drogen bonds since only relatively few $CHCl_3$ molecules are present (*3*, *4*). The net increase in interaction that results should cause η^E to be positive. This does occur for the methanol-chloroform system, which shows η^E to be mainly positive with a maximum value of +0.1 cP. It also occurs to a lesser extent for ethanol (η^E_{max} = +0.02 cP).

The 1-propanol system never exhibits a positive excess viscosity. Apparently the longer alkyl chain diminishes the chloroform-alcohol interactions enough that all η^E are negative. Thus, it is likely that higher straight-chain alcohols will all exhibit negative excess viscosities throughout the entire range of compositions.

The effect of a temperature increase is, in all cases, to break interactions and permit easier flow. This tends to diminish differences between solutions. The result is low absolute values of η^E at higher temperatures. This can be seen in all three of the figures. It is particularly striking in the case of ethanol-chloroform. Figure 2 exhibits a crossover point at $X_{CHCl_3} \sim 0.4$. The high-temperature η^E values are less positive and less negative.

Glossary

d	density (g/mL)
ΔH_{mix}	enthalpy of mixing
ΔV_{mix}	volume of mixing
η	viscosity (cP) of a mixture
η^E	excess viscosity (cP) as defined in eq 1
X_{CHCl_3}	mole fraction of chloroform

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Temperature and Concentration Dependence of Electrical Conductance of a Mixture of Sodium and Potassium Thiocyanates in Aqueous Medium

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Molar conductance and density of the [xNaSCN + (1 − x)KSCN] + RH_2O system were measured as functions of x, R, and temperature (283–323 K). Deviation of molar conductance from additivity occurs at all the temperatures in the region $R \leq 10$. The amount of this deviation is found to be independent of temperature. The isothermal concentration dependence of molar conductance was described by the expression $\Lambda = \Lambda_{FLK} \exp(Bc + Cc^2)$, where Λ_{FLK} is the Falkenhagen–Leist–Kelbg equation for Λ. B and C are empirical constants, and c is the molar concentration. The temperature dependence of Λ has been described by the Vogel–Tammann–Fulcher equation.

Introduction

Data on the transport properties of mixed electrolytes in the aqueous medium are scarce in the literature. Recently, we reported (*1*) the electrical conductance of the [xNaSCN + (1 − x)KSCN] + RH_2O system as functions of x and R at 298 K. Deviation of molar conductance from additivity known as the mixed-alkali-metal effect was observed in this system in the region where $R \leq 10$. Reported here are the molar conductance and density values of this mixed electrolytic system at various other temperatures, from 283 to 323 K.

Experimental Section

Molal solutions were prepared by using recrystallized NaSCN (SD, reagent grade) and KSCN (SD, reagent grade). Conductivity measurements were made at 1 kHz with use of the CDM83 conductivity meter (Radiometer, Copenhagen) and a dip-type CDC304 conductivity cell. This cell has three electrodes in the form of pure platinum bands on a glass tube. Densities of the solutions were measured by using a calibrated glass pycnometer of about 7-cm^3 capacity. All measurements were made in a thermostated (±0.02 °C) water bath.

Results and Discussion

The experimental values of molar conductance, Λ, of the [xNaSCN + (1 − x)KSCN] + RH_2O system as functions of x, R, and temperature are presented in Table I. The density data are presented as a linear function of temperature in Table II. In order to examine the occurrence of deviation of Λ from additivity, the r factor, defined as $r = \Lambda_{add}/\Lambda$, is plotted against R in Figure 1 for x = 0.5. Λ_{add} is the molar conductance of the mixture of thiocyanates calculated by using the additivity principle. It is apparent from Figure 1 that at all the experimental temperatures significant deviation of Λ from additivity occurs around $R \leq 10$ only. The amount of deviation is also found to be almost independent of temperature in the range from 283 to 323 K, as evident from Figures 2 and 3.

Earlier we reported (*1*) a new semiempirical equation to describe the isothermal concentration dependence of Λ, which is of the form

$$\Lambda = \Lambda_{FLK} \exp(Bm + Cm^2) \quad (1)$$

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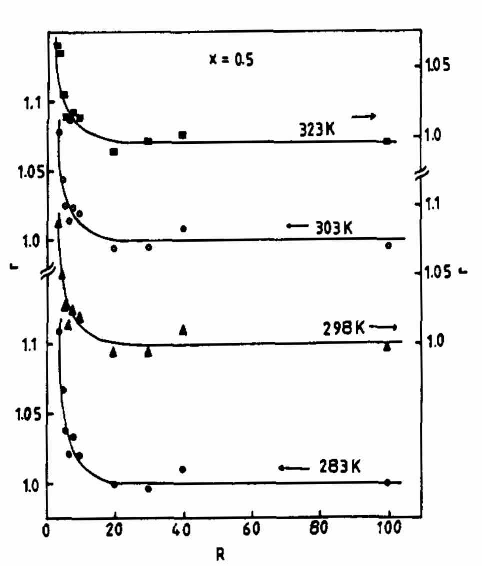

Figure 1. Variations of r for the $[x\text{NaSCN} + (1 - x)\text{KSCN}] + R\text{H}_2\text{O}$ system with R at different temperatures.

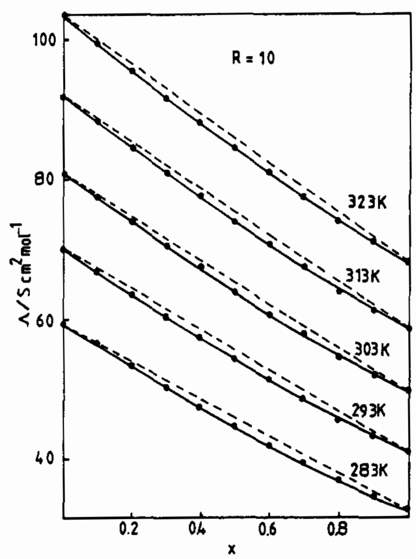

Figure 2. Plot of Λ of the $[x\text{NaSCN} + (1 - x)\text{KSCN}] + R\text{H}_2\text{O}$ system vs x at different temperatures for $R = 10$.

where Λ_{FLK} is the Falkenhagen-Leist-Kelbg (2) equation for Λ and it is of the form

$$\Lambda_{\text{FLK}} = \left(\Lambda_0 - \frac{B_1 c^{1/2}}{1 + B_0 a_0 c^{1/2}}\right)\left(1 - \frac{B_2 c^{1/2} F}{1 + B_0 a_0 c^{1/2}}\right) \quad (2)$$

$B_0 = 50.29 \times 10^8/(\epsilon_0 T)^{1/2}$, $B_1 = 82.5/(\eta_0(\epsilon_0 T)^{1/2})$, $B_2 = 8.204 \times 10^5/(\epsilon_0 T)^{3/2}$, and $F = (\exp(0.2929 B_0 a_0 c^{1/2}) - 1)/(0.2929 B_0 a_0 c^{1/2})$. Λ_0 is the molar conductance of the solution at infinite dilution, c is the concentration in mol·dm^{-3}, a_0 is the ion-size parameter, ϵ_0 is the dielectric constant of water, η_0 is the viscosity of water, and T is the absolute temperature. In eq 1, B and C are empirical constants. It may be noticed that in eq 1 the molal concentration (m) unit is used in the exponential part, whereas in the Λ_{FLK} part the molar concentration (c) unit is used. Since B and C are employed as freely adjustable parameters during least-squares fitting, it is expected that in the exponential part of eq 1 also it is possible to use the molar concentration scale. Therefore in the present study using two different concentration units in the same equation is avoided by least-squares fitting, using the iteration program, the Λ data to an equation of the form

$$\Lambda = \Lambda_{\text{FLK}} \exp(Bc + Cc^2) \quad (3)$$

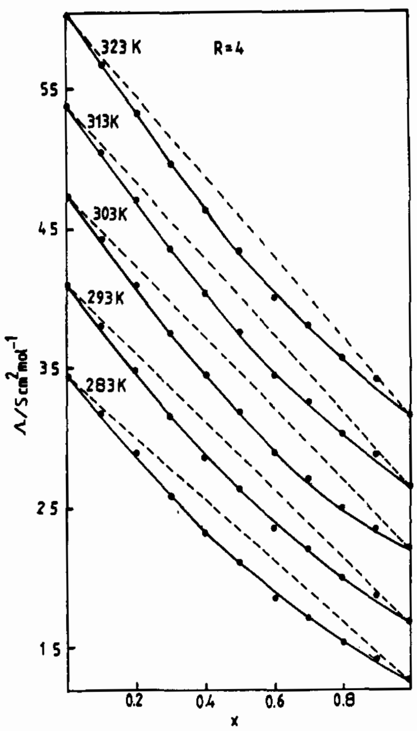

Figure 3. Plot of Λ of the $[x\text{NaSCN} + (1 - x)\text{KSCN}] + R\text{H}_2\text{O}$ system vs x at different temperatures for $R = 4$.

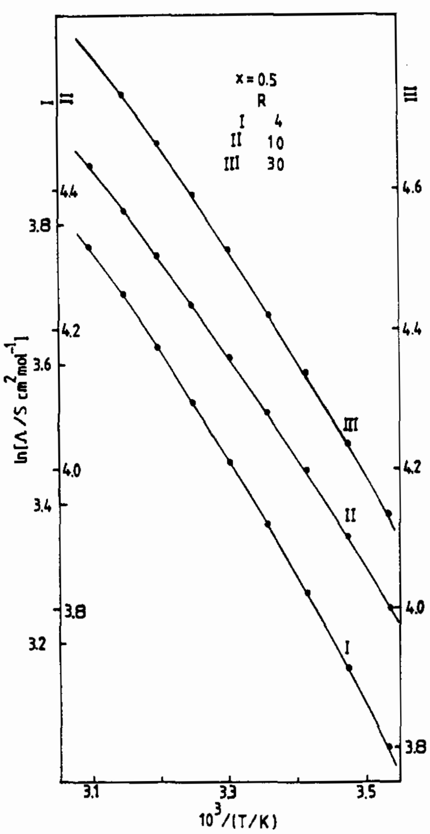

Figure 4. Plot of ln Λ of the $[x\text{NaSCN} + (1 - x)\text{KSCN}] + R\text{H}_2\text{O}$ system vs $1/T$ at different R values for $x = 0.5$.

During data fitting, the reported values (3) of the molar conductance at infinite dilution (Λ_0) were introduced into eq 3, as described earlier (1). The best-fit values of the three parameters of eq 3, viz., a_0, B, and C, are listed in Table III (supplementary material). No regular trends in the variations of these three parameters with x and temperature have been observed. At all the temperatures and x values, C has negative values. On the other hand, at all x values, B is found to be

Table I. Molar Conductance Data for [xNaSCN + (1 - x)KSCN] + RH_2O System

	$\Lambda/(S\ cm^2\ mol^{-1})$								
R	283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.0				
100	80.0	89.0	98.7	108.2	118.2	128.4	139.1	149.6	160.4
40	75.1	83.2	91.4	99.7	108.2	116.9	125.6	134.2	142.7
30	72.7	80.2	87.9	95.8	103.7	111.6	119.7	127.9	135.8
20	68.7	75.4	82.3	89.3	96.4	103.5	110.7	117.9	125.2
10	59.3	64.5	69.9	75.4	81.1	86.6	92.1	97.7	103.3
8	54.3	59.0	63.9	68.8	73.7	78.6	83.3	88.2	93.2
7	51.5	55.9	60.5	65.0	69.6	74.2	78.8	83.5	88.1
6	47.5	51.7	55.9	60.2	64.5	68.8	73.0	77.4	81.6
5	41.8	45.5	49.3	53.1	56.8	60.5	64.3	68.0	71.8
4	34.4	37.7	40.9	44.1	47.3	50.5	53.7	56.9	60.1
3					36.0	38.6	41.2	43.8	46.4
					x = 0.1				
200	80.3	90.3	100.3	110.3	120.8	131.6	142.6	153.7	165.3
100	76.7	85.4	94.2	103.7	113.4	123.4	133.7	144.1	154.5
40	72.7	80.7	88.8	97.1	105.4	113.9	122.8	131.6	140.1
20	66.0	72.0	79.5	86.3	93.3	100.3	107.2	114.5	121.7
10	56.4	61.5	66.8	72.2	77.6	83.0	88.4	93.9	99.6
8	51.5	56.2	61.0	65.8	70.5	75.4	80.3	85.4	90.2
7	48.4	52.8	57.2	61.7	66.2	70.3	74.8	79.3	83.8
6	44.4	48.4	52.5	56.6	60.8	65.0	69.1	73.3	77.5
5	39.1	42.7	46.3	50.0	53.6	57.3	61.0	64.8	68.5
4	31.8	34.8	37.9	41.1	44.2	47.3	50.5	53.7	56.8
3					32.4	35.0	37.5	40.0	42.6
					x = 0.2				
200	79.3	88.7	98.7	108.8	119.1	130.0	140.7	151.9	163.3
100	76.0	84.7	94.0	103.5	113.0	122.9	133.1	143.6	153.9
40	71.6	79.3	87.6	95.3	103.7	112.0	120.4	128.8	137.0
30	67.8	74.9	82.4	90.0	97.6	105.4	113.1	120.4	128.0
20	63.4	69.8	76.4	83.2	90.1	96.9	103.8	110.8	118.0
10	53.3	58.3	63.4	68.7	74.0	79.4	84.6	90.0	95.5
8	48.5	53.0	57.8	62.4	67.2	71.9	76.7	81.5	86.4
7	45.3	49.6	53.9	58.3	62.7	67.1	71.6	76.2	80.6
6	41.2	45.1	49.1	53.1	57.2	61.3	65.4	69.5	73.7
5	35.9	39.4	43.0	46.5	50.1	53.7	57.4	61.1	64.7
4	28.9	31.8	34.8	37.8	40.9	44.0	47.0	50.1	53.2
3					29.5	32.0	34.5	37.0	39.5
					x = 0.3				
200	76.9	86.5	96.1	106.1	116.2	126.7	137.4	148.4	159.4
40	67.7	75.2	83.0	90.9	99.1	107.3	115.3	123.7	132.0
30	65.2	72.0	79.3	86.7	94.1	101.7	109.3	117.1	124.2
20	61.8	68.3	74.8	81.4	88.1	95.0	101.9	108.8	115.9
10	50.3	55.2	60.3	65.3	70.5	75.7	80.9	86.2	91.5
8	44.7	49.1	53.6	58.1	62.7	67.2	71.9	76.6	81.3
7	42.1	46.3	50.5	54.8	59.1	63.4	67.7	72.1	76.5
6	38.0	41.8	45.7	49.6	53.6	57.7	61.7	65.8	69.9
5	32.9	36.3	39.7	43.2	46.8	50.3	53.9	57.5	61.1
4	25.9	28.6	31.6	34.5	37.5	40.5	43.5	46.6	49.7
3					26.7	29.0	31.5	33.9	36.4
					x = 0.4				
200	74.9	84.3	93.7	103.3	113.2	123.5	133.9	145.0	156.2
100	71.7	80.1	89.0	97.6	107.1	116.8	126.4	136.4	146.7
40	67.2	74.2	82.0	89.9	97.9	106.1	114.5	123.0	131.6
20	59.1	65.4	71.8	78.3	84.9	91.6	98.3	105.1	112.1
10	47.6	52.5	57.4	62.5	67.5	72.6	77.7	82.9	88.1
8	41.9	46.1	50.5	54.9	59.4	63.9	68.4	73.0	77.7
7	39.3	43.3	47.5	51.6	55.8	60.1	64.3	68.5	72.9
6	35.3	39.0	42.7	46.6	50.5	54.4	58.3	62.3	66.3
5	30.2	33.4	36.7	40.2	43.6	47.0	50.5	54.1	57.7
4	23.2	25.9	28.6	31.5	34.4	37.3	40.3	43.3	46.3
3					24.3	26.7	29.0	31.5	33.9
					x = 0.5				
200	73.3	82.3	91.9	101.5	111.3	121.2	131.7	142.2	153.1
100	69.7	78.0	86.5	95.5	104.6	114.0	123.5	133.6	143.5
40	64.3	71.5	79.2	86.8	94.6	102.6	110.7	119.0	127.4
30	62.5	69.3	76.5	83.8	91.3	98.8	106.3	114.0	121.4
20	57.3	63.5	69.8	76.3	82.9	89.5	96.3	103.3	110.2
10	44.8	49.4	54.2	59.1	64.0	69.1	74.1	79.1	84.4
8	39.3	43.5	47.8	52.1	56.4	60.9	65.3	69.7	74.3
7	36.7	40.5	44.5	48.5	52.6	56.7	60.8	65.0	69.2
6	32.5	36.0	39.7	43.4	47.2	51.0	54.8	58.8	62.7
5	27.6	30.7	34.0	37.2	40.6	44.0	47.4	50.9	54.4
4	21.1	23.6	26.3	29.0	31.8	34.6	37.5	40.4	43.3
3					21.7	24.0	26.3	28.6	31.0

Table I (Continued)

R	Λ/(S cm² mol⁻¹) 283K	288K	293K	298K	303K	308K	313K	318K	323K
					x = 0.6				
200	72.4	81.4	90.6	100.1	109.9	120.2	130.3	140.6	151.8
100	67.7	75.8	84.3	93.0	101.9	111.0	120.4	130.2	140.1
30	60.4	67.1	74.1	81.2	88.4	95.9	103.3	110.7	118.2
20	54.8	60.6	66.8	73.1	79.7	86.0	92.5	99.1	106.0
10	41.9	46.6	51.3	56.0	60.8	65.7	70.7	75.8	80.9
8	36.7	40.7	44.8	49.0	53.3	57.7	62.0	66.5	71.0
7	33.6	37.3	41.1	45.0	49.0	53.0	57.0	61.1	65.2
6	29.9	33.3	36.9	40.5	44.2	47.9	51.7	55.5	59.4
5	25.1	28.1	31.3	34.5	37.7	41.0	44.3	47.9	51.1
4	18.6	21.0	23.6	26.2	28.9	31.6	34.4	37.2	40.1
3					19.4	21.5	23.7	26.0	28.4
					x = 0.7				
200	70.1	78.7	87.8	97.2	106.9	116.8	126.7	137.2	148.0
100	65.5	73.4	81.6	88.4	98.0	106.7	116.1	125.4	134.7
40	61.0	68.2	75.4	83.0	90.7	98.4	106.3	114.5	122.6
30	58.7	65.4	72.2	79.3	86.5	93.8	101.0	108.5	116.1
20	51.4	57.1	63.0	68.8	75.0	81.1	87.3	93.9	100.2
10	39.6	44.0	48.6	53.2	57.9	62.7	67.6	72.5	77.4
8	34.4	38.3	42.2	46.4	50.6	54.8	59.0	63.4	67.7
7	30.9	34.5	38.2	41.9	45.7	49.6	53.5	57.5	61.5
6	27.1	30.3	33.7	37.1	40.7	44.3	48.0	51.7	55.3
5	23.1	25.9	28.9	32.0	35.2	38.3	41.6	44.9	48.3
4	17.1	19.4	21.9	24.5	27.1	29.8	32.5	35.2	38.1
3					17.2	19.2	21.4	23.5	25.8
					x = 0.8				
200	68.8	77.4	86.2	95.6	105.9	115.3	125.4	135.7	146.2
40	58.9	65.9	73.1	80.7	88.2	95.6	103.6	111.9	120.1
30	57.0	63.5	70.3	77.2	84.4	91.7	98.9	106.3	113.8
20	50.0	55.8	61.5	67.4	73.5	79.7	86.0	92.4	98.8
10	37.0	41.2	45.6	50.1	54.7	59.4	64.1	69.0	73.8
8	31.8	35.5	39.4	43.5	47.6	51.7	55.8	60.1	64.5
7	28.0	31.5	35.2	38.8	42.6	46.4	50.2	54.2	58.2
6	24.7	27.9	31.1	34.4	37.9	41.4	44.9	48.5	52.2
5	20.9	23.7	26.6	29.6	32.6	35.7	38.9	42.2	45.5
4	15.3	17.5	19.9	22.4	24.9	27.6	30.2	33.0	35.7
3					15.3	17.3	19.3	21.4	23.6
					x = 0.9				
100	61.9	69.4	77.4	85.4	93.7	102.1	110.8	120.6	130.7
30	55.2	61.5	68.1	75.0	82.1	89.0	95.9	103.3	110.8
20	47.4	53.1	58.8	64.7	70.7	76.8	83.0	89.3	95.6
10	34.8	38.9	43.2	47.6	52.1	56.7	61.4	66.2	71.0
8	29.4	33.0	36.7	40.6	44.5	48.6	52.6	56.8	61.1
7	25.7	29.1	32.5	36.1	39.7	43.4	47.2	51.1	55.0
6	22.4	25.4	28.6	31.8	35.1	38.5	42.0	45.5	49.2
5	18.8	21.5	24.3	27.1	30.1	33.1	36.2	39.3	42.4
4	14.2	16.4	18.7	21.1	23.6	26.2	28.8	31.5	34.2
3					13.7	15.6	17.6	19.6	21.7
					x = 1.0				
200	65.0	73.2	82.0	90.8	99.9	109.2	119.1	129.0	139.0
100	59.4	66.7	74.5	82.4	90.3	99.0	107.4	116.1	124.9
40	55.1	61.4	68.4	75.3	82.5	89.9	97.4	105.1	112.8
30	51.9	57.8	64.5	71.1	77.8	84.6	92.1	99.3	106.5
20	45.9	51.3	56.9	62.7	68.6	74.7	80.8	87.1	93.3
10	32.5	36.6	40.8	45.1	49.4	54.0	58.5	63.3	67.9
8	27.2	30.6	34.3	38.0	41.9	45.8	49.8	53.9	58.0
7	23.6	26.8	30.1	33.5	37.1	40.7	44.3	48.2	52.0
6	20.1	23.0	26.0	29.0	32.2	35.5	38.9	42.3	45.8
5	17.2	19.8	22.5	25.3	28.1	31.0	34.0	37.1	40.2
4	12.5	14.5	16.7	19.0	21.4	23.9	26.4	29.0	31.6
3					12.0	13.8	15.6	17.6	19.6

negative only above 303 K. At temperatures ≤303 K, B has positive values for x = 0.0 and negative values for x = 1.0. In this temperature range, the values of x at which B changes its sign is dependent on the temperature. For example, B changes its sign between x = 0.5 and 0.6 at 283 K, whereas at 293 K it changes between x = 0.3 and 0.4. This type of dependence of B on x may be explained by correlating, in the light of the Wishaw–Stokes equation (*4*), the exponential part of eq 3 to the reciprocal of the viscosity of the system. Accordingly, a positive value of B and a negative value of C may indicate that the solution has lower viscosity than water up to a concentration equal to B/C. In fact, KSCN solution (x = 0.0) is known to have relative viscosity <1 (*5*). For example, at 293 K the viscosity of KSCN solution is less than that of water up to $c \simeq$ 1.7 mol·dm^{-3} (*5*), which is in good agreement with the value of the B/C ratio of 1.67 at that temperature.

In order to analyze the temperature dependence of Λ, ln Λ has been plotted versus $1/T$ in Figure 4 for x = 0.5 at three different R values. The plots look similar at other x and R values also. From the shape of these plots, it is apparent that

Table II. Best Fit Parameters of the Density Equation $\rho = a - bt$ for $[x\text{NaSCN} + (1 - x)\text{KSCN}] + R\text{H}_2\text{O}$ System

x	$a/(\text{g}\cdot\text{cm}^{-3})$	$b \times 10^4/(\text{g}\cdot\text{cm}^{-3}\cdot{}^\circ\text{C}^{-1})$	−(corr coeff)	x	$a/(\text{g}\cdot\text{cm}^{-3})$	$b \times 10^4/(\text{g}\cdot\text{cm}^{-3}\cdot{}^\circ\text{C}^{-1})$	−(corr coeff)
			$R = 200$				
0.1	1.0079	2.9845	0.9833	0.2	1.0087	3.4977	0.9956
0.3	1.0091	3.3661	0.9919	0.4	1.0095	3.4651	0.9932
0.5	1.0094	3.0735	0.9817	0.6	1.0076	3.1113	0.9879
0.7	1.0070	3.1870	0.9898	0.8	1.0065	2.9275	0.9748
1.0	1.0076	3.2406	0.9899				
			$R = 100$				
0.0	1.0197	3.5334	0.9941	0.1	1.0185	3.6217	0.9960
0.2	1.0186	3.5125	0.9935	0.4	1.0181	3.4623	0.9925
0.5	1.0184	3.6390	0.9946	0.6	1.0178	3.6587	0.9954
0.7	1.0181	3.6298	0.9965	0.9	1.0175	3.7118	0.9975
1.0	1.0171	3.6621	0.9942				
			$R = 40$				
0.0	1.0588	4.8800	0.9992	0.1	1.0559	4.6008	0.9994
0.2	1.0554	4.6084	0.9997	0.3	1.0576	4.8064	0.9994
0.4	1.0542	4.8729	0.9993	0.5	1.0543	4.9968	0.9993
0.7	1.0539	4.5840	0.9993	0.8	1.0510	4.9000	0.9996
1.0	1.0511	4.9143	0.9992				
			$R = 30$				
0.0	1.0756	4.6868	0.9974	0.2	1.0737	4.7249	0.9988
0.3	1.0718	4.7348	0.9988	0.5	1.0684	4.7637	0.9982
0.6	1.0681	4.9520	0.9991	0.7	1.0673	4.8004	0.9978
0.8	1.0667	5.0041	0.9995	0.9	1.0665	4.9395	0.9988
1.0	1.0699	5.4789	0.9995				
			$R = 20$				
0.0	1.1090	5.3707	0.9992	0.1	1.1062	5.4275	0.9995
0.2	1.1079	5.4345	0.9996	0.3	1.1067	5.5192	0.9995
0.4	1.1037	5.3477	0.9996	0.5	1.1070	5.5286	0.9994
0.6	1.1045	5.3934	0.9995	0.7	1.1062	5.5395	0.9997
0.8	1.1054	5.6278	0.9997	0.9	1.1041	5.7130	0.9997
1.0	1.1094	5.9111	0.9999				
			$R = 10$				
0.0	1.1862	6.3123	1.0000	0.1	1.1871	6.3737	0.9999
0.2	1.1849	6.3898	0.9999	0.3	1.1833	6.4513	1.0000
0.4	1.1819	6.4872	0.9999	0.5	1.1813	6.5069	0.9996
0.6	1.1785	6.6530	1.0000	0.7	1.1721	6.6171	0.9989
0.8	1.1795	6.9425	0.9999	0.9	1.1730	6.8053	1.0000
1.0	1.1728	6.9783	1.0000				
			$R = 8$				
0.0	1.2169	6.5779	1.0000	0.1	1.2192	6.5642	1.0000
0.2	1.2148	6.6598	1.0000	0.3	1.2131	6.7436	1.0000
0.4	1.2127	6.7952	1.0000	0.5	1.2104	6.7909	0.9999
0.6	1.2101	7.0742	1.0000	0.7	1.2033	6.9943	0.9999
0.8	1.2010	7.1196	1.0000	0.9	1.2093	7.3642	0.9999
1.0	1.2066	7.2897	1.0000				
			$R = 7$				
0.0	1.2401	6.7318	1.0000	0.1	1.2369	6.6376	1.0000
0.2	1.2340	6.7586	1.0000	0.3	1.2331	6.8458	0.9999
0.4	1.2297	6.9695	1.0000	0.5	1.2287	6.8503	1.0000
0.6	1.2305	7.0575	1.0000	0.7	1.2299	7.0441	1.0000
0.8	1.2304	7.4150	1.0000	0.9	1.2272	7.3211	0.9999
1.0	1.2267	7.5112	1.0000				
			$R = 6$				
0.0	1.2734	6.7688	0.9999	0.1	1.2692	6.8450	0.9999
0.2	1.2665	6.9138	1.0000	0.3	1.2653	6.9731	0.9999
0.4	1.2555	7.1625	0.9999	0.5	1.2571	7.1450	0.9999
0.6	1.2529	7.2151	1.0000	0.7	1.2557	7.3465	0.9999
0.8	1.2534	7.4197	1.0000	0.9	1.2523	7.5166	1.0000
1.0	1.2544	7.6175	1.0000				
			$R = 5$				
0.0	1.3019	6.8479	0.9999	0.1	1.2967	6.9971	1.0000
0.2	1.2959	7.1943	1.0000	0.3	1.2911	7.1535	0.9998
0.4	1.2907	7.1398	0.9999	0.5	1.2876	7.4187	0.9999
0.6	1.2828	7.3719	0.9999	0.7	1.2774	7.4696	0.9999
0.8	1.2735	7.4906	0.9999	0.9	1.2710	7.5962	0.9999
1.0	1.2646	7.7356	0.9999				

Table II (Continued)

x	a/(g·cm^{-3})	$b \times 10^4$/ (g·cm^{-3}·°C^{-1})	−(corr coeff)	x	a/(g·cm^{-3})	$b \times 10^4$/ (g·cm^{-3}·°C^{-1})	−(corr coeff)
			$R = 4$				
0.0	1.3422	6.9996	1.0000	0.1	1.3405	7.1737	1.0000
0.2	1.3369	7.2828	0.9999	0.3	1.3350	7.2534	1.0000
0.4	1.3327	7.3685	1.0000	0.5	1.3263	7.2100	1.0000
0.6	1.3249	7.5644	0.9999	0.7	1.3179	7.6162	1.0000
0.8	1.3135	7.5513	0.9999	0.9	1.3048	7.7441	0.9999
1.0	1.3022	7.7850	0.9999				
			$R = 3$				
0.0	1.3917	7.3349	0.9999	0.1	1.3898	7.1605	0.9999
0.2	1.3866	7.2466	0.9999	0.3	1.3848	7.4402	0.9999
0.4	1.3814	7.3622	0.9999	0.5	1.3793	7.4856	0.9999
0.6	1.3769	7.5452	0.9999	0.7	1.3767	7.6426	0.9999
0.8	1.3750	7.7360	0.9999	0.9	1.3719	7.7881	1.0000
1.0	1.3725	7.9718	1.0000				

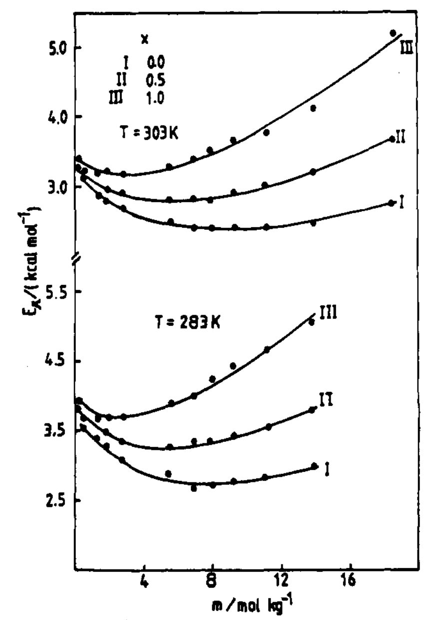

Figure 5. Plot of E_Λ of the [xNaSCN + (1 − x)KSCN] + RH_2O system vs concentration at different x and T.

the variation of Λ with T in the experimental range of temperature is a slightly non-Arrhenius type. This is an expected behavior, and it becomes more pronounced as one extends the temperature range to further low values. The Λ vs T data were therefore least-squares-fitted by using an iteration program to the Vogel–Tammann–Fulcher (VTF) equation of the form

$$\ln \Lambda = \ln A_\Lambda - B_\Lambda(T - T_0) \quad (4)$$

The best fit values of the empirical parameters in A_Λ, B_Λ, and T_0 are listed in Table IV (supplementary material). No regular trend in the variation of ln A_Λ or B_Λ or T_0 with R and x is observed. However, in the higher concentration region (at low R values), the value of T_0, in general, shows an increase with a decrease in R for all x values. Although the value of T_0 gives an idea about the glass-transition temperature of a system, in the present, case due to the smallness of the non-Arrhenius behavior, the values of T_0 may not reflect correctly on the glass-transition temperatures of the solutions.

With use of the best fit values of B_Λ and T_0, the activation energy (E_Λ) for conductance flow was calculated from the relation $E_\Lambda = B_\Lambda R'[T/(T - T_0)]^2$ where R' is the gas constant. The dependence of E_Λ on concentration is illustrated in Figure 5 for x = 0.0, 0.5, and 1.0 at 283 and 303 K. The shape of this type of plot is found to be similar for systems of other x values. The broad minimum in the plot of E_Λ vs concentration is a general feature of electrolytic solutions containing single salts. The present study reveals that the appearance of a broad minimum in the plot of E_Λ vs concentration is a general trend in the case of mixed electrolytic solutions also (*6*).

Registry No. NaSCN, 540-72-7; KSCN, 333-20-0.

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Supplementary Material Available: Tables of the best fit values of the parameters of eq 3 (Table III) and of eq 4 (Table IV) (17 pages). Ordering information is given on any current masthead page.