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Electrical Conductance of a Mixture of Sodium and Potassium Thiocyanates in Aqueous Medium at 25 °C

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Electrical conductance measurements of $[x\text{NaSCN}+(1-x)\text{KSCN}]+R\,\text{H}_2\text{O}$ system were made as functions of x and R at 25 °C. The mixed alkali effect was found to be negligible when $R>10$ and it increased sharply with increase in concentration in the range $R\leqslant 10$. The concentration dependence of molar conductance (Λ) has been described satisfactorily by the expression, $\Lambda=\Lambda_{\text{FH}}\exp(Bm+Cm^2)$ where Λ_{FH} is the Falkenhagen-Leist-Kelbg equation for Λ, m is the molality and the parameters B and C are the empirical constants.

In a glassy or molten medium containing mixed alkali ions deviations from additivity are observed in isotherms of various physical properties as a function of composition which is varied by progressively replacing one alkali ion by another.[1,2] This phenomenon is termed as the mixed alkali effect (MAE) and it is most pronounced for properties related to ionic transport. For instance, in glasses of constant alkali content the electrical conductivity of mixed glasses can be reduced by a factor of about 10^4 or 10^5 in comparison with the conductivity of single alkali glasses measured at the same temperature.[3] According to Ingram et al.[4] such large departures from additivity indicate a major breakdown of the principle of independent migration of ions which works well for dilute aqueous electrolytes.

Recently attempts have been made to look for MAE in media other than glassy or molten media. Aqueous medium is one of such suitable medium. There are some very old reports on the conductivities of mixed aqueous electrolytes containing alkali halides and nitrates.[5] In recent years only one report is made on the study of MAE in aqueous medium.[4] One of the characteristics of MAE is that it shows a complicated dependence on the total alkali ion concentration.[6] With a view to understanding better the dependence of MAE on the total alkali ion concentration we have made in the present study measurement of electrical conductance of a mixture of NaSCN and KSCN in aqueous medium with varying amounts of water.

Experimental

Molal solutions were prepared using recrystallized NaSCN (SD, R grade) and KSCN (SD, R grade). Before using these salts they were dried for several days over CaCl_2 in vacuum desiccator. Conductivity measurements were made using the CDM83 conductivity meter (Radiometer, Copenhagen) and a dip-type CDC304 conductivity cell. The instrument was calibrated by adjusting the cell constant knob of the instrument till the specific conductance value of the reference solution (0.1 M KCl (1 M=1 mol dm^{-3})) was displayed. For measuring density a calibrated glass pycnometer was used. All measurements were made in a thermostated (±0.02 °C) water bath.

Results and Discussion

The experimental values of molar conductance (Λ) at 25 °C of $[x\ \text{NaSCN}+(1-x)\ \text{KSCN}]+R\text{H}_2\text{O}$ system as functions of x and R are presented in Table 1. The molar concentrations (c) of these solutions are also evaluated using the measured density values and are included in Table 1. The present values of Λ of NaSCN and KSCN solutions are found to be in good agreement with the reported data[7,8] as apparent from Fig. 1. In the case of KSCN solution since the literature values of Λ at 25 °C were not readily available, the comparison of the experimental and reported data[8] was made at 20 °C. The measured values of conductance were found to be reproducible within ±0.75% accuracy.

Variation of Λ with x. The variation of Λ with x at different R values is shown in Fig. 2. Λ tends to deviate more and more from additivity as R decreases. The non-additivity in Λ are represented here in terms of r-factor defined as $r=[x\Lambda_1+(1-x)\Lambda_2]/\Lambda$, where Λ_1 is

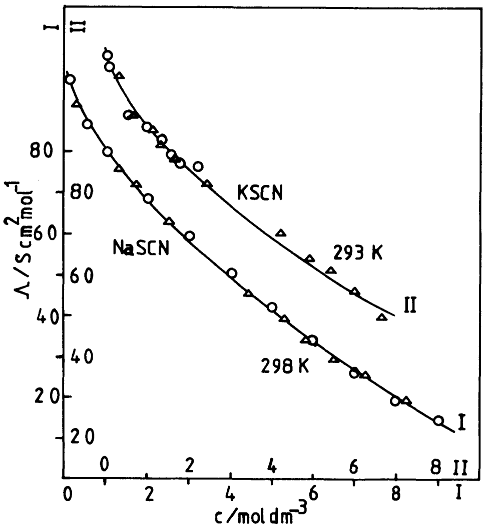

Fig. 1. Plots of Λ vs. molar concentration for NaSCN and KSCN solutions (Δ-experimental, O-reported).

Table 1. Molar Conductance of $[x\ \mathrm{NaSCN}+(1-x)\mathrm{KSCN}]+R\mathrm{H_2O}$ System at 25 °C as Functions of x and R

x	$\Lambda\pm0.75\%/\mathrm{S\,cm^2\,mol^{-1}}$				
	R=4	R=5	R=6	R=7	R=8
0.0	44.1	53.1	60.2	65.0	68.8
	(7.8275)	(6.8685)	(6.1212)	(5.4788)	(4.9751)
0.1	41.1	50.0	56.6	61.7	65.8
	(7.8902)	(6.898)	(6.1481)	(5.5052)	(5.0184)
0.2	37.8	46.5	53.1	58.3	62.4
	(7.9436)	(6.9511)	(6.1832)	(5.5310)	(5.0329)
0.3	34.5	43.2	49.6	54.8	58.1
	(8.0101)	(6.987)	(6.2264)	(5.5665)	(5.0591)
0.4	31.5	40.2	46.6	51.6	54.9
	(8.0733)	(7.0397)	(6.2246)	(5.5909)	(5.0913)
0.5	29.0	37.2	43.4	48.5	52.1
	(8.1166)	(7.0815)	(6.2838)	(5.6295)	(5.1169)
0.6	26.2	34.5	40.5	45.0	49.0
	(8.1845)	(7.1194)	(6.3132)	(5.678)	(5.1478)
0.7	24.5	32.0	37.1	41.9	46.4
	(8.2228)	(7.1529)	(6.3786)	(5.7185)	(5.1554)
0.8	22.4	29.6	34.4	38.8	43.5
	(8.2805)	(7.1959)	(6.4192)	(5.7601)	(5.226)
0.9	21.1	27.1	31.8	36.1	40.6
	(8.3073)	(7.2473)	(6.4659)	(5.7903)	(5.2509)
1.0	19.0	25.3	29.0	33.5	38.0
	(8.3774)	(7.2761)	(6.5308)	(5.8305)	(5.2775)

x	$\Lambda\pm0.75\%/\mathrm{S\,cm^2\,mol^{-1}}$				
	R=10	R=20	R=30	R=100	R=200
0.0	75.4	89.3	95.8	108.2	—
	(4.2205)	(2.3948)	(1.6684)	(0.5324)	
0.1	72.2	86.3	—	—	110.3
	(4.2479)	(2.3968)			(0.2705)
0.2	68.7	83.2	90.0	103.4	108.8
	(4.2647)	(2.409)	(1.6738)	(0.5328)	(0.2705)
0.3	65.3	81.3	—	—	106.1
	(4.2835)	(2.4145)			(0.2708)
0.4	62.5	78.3	—	97.6	103.3
	(4.3022)	(2.4175)		(0.5334)	(0.2710)
0.5	59.1	76.3	83.8	95.5	101.5
	(4.3268)	(2.4325)	(1.6781)	(0.5338)	(0.2713)
0.6	56.0	73.1	81.2	93.0	100.1
	(4.341)	(2.4365)	(1.6812)	(0.534)	(0.2709)
0.7	53.2	—	79.3	—	97.2
	(4.3434)		(1.6849)		(0.2708)
0.8	50.1	67.4	77.2	86.6	95.6
	(4.3949)	(2.4546)	(1.6874)	(0.5342)	(0.2710)
0.9	47.6	64.7	75.0	85.3	—
	(4.3983)	(2.4603)	(1.6917)	(0.5351)	
1.0	45.1	62.7	71.1	82.4	90.8
	(4.4232)	(2.4801)	(1.6994)	(0.5359)	(0.2713)

Molar concentration data are within the parentheses.

the molar conductance of NaSCN solution and Λ_2 that of KSCN solution. The dependence of r on concentration is illustrated in Fig. 3 for x=0.5. r varies negligibly upto a particular concentration and thereafter increases sharply with increasing concentration. Similar trend in the variation of r-factor with R is found at other x values also. Such a dependence of r on R therefore clearly indicates that the MAE is dependent on the total alkali ion concentration. For the system under study the value of r appears to increase sharply above ca. 10R (ca. 5.6 m) concentration. It is interesting to note that this concentration falls in the range where the specific conductance of NaSCN solution becomes maximum. Moreover, in this concentration range the viscosity of NaSCN solution starts increasing exponentially with concentration.[7,9] Every electrolytic solution exhibits a particular concentration range of this type and it is identified as the region where a transition from primitive structure to quasi-crystalline structure takes place.[10,11] For KSCN solution such a concentration range of structural transition falls around ca. 6*R* (ca. 9.2 m). In a mixed electrolyte containing NaSCN and KSCN a quasi-crystalline type structure may therefore be considered to start appearing from ca. 10*R* and the extent of quasi-crystallinity keeps on increasing beyond this concentration. Therefore in aqueous medium the MAE seems to become significant when the solution attains a quasi-crystalline type structure. This inference is in accordance with the empirical fact that the MAE is much prominant in the glassy media having very rigid-like structure. In the present system of interest the MAE observed for the highest concentration (=4*R*) studied is about 8.6%, i.e., the percentage of deviation of Λ from additivity.

The dependence of *r*-factor or MAE on concentration may be explained in terms of the anion polarization model.[12,13] According to this model, the MAE is due to the asymmetry created in the electrical field around the thiocyanate ion owing to its competitive polarization by the unlike cations. Such a competitive polarization can cause significant MAE only when the ionic concentration is large enough. Moreover, the effect of competitive polarization is expected to be maximum when the two cations are in equal concentration. This is, in fact, observed as evident from the plot (Fig. 3) of *r* vs. *x* which passes through a maximum in the range *x*=ca. 0.5.

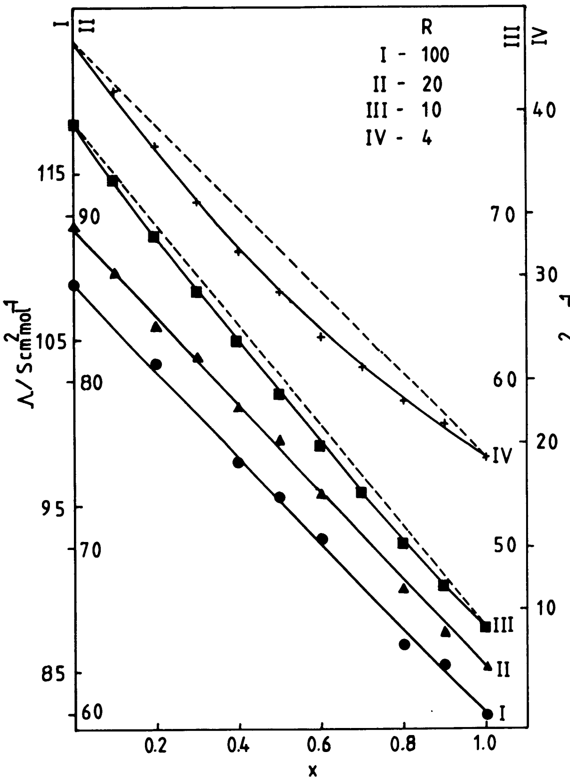

Fig. 2. Variation of Λ of [*x* NaSCN+(1−*x*)KSCN]+ *R*H$_2$O system with *x* at different *R* values.

Variation of Λ with *R*. A successful theoretical expression is not available to describe the concentration dependence of Λ in the higher concentration range. Recently we have reported[11] an expression of the form

$$\Lambda = \Lambda \exp(Bm + Cm^2) \qquad (1)$$

for describing the conductance of aqueous electrolytes upto very high concentrations. In Eq. 1 Λ, B, and C are adjustable parameters. This equation was shown to be obtainable from the Adam–Gibbs configurational entropy model.[14] However, Eq. 1 was found to be only partly successful in describing the conductance data of concentrated aqueous solutions. The incomplete success of Eq. 1 was attributed to the fact that this expression accounts only for the short-range interactions in the solution. An attempt has been made here to improve Eq. 1 by accounting for the long-range interactions. This is achieved by substituting Λ_{FH} term for Λ where Λ_{FH} refers to the Falkenhagen–Leist–Kelbg[15] equation for Λ and is of the form

$$\Lambda_{FH} = \left(\Lambda_o - \frac{B_1 c^{1/2}}{1 + B_o a_o c^{1/2}}\right)\left(1 - \frac{B_2 c^{1/2} F}{1 + B_o a_o c^{1/2}}\right) \qquad (2)$$

B_1=82.501/$\eta_o(DT)^{1/2}$, B_2=82.04×10^4/$(DT)^{3/2}$, B_o=50.29/$(DT)^{1/2}$, and F=(exp(0.2929$B_o a_o$)−1)/0.2929$B_o a_o$. Λ_o is the equivalent conductance of the solution at infinite dilution, η_o is the vicosity of water, D is the dielectric constant of water, and T is the absolute temperature. a_o is a term which accounts for the finite size of the ions and is known as the ion-size parameter. The conductance data of the system under study were therefore least squares fitted to the equation

$$\Lambda = \Lambda_{FH} \exp(Bm + Cm^2). \qquad (3)$$

For least-squares fitting the conductance data to Eq. 3,

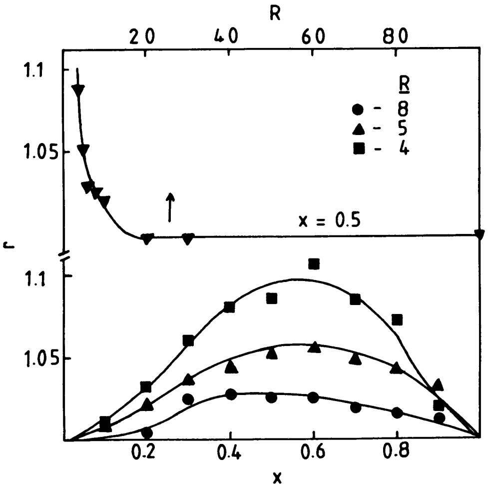

Fig. 3. Variation of *r* of [*x*NaSCN+(1−*x*)KSCN]+ *R*H$_2$O system with *R* and *x*.

Table 2. Best-Fit Values of the Parameters of Eq. 3 for the Molar Conductance of $[x\mathrm{NaSCN}+(1-x)\mathrm{KSCN}]+R\mathrm{H_2O}$ System at 25 °C

x	$\Lambda_0/\mathrm{S\,cm^2\,mol^{-1}}$	$a_0\times10^8$	B	$C\times10^2$	Std. dev. in Λ
0.0	139.6[a)]	5.78	−0.0325	−0.1022	0.212
0.1	137.3[b)]	5.05	−0.0293	−0.1394	0.270
0.2	135.0[b)]	5.57	−0.0403	−0.0984	0.150
0.3	132.7[b)]	5.28	−0.0418	−0.1193	0.511
0.4	130.4[b)]	4.99	−0.0425	−0.1423	0.520
0.5	128.1[b)]	5.25	−0.0490	−0.1338	0.877
0.6	125.7[b)]	5.58	−0.0588	−0.1059	0.737
0.7	123.4[b)]	5.57	−0.0661	−0.0791	0.999
0.8	121.1[b)]	5.31	−0.0677	−0.1026	1.4111
0.9	118.8[b)]	5.43	−0.0780	−0.0499	1.478
1.0	116.5[a)]	5.27	−0.0798	−0.0799	1.257

a) Literature value. b) Estimated values using additivity principle.

we have chosen in the case of solutions with $x=0$ and $x=1$ the reported values of Λ_0 and for compositions with x values other than 0 or 1 the Λ_0 values are estimated using the additivity principle. Therefore Eq. 3 becomes an expression with three adjustable parameters. The best-fit values of a_0, B, and C corresponding to the lowest standard deviations were computed and are given in Table 2.

The value of $a_0=5.27$ Å for NaSCN solution is comparable with the value 5.5 Å reported for this solution by Janz et al.[7)] The higher value for $a_0=5.78$ Å of KSCN is expected due to the larger ionic size of the $\mathrm{K^+}$ ion. For the mixed electrolyte, however, no regular trend in the variation of a_0 with x has been observed. It may be pointed out as suggested by others[17)] also that a_0 behaves more like an adjustable parameter than a physically significant parameter.

The value of B appears to decrease with increasing x. A comparison of Eq. 3 with the Wishaw-Stokes[18)] equation reveals that the exponential part of Eq. 3 is related to the viscosity of the solution. Accordingly, a decrease in the value of B with increasing x appears to be due to the increasing viscosity of the solution as the content of NaSCN increases. We also made an attempt to estimate the viscosity of NaSCN solution at different concentrations by equating $\exp(Bm+Cm^2)$ to the reciprocal of the relative viscosity. The viscosity of NaSCN solution estimated in this fashion was found to be in agreement with the experimental values[7)] only at lower concentrations. This envisages that the Wishaw-Stokes equation[18)] can describe the conductance data only at concentrations where the relative viscosity is low.[19)] Furthermore, it may be seen that Eq. 3 reduces to the form of Postler equation[20)] at low concentrations.

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