

Conductances of Sodium Perchlorate & Thiocyanate in Tetramethylurea

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Conductances of NaClO_4 and NaSCN have been determined in tetramethylurea (TMU) at 25°, 30°, 35° and 40°C. Limiting equivalent conductances (Λ_0) and association constants (K_A) of these salts have been determined by Fuoss-Onsager-Skinner equation as well as by Fuoss-Hsia equation as expanded by Fernandez-Prini. Transference numbers of NaSCN have also been measured in TMU at various temperatures to calculate limiting ionic conductances ($\lambda_{\pm}^0$). The $\lambda_{\pm}^0$ increases by about 2.2% per degree rise in temperature for all the ions in TMU.

Conductances and transference numbers of sodium perchlorate and thiocyanate in tetramethylurea (TMU) have been measured at 25°, 30°, 35° and 40°C to throw light on the effect of temperature on ion-solvent interactions. This investigation is in continuation of our earlier similar work¹⁻³.

Tetramethylurea (Fluka AG) was purified as reported earlier¹. Sodium perchlorate (Riedel) was recrystallised twice from conductivity water, dried at 250°C for two hr and cooled in a vacuum desiccator over phosphorus pentoxide. Sodium thiocyanate (BDH, AR) was used after drying *in vacuo* for 2-3 hr.

Conductance⁴ and transference number¹ were measured as reported. The viscosities and densities of TMU needed for calculations at different temperatures were measured as described previously⁵. Dielectric constants were measured with a dielectrometer based on heterodyne beat method⁶ at a frequency of 100 KHz. The liquid cell was calibrated

using purified and dried decalin, chlorobenzene and nitrobenzene.

Conductances of NaClO_4 and NaSCN have been measured in the concentration range $5-53 \times 10^{-4}$ g equiv. litre⁻¹ in TMU at 25°, 30°, 35° and 40°C. The conductance data have been analysed by the Fuoss-Onsager-Skinner (FOS) equations⁷ as described previously⁸. The analysis of the data reveals that NaClO_4 is unassociated while NaSCN is associated at all temperatures (Table 1).

The conductance data have also been treated by more accepted⁹ expressions (Eqs 1-3) for conductance of symmetrical electrolytes in dilute solutions:

$$\Lambda = \gamma[\Lambda_0 - S(C\gamma)^{1/2} + EC\gamma \log C\gamma + JC\gamma + J_{3/2}(C\gamma)^{3/2}] \quad \dots (1)$$

$$K_A = \frac{1-\gamma}{\gamma^2 C f_{\pm}^2} \quad \dots (2)$$

$$\ln f_{\pm} = -\frac{A(C\gamma)^{1/2}}{1 + BR(C\gamma)^{1/2}} \quad \dots (3)$$

The above equations are obtained by expanding¹⁰⁻¹² the Fuoss-Hsia expression¹³, where the symbols have the usual significance. The distance parameters in Eq. (1), i.e. J and $J_{3/2}$ have been taken to be equal to Bjerrum critical distance, $q = z^2 e^2 / 2DkT$. The expressions for J and $J_{3/2}$ used here are those given by Fernandez-Prini¹⁰. Under these conditions, conductance depends upon two parameters Λ_0 and K_A which were adjusted by the least squares method to fit the experimental data. The values of Λ_0 and K_A obtained by this method are also reported in Table 1.

It is apparent from Table 1 that unlike K_A values, the Λ_0 values obtained by the two methods do not differ significantly. NaClO_4 has been found to be dissociated

Table 1—Conductance Parameters of NaClO_4 and NaSCN at Different Temperatures in TMU Obtained by⁴ Fuoss-Onsager-Skinner (FOS) and Fuoss-Hsia-Fernandez-Prini (FHFP) Treatment

Temp. 0°C	FOS			FHFP		
	Λ_0	K_A	$\sigma\Lambda$	Λ_0	K_A	$\sigma\Lambda$
NaClO_4						
25	44.57 ± 0.09	—	0.12	44.40 ± 0.05	41.0 ± 1.0	0.05
30	49.67 ± 0.11	—	0.13	49.56 ± 0.09	51.6 ± 1.6	0.09
35	54.53 ± 0.11	—	0.11	54.40 ± 0.09	55.9 ± 1.5	0.09
40	59.20 ± 0.09	—	0.11	58.97 ± 0.08	57.3 ± 1.2	0.07
NaSCN						
25	48.94 ± 0.05	47.4 ± 7.2	0.04	49.16 ± 0.06	126.9 ± 2.6	0.06
30	53.29 ± 0.06	60.8 ± 8.2	0.06	53.57 ± 0.06	134.1 ± 1.3	0.05
35	57.71 ± 0.03	72.3 ± 2.4	0.02	57.96 ± 0.01	145.0 ± 0.2	0.01
40	64.14 ± 0.08	84.0 ± 11.0	0.05	64.32 ± 0.06	152.5 ± 1.4	0.04

by FOS treatment but associated according to Fuoss-Hsia-Fernandez-Prini (FHFP) treatment. NaSCN has higher K_A values at all temperatures by FHFP treatment as compared to those obtained by FOS treatment. The differences in K_A may be attributed to the influence of terms of the order $(C\gamma)^{3/2}$, the Bjerrum distance used in J and $J_{3/2}$ and the use of more complete Debye-Huckel expression for the activity coefficients in the second treatment. This is in agreement with the views expressed by many other workers^{11,12,14}.

During the last decade, a number of equations have been proposed to analyse the conductance data. The precision of these equations is of a very high degree. As the precision of our conductance data is $\Lambda_0 \approx \pm 0.02$ which can provide sufficient data for comparative study, the use of other equations has not been thought appropriate to analyse the present data.

The association constants increase with temperature. This observation is similar to one recorded earlier by Banewicz *et al.*¹⁵ in the case of Et_4NClO_4 in valeronitrile, a solvent having a dielectric constant ($D = 20.3$ at 25°C) very close to that of TMU. Increase in K_A values with increase in temperature may be due to a decrease in the dielectric constant.

Transference numbers of NaSCN have been measured in the concentration range $2.1\text{--}7.1 \times 10^{-2}$ gequiv. litre⁻¹ at 30° , 35° and 40°C . The cation transference number has been found to decrease linearly with $\sqrt{C}$ and limiting cation transference number (t_+^0) has been obtained by extrapolation of the plots of t_+ versus $c^{1/2}$ and the values are 0.327, 0.338, 0.347 and 0.356 at 25° , 30° , and 40°C respectively. The values at 25°C are taken from our previous publication¹. It is observed that t_+^0 increases with increase in temperature. A similar behaviour has already been observed in other solvents including water^{16,17}.

Limiting ionic conductances of Na^+ and SCN^- ions at all temperatures have been calculated from t_+^0 and Λ_0 of NaSCN from the reaction,

$$\lambda_+^0 = \Lambda_0 \times t_+^0 \quad \dots (4)$$

The limiting equivalent conductances of ClO_4^- ion are obtained from corresponding Λ_0 values of NaClO_4 and λ_+^0 of Na^+ ion at that temperature employing Kohlrausch law of independent migration of ions. The

Table 2—Limiting Ionic Conductances* of Na^+ , SCN^- and ClO_4^- in TMU at Different Temperatures

Ion	$\lambda_{\pm}^0$ at			
	25°	30°	35°	40°
Na^+	16.08	18.11	20.11	22.90
SCN^-	33.08	35.46	37.85	41.42
ClO_4^-	28.32	31.45	3.29	36.07

*Values used for calculating

$\lambda_{\pm}^0$ are those obtained by FHFP analysis.

results, given in Table 2, show that the ionic mobility of the ClO_4^- ion is less than that of the SCN^- ion at all temperatures. This may be attributed to the larger solvation of the ClO_4^- due to its tetrahedral geometry; the SCN^- ion is linear. Further the limiting ionic conductances of an ion increase with the rise in temperature. The increase is of about 2.2% per degree for all ions in TMU and is the same order of magnitude as in other amide solvents^{16,17}.

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