. The three-way stopcock [3] was turned to form a liquid junction between compartments and the cell was tempered for another 30 minutes. After that the pd of two AgCl│Ag electrodes was recorder at intervals of 10 minutes till its steady value recordings; that value would have remained steady for several hours.

3. RESULTS AND DISCUSSION

A summary of the values obtained for NaCl solutions is given in Table 1 as a function of working concentration against a reference one (both in Z).

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

$$E_t / (V) = a_0 + a_1 E + a_2 E^2 \qquad (5)$$

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. (5) to the experimental results are presented in Table 2, together with their standard deviations.

From the first derivate of Eq. (5), according to Eq. (3),

$$t_{\mathrm{Na^+}} = \left(\frac{\mathrm{d}E_{\mathrm{t}}}{\mathrm{d}E}\right)_{\mathrm{m}} = a_1 + 2a_2E \qquad (6)$$

the transference number of Na$^+$ ($t_{\mathrm{Na^+}}$) in all solvent systems studied were evaluated. The resulting transference numbers at 298.15 K are given in Table 1. As seen in Table 1, the values for $t_{\mathrm{Na^+}}$ decrease slightly with increasing NaCl concentration in all solvent systems. Earlier studies of the same electrolyte in water medium have led to similar observations [17].

Using numerical analysis, a third-order polynomial of the general form

$$Y(X) = b_0 + b_1X + b_2X^2 + b_3X^3 \qquad (7)$$

was found to fit the experimental data over the entire concentration range with a very good correlation coefficient, $R^2 \geq 0.9970$. In this expression, Y is the transference number, X is the square-root of molarity, and the coefficients b_0, b_1, b_2, and b_3 were evaluated by the least-squares method and are reported in Table 3, together with their standard deviations. The extrapolation of Eq. (7) to infinite dilution (no ion-ion interactions) gives the limiting transference number of sodium ion ($t^{\mathrm{o}}_{\mathrm{Na^+}}$), *i.e.*, from Eq. (7) follows: $Y(X = 0) = b_0 \equiv t^{\mathrm{o}}_{\mathrm{Na^+}}$. Cation transference numbers of NaCl in water and in Z with $w_{\mathrm{F}} = 0.2$ are also plotted in Fig. 2 as examples. The limiting transference number of sodium ion, determined in aqueous solutions in our laboratory (0.3934), are in good agreement with published data obtained by potentiometric method (0.3959 [4], 0.3910 [5], 0.3962 [18]).

Table 1. Experimental results on solutions of NaCl in (w_{F}) formamide + (1 – w_{F}) water mixtures (Z) at 298.15 K^a

m	ρ	c^b	$a_\pm{}^c$	E^d	E_{t}(obs.)^e	E_{t}(calc.)^f	$t_{\mathrm{Na^+}}{}^g$
w_{F}= 0.2 ($m_{\mathrm{ref.}}$ = 0.0549; $\rho_{\mathrm{ref.}}$ = 1.02767; $c_{\mathrm{ref.}}$ = 0.0562; $a_{\pm,\,\mathrm{ref.}}$ = 0.0457)							
0.0045	1.02566	0.0046	0.0038	–0.12780	–0.05010	–0.05012	(0.3969)
0.0094	1.02584	0.0096	0.0080	–0.08955	–0.03497	–0.03496	0.3946
0.0361	1.02690	0.0370	0.0303	–0.02112	–0.00812	–0.00811	(0.3903)
0.0789	1.02859	0.0808	0.0650	0.01808	0.00717	0.00714	(0.3879)
0.1022	1.02954	0.1046	0.0833	0.03081	0.01210	0.01208	0.3871
0.3513	1.03933	0.3578	0.2621	0.08971	0.03478	0.03477	0.3834
0.5255	1.04590	0.5332	0.3857	0.10957	0.04230	0.04237	(0.3822)
0.7869	1.05582	0.7943	0.5705	0.12968	0.05015	0.05004	0.3809
0.9903	1.06332	0.9954	0.7170	0.14143	0.05433	0.05452	0.3804
1.2043	1.07103	1.2050	0.8803	0.15197	0.05867	0.05852	0.3795
1.3977	1.07801	1.3930	1.0301	0.16005	0.06151	0.06158	0.3790
1.6715	1.08769	1.6563	1.2520	0.17007	0.06532	0.06538	0.3784
1.8281	1.09308	1.8054	1.3857	0.17529	0.06741	0.06735	0.3781
2.0253	1.09983	1.9917	1.5575	0.18129	0.06970	0.06962	0.3777
2.3126	1.14130	2.3251	1.8177	0.18923	0.07258	0.07262	0.3772
w_{F}= 0.4 ($m_{\mathrm{ref.}}$ = 0.0503; $\rho_{\mathrm{ref.}}$ = 1.05449; $c_{\mathrm{ref.}}$ = 0.0529; $a_{\pm,\,\mathrm{ref.}}$ = 0.0413)							

0.0042	1.05266	0.0044	0.0035	–0.12682	–0.05009	–0.05007	0.3970
0.0082	1.05283	0.0086	0.0068	–0.09270	–0.03660	–0.03656	0.3949
0.0114	1.05299	0.0120	0.0094	–0.07606	–0.02991	–0.03000	0.3939
0.0366	1.05396	0.0385	0.0301	–0.01626	–0.00656	–0.00655	0.3904
0.0740	1.05543	0.0778	0.0605	0.01962	0.00742	0.00742	0.3882
0.0978	1.05635	0.1027	0.0796	0.03372	0.01279	0.01288	0.3874
0.3172	1.06481	0.3316	0.2487	0.09226	0.03544	0.03546	(0.3839)
0.5326	1.07295	0.5542	0.4106	0.11802	0.04548	0.04532	(0.3823)
0.7517	1.08111	0.7785	0.5871	0.13639	0.05220	0.05234	0.3812
1.0035	1.09018	1.0334	0.7928	0.15183	0.05839	0.05822	0.3803
1.1994	1.09725	1.2298	0.9571	0.16151	0.06182	0.06190	0.3797
1.4558	1.10626	1.4842	1.1836	0.17242	0.06601	0.06603	0.3791
1.6883	1.11430	1.7123	1.4013	0.18110	0.06926	0.06932	0.3786
1.7966	1.11803	1.8178	1.5055	0.18478	0.07078	0.07071	0.3784
2.1189	1.12915	2.1289	1.8286	0.19477	0.07447	0.07449	(0.3778)
w_F= 0.6 ($m_{ref.}$ = 0.0500; $\rho_{ref.}$ = 1.08037; $c_{ref.}$ = 0.0539; $a_{\pm, ref.}$ = 0.0437)							
0.0059	1.07868	0.0064	0.0052	–0.10938	–0.04380	–0.04385	0.4009
0.0104	1.07882	0.0112	0.0092	–0.08007	–0.03221	–0.03213	0.3985
0.0286	1.07950	0.0308	0.0251	–0.02849	–0.01187	–0.01169	(0.3941)
0.0652	1.08100	0.0702	0.0568	0.01347	0.00499	0.00477	(0.3906)
0.1004	1.08239	0.1080	0.0869	0.03532	0.01344	0.01328	0.3887
0.2004	1.08622	0.2152	0.1700	0.06980	0.02667	0.02664	0.3858
0.3014	1.09002	0.3228	0.2538	0.09040	0.03453	0.03457	0.3841
0.3998	1.09376	0.4273	0.3362	0.10484	0.04002	0.04010	0.3829
0.6072	1.10144	0.6459	0.5138	0.12664	0.04835	0.04843	0.3810
0.8201	1.10924	0.8681	0.7043	0.14284	0.05441	0.05459	0.3796
1.0055	1.11592	1.0598	0.8753	0.15401	0.05886	0.05883	0.3787
1.2199	1.12353	1.2794	1.0846	0.16503	0.06290	0.06299	0.3778
1.4094	1.13013	1.4716	1.2785	0.17348	0.06619	0.06618	0.3771
1.6041	1.13685	1.6673	1.4867	0.18123	0.06929	0.06910	0.3764
1.8088	1.14374	1.8710	1.7012	0.18816	0.07175	0.07171	0.3758

Table 1. (continued)

m	ρ	c^b	$a_\pm{}^c$	E^d	E_t(obs.)^e	E_t(calc.)^f	$t_{Na^+}{}^g$
w_F= 0.8 ($m_{ref.}$ = 0.0503; $\rho_{ref.}$ = 1.10559; $c_{ref.}$ = 0.0554; $a_{\pm, ref.}$ = 0.0452)							
0.0051	1.10377	0.0056	0.0046	–0.11742	–0.04541	–0.04548	(0.3886)
0.0122	1.10409	0.0135	0.0110	–0.07262	–0.02837	–0.02814	0.3859
0.0391	1.10511	0.0431	0.0352	–0.01285	–0.00508	–0.00518	0.3824
0.0666	1.10619	0.0734	0.0599	0.01447	0.00542	0.00524	0.3807
0.1010	1.10747	0.1112	0.0906	0.03573	0.01337	0.01332	0.3795
0.2515	1.11318	0.2759	0.2239	0.08222	0.03094	0.03090	0.3767
0.3081	1.11528	0.3375	0.2749	0.09277	0.03477	0.03487	0.3761
0.4016	1.11873	0.4390	0.3593	0.10653	0.03994	0.04004	0.3753
0.6041	1.12626	0.6572	0.5472	0.12814	0.04804	0.04813	0.3740
0.8069	1.13362	0.8735	0.7469	0.14413	0.05398	0.05411	0.3731
1.0024	1.14059	1.0788	0.9479	0.15637	0.05884	0.05867	0.3723
1.2030	1.14761	1.2899	1.1476	0.16620	0.06225	0.06233	0.3718

1.4077	1.15473	1.5019	1.3542	0.17470	0.06557	0.06548	0.3713
1.6065	1.16160	1.7059	1.5390	0.18128	0.06790	0.06792	0.3709
1.9976	1.17521	2.1022	1.8857	0.19172	0.07185	0.07179	0.3702

[a]Units: m in mol·kg^{-1}; ρ in g·cm^{-3}; c in mol·dm^{-3}; E and E_t in V. [b]Calculated from the density data (ρ) using Eq. (4). [c]Calculated by taking interpolated or extrapolated $\gamma_\pm$ values from Ref. [9]. [d]Calculated pd values for the cell II using Eq. (2). [e]Observed pd values for the cell I. [f]Calculated pd values for the cell I using a second-order polynomial (see Eq. 5). [g]Transference number data for investigated systems (see Eq. 6); calculations of the limiting transference numbers, according Eq. (7), does not include values in brackets.

Table 2. Adjustable coefficients a_0, a_1, and a_2 of Eq. (5) for NaCl in Z at 298.15 K

w_F	a_0	a_1	a_2	$s_f(E_t)$[a]
0.00[b]	–0.00013 ± 0.00002	0.3819 ± 0.0003	–0.0402 ± 0.0029	0.00008
0.20	0.00012 ± 0.00004	0.3890 ± 0.0003	–0.0311 ± 0.0028	0.00009
0.40	–0.00021 ± 0.00004	0.3894 ± 0.0003	–0.0299 ± 0.0029	0.00010
0.60	–0.00049 ± 0.00006	0.3917 ± 0.0006	–0.0422 ± 0.0045	0.00010
0.80	–0.00027 ± 0.00005	0.3816 ± 0.0005	–0.0296 ± 0.0041	0.00010

[a]$s_f(E_t)$ is the standard deviation in V for the fitting of observed data into Eq. (5); calculated E_t values are shown in Table 1. [b]Coefficients for water medium are determined in our laboratory [17].

Table 3. Adjustable coefficients b_0, b_1, b_2, and b_3 of equation of type (7) for NaCl in Z at 298.15 K ($Y = t_{\mathrm{Na}^+}$, $X = c^{1/2}$)

w_F	b_0[a]	b_1	b_2	b_3	$s_f(Y)$[b]
0.00[c]	0.3934 ± 0.0004	–0.0434 ± 0.0022	0.0327 ± 0.0031	–0.0096 ± 0.0013	0.0003
0.20	0.3980 ± 0.0006	–0.0414 ± 0.0035	0.0336 ± 0.0048	–0.0102 ± 0.0019	0.0004
0.40	0.3997 ± 0.0005	–0.0548 ± 0.0036	0.0549 ± 0.0057	–0.0194 ± 0.0025	0.0004
0.60	0.4049 ± 0.0006	–0.0632 ± 0.0035	0.0562 ± 0.0059	–0.0189 ± 0.0027	0.0005
0.80	0.3892 ± 0.0005	–0.0371 ± 0.0027	–0.0296 ± 0.0040	–0.0091 ± 0.0017	0.0003

[a]Coefficient b_0 is equal to the limiting transference number of Na$^+$.[b]$s_f(Y)$ is the standard deviation for the fitting of data into Eq. (7). [c]Values from Ref. [17].

The limiting transference number of Na$^+$ in several different mixtures of (F + W) are given in Fig. 3. Also, the data [5,6,8] for aqueous mixtures of ethylene glycol (EG), acetonitrile (ACN), 1,4-dioxane (D), ethanol (E) and methanol (M) are presented here for comparison.

As it is seen from Fig. 3, additions of co-solvents to water influence $t^{\mathrm{o}}_{\mathrm{Na}^+}$ differently. The position and shape of the upper five curves were interpreted [8] assuming a gradual substitution of water molecules by that of co-solvent in the primary solvation shell around Na$^+$ ion. Such an aggregate interacts with the bulk solvent through the H-bond donor or acceptor sites at the outer positive ends of the new dipoles. Since a formamide molecule has two donor sites as water, $t^{o}_{Na^+}$ departs only slightly from the water value, 0.3934.

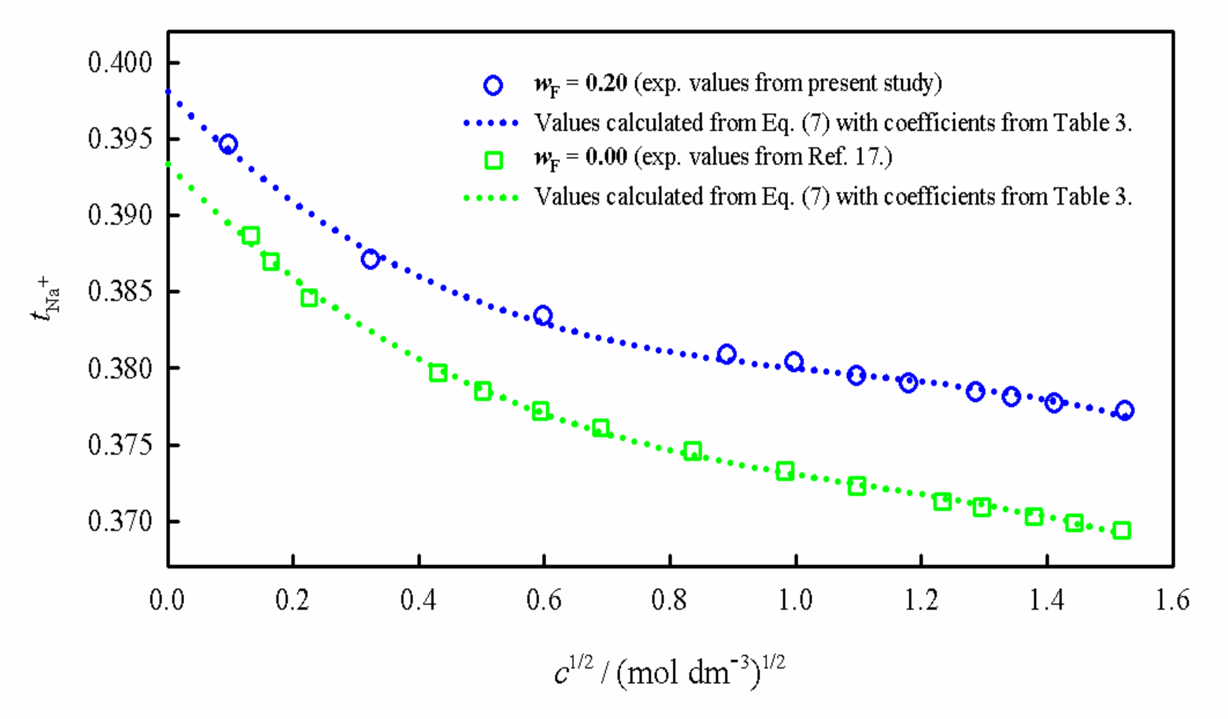

Figure 2. Plots of transference number against (molarity)$^{1/2}$ of NaCl at 298.15 K in Z with formamide mass fraction w_F = 0.00 and w_F = 0.20. The values of $t^{o}_{Na^+}$ are obtained from curve intercept on y-axe

Curves for aqueous mixtures of formamide and ethylene glycol are very similar in shape and position of maxima. It seems that the ratio of aqueous to organic molecules of 2:1, corresponding to w_F = 0.56 and to w_{EG} = 0.63, favors the formation of the most developed three-dimensional structure containing the greatest fraction of saturated bonds, because Na^+ would exhibit the highest mobility in such a mixture (Fig. 3).

The limiting ion conductances of Na^+ and Cl^- (λ^o) have been calculated using $t^{o}_{Na^+}$ from the present work and interpolated Λ^o values of NaCl from literature [14]. The values obtained for investigated systems are reported in Table 4, together with literature values for water [19], and formamide [20]. As can be observed each λ^o for sodium ion is lower than the corresponding value for chloride ion; stronger solvation of Na^+ enlarges its hydrodynamic radius. For both ions λ^o decreases with increasing formamide content in the mixture, which is mainly determined by an opposite trend in viscosity. Differences in hydrodynamic radius are reflected in the ionic Walden product ($\lambda^o\eta$). The variation of Walden product with solvent composition can be explained through change in ion solvation. For both ions Walden product decreases in direction of increasing formamide content in the mixture, and consequently the solvation is strengthened in that direction.

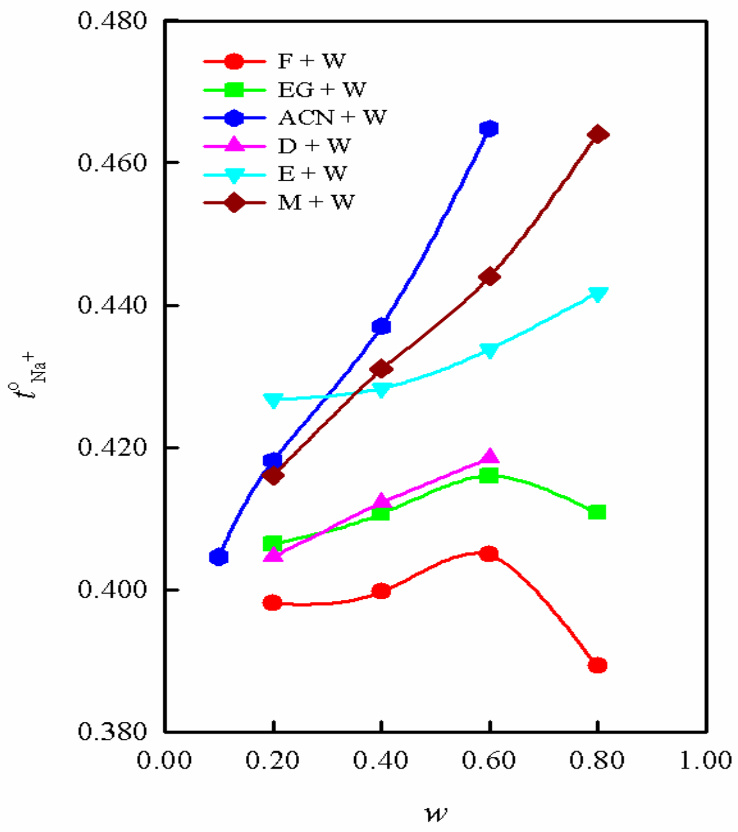

Figure 3. Limiting transference number of Na^+ (NaCl) in different aqueous mixtures with formamide (F; our data), ethylene glycol (EG; [8]), acetonitrile (ACN; [8]), 1,4-dioxane (D; [8]), ethanol (E; [6]), and methanol (M; [5]) at 298.15 K; w denotes mass fraction of non-aqueous solvent in mixture.

Table 4. Limiting molar conductivities of Na^+ and Cl^- ions in formamide + water mixtures at 298.15 K

w_F	λ^o / S cm^2 mol^{-1}	
	Na^+	Cl^-
0.00[a]	50.20	76.34
0.20	45.97	69.53
0.40	39.05	58.65
0.60	30.00	44.10
0.80	19.42	30.48
1.00[b]	9.88	17.46

[a]Values from Ref. [19]. [b]Values from Ref. [20].

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