

# Conductivities, Partial Molar Volumes, and Isentropic Compressibilities of Sodium, Potassium and Ammonium Thiocyanates in Water + *N,N*-Dimethylformamide Mixtures at 20 °C

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*Association Constant / Partial Molar Volume / Adiabatic Compressibility /  
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Conductance, ultrasonic velocity, and density measurements are reported for NaSCN, KSCN and NH<sub>4</sub>SCN in water, *N,N*-dimethylformamide (DMF), and water + DMF mixtures at 20 °C. The limiting molar conductances and association constants have been derived from the Lee–Wheaton conductivity equation. The single-ion conductances have been evaluated using Bu<sub>4</sub>NBPh<sub>4</sub> as the “reference electrolyte”. The limiting molar volumes and apparent isentropic compressibilities have been calculated. The ion–ion and ion–solvent interactions have been discussed.

## 1. Introduction

The conductometric method is of great importance for obtaining information concerning ion–ion and ion–solvent interactions of electrolytes in mixed solvents. The volumetric properties of electrolytes, such as partial molar volumes and compressibilities are known to be sensitive to the extent and nature of the solvation of the ions. The use of mixed solvents enables the variation of properties such as dielectric constant or viscosity and therefore the interactions can be better studied.

Conductance and density measurements of alkali-metal halides and alkali-metal perchlorates in pure DMF [1,2] and binary mixtures containing

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DMF [3–5] are now plentiful in the literature, but such studies for alkali-metal thiocyanates are lacking. In the literature appear reports of conductivity studies for NaSCN and KSCN in 1-propanol and 2-propanol [6, 7].

We have recently reported conductance measurements of 2:2 electrolytes in water + methanol [8] and water + DMF [9] mixtures. Extending our investigation we present measured values of conductance, ultrasonic velocity and density of NaSCN, KSCN and  $\text{NH}_4\text{SCN}$ , in water, DMF, and water + DMF mixtures at 20 °C. The limiting molar conductivities ( $\Lambda_\circ$ ), the ionic conductances ( $\lambda_\pm^\circ$ ), the association constants ( $K_A$ ) as well as the limiting partial molar volumes ( $V_\circ$ ) and apparent isentropic compressibilities ( $k_\phi^\circ$ ) of the electrolytes, have been derived.

## 2. Experimental

*N,N*-dimethylformamide (Fluka, 99.8%) was used without further purification. The purity was checked by measuring the density ( $\rho = 0.94881 \text{ g cm}^{-3}$ ), and the relative permittivity ( $\epsilon = 38.5$ ) at 20 °C. The agreement between our and literature values ( $\rho = 0.9500 \text{ g cm}^{-3}$ ,  $\epsilon = 38.48$  at 20 °C [2, 10]) is good. The water was doubly distilled, and the specific conductivity was found to be better than  $0.40 \mu\text{S cm}^{-1}$  at 20 °C. The chemicals, NaSCN (Fluka, > 98.0%), KSCN (Merck, > 98.5%),  $\text{NH}_4\text{SCN}$  (Fluka, > 99%), NaBr (Riedel-de Haën, > 99%),  $\text{Bu}_4\text{NBr}$  (Carlo Erba, > 99.0%), and NaBPh<sub>4</sub> (Aldrich, > 99.5%), were used without further purification.

The water + DMF mixtures were prepared by mass. The mole fractions were known from  $\pm 0.0001$  to  $\pm 0.0005$  in all cases. All solutions were prepared by mass from a stock solution. Molar concentrations were obtained from molality and density values. The uncertainty of the molar concentrations was  $\pm 0.00001 \text{ mol dm}^{-3}$ .

Densities were measured with an Anton Paar (DMA 58) micro-computer controlled precision densimeter with built-in solid state thermostat at  $(20.00 \pm 0.01) \text{ }^\circ\text{C}$ . The densimeter was calibrated with distilled water and air. The estimated uncertainty of the measured densities was  $\pm 0.00001 \text{ g cm}^{-3}$ .

The speeds of sound were measured with an Anton Paar (DSA 48) sound analyser. The temperature was maintained constant within  $\pm 0.01 \text{ }^\circ\text{C}$ . The sound analyser was calibrated with distilled water and air at the experimental temperatures. The uncertainty of the measured speeds of sound was  $\pm 1 \text{ m s}^{-1}$ .

The conductance measurements were carried out using a digital bridge-type conductivity meter (Jenway, PCM 3) working at a frequency of 1 kHz. A dipping type conductance cell with platinized electrodes was used. The temperature was maintained constant within  $\pm 0.01 \text{ }^\circ\text{C}$ . All data were corrected with the specific conductance of each solvent mixture. The uncertainty of the specific conductance was  $\pm 0.3\%$ . Details of the experimental procedure have been described previously [8, 9].

### 3. Results and discussion

#### 3.1 Association constants

The experimental data were analyzed using the mass action law, the Debye–Hückel law, and the Lee–Wheaton [11, 12] conductivity equation in the form suggested by Pethybridge and Taba [13] which can be expressed as:

$$\Lambda = \alpha_d \left[ \Lambda_o \left( 1 + \frac{\Delta x}{x} \right) - \Delta \Lambda_e \right] \quad (1)$$

where  $\Delta x/x$  and  $\Delta \Lambda_e$  are the relaxation and electrophoretic term respectively,  $\alpha_d$ : is the degree of dissociation. The mean ion activity coefficient ( $y_{\pm}$ ) and the degree of dissociation were determined, from the equations

$$-\log y_{\pm} = \frac{2z_+z_-A_y\sqrt{\alpha_d c}}{1 + 2B_y q \sqrt{\alpha_d c}} \quad (2)$$

$$K_A = \frac{(1 - \alpha_d)}{\alpha_d^2 c y_{\pm}^2} \quad (3)$$

where  $A_y$ ,  $B_y$  are the Debye–Hückel coefficients and  $q$  the ion-size parameter, which was set equal to Bjerrum's critical distance [14]. The other symbols have the usual meaning.

The values of limiting molar conductances ( $\Lambda_o$ ) and association constants ( $K_A$ ), given in Table 1, were obtained as the best fit parameters which minimize the standard deviation ( $\sigma_A$ ).

The association constants are presented graphically in Fig. 1. The variation of the association constants with the DMF composition shows the same qualitative behaviour in all electrolytes used. The curves pass through a maximum in the region 40–60% w/w DMF and indicate that association is most pronounced for all salt solutions. In previous works [9, 15–17] has been reported that in this region predominate the interactions between unlike molecules. As a consequence, the ion solvation weakens and the ion-ion interaction dominates, leading to large values of the association constant. The most pronounced maximum appears for NaSCN and can be attributed to the smaller ionic radius of the  $\text{Na}^+$ .

These conclusions are supported by the results obtained for limiting apparent isentropic compressibilities and molar volumes, which follow in the next pages.

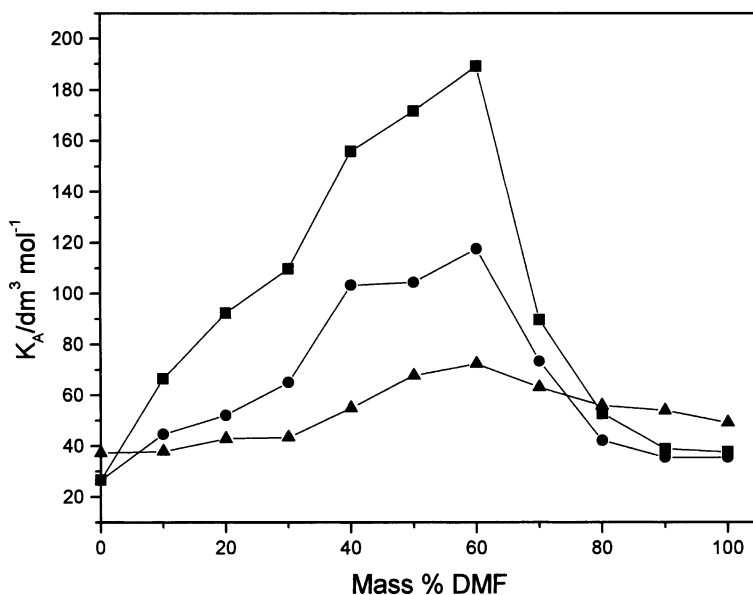
#### 3.2 Ionic conductances

For the calculation of the ion conductances we have used  $\text{Bu}_4\text{NBPh}_4$  as a “reference” electrolyte for the division of  $\Lambda_o$  values into single ion conductivities ( $\lambda_{\pm}^o$ ). The method is similar to that proposed by Krumgalz [18] for

**Table 1.** Limiting molar conductances ( $\Lambda_{\circ}$ ), association constants ( $K_A$ ) and standard deviations ( $\sigma_{\Lambda}$ ) for NaSCN, KSCN and  $\text{NH}_4\text{SCN}$  in water + DMF mixtures at 20 °C.

% w/w DMF	$\Lambda_{\circ}/\text{S cm}^2 \text{ mol}^{-1}$	$K_A/\text{dm}^3 \text{ mol}^{-1}$	$\sigma_{\Lambda}$
NaSCN			
0.00	109.7 ± 0.9	26.6 ± 0.1	1.3805
10.00	95.4 ± 0.8	66.5 ± 0.1	1.1443
20.00	81.5 ± 0.7	92.2 ± 0.2	0.7694
30.00	74.7 ± 0.6	109.8 ± 0.2	0.3512
40.00	63.2 ± 0.5	155.9 ± 0.3	0.3849
50.00	52.0 ± 0.4	171.6 ± 0.3	0.3226
60.00	47.4 ± 0.4	189.3 ± 0.4	0.4001
70.00	40.4 ± 0.3	89.7 ± 0.2	0.4355
80.00	38.8 ± 0.3	52.7 ± 0.1	0.3956
90.00	52.0 ± 0.4	38.9 ± 0.1	0.4390
100.00	88.2 ± 0.7	37.7 ± 0.1	1.0174
KSCN			
0.00	136.6 ± 1.1	26.5 ± 0.1	1.5462
10.00	104.0 ± 0.8	44.6 ± 0.1	1.4515
20.00	89.3 ± 0.7	52.0 ± 0.1	0.8928
30.00	77.1 ± 0.6	65.0 ± 0.1	0.4838
40.00	66.7 ± 0.5	103.3 ± 0.2	0.5494
50.00	57.3 ± 0.5	104.4 ± 0.2	0.6434
60.00	49.7 ± 0.4	117.7 ± 0.2	0.6451
70.00	40.6 ± 0.3	73.4 ± 0.2	0.4211
80.00	43.0 ± 0.3	42.2 ± 0.1	0.3743
90.00	56.4 ± 0.5	35.6 ± 0.1	0.2692
100.00	88.9 ± 0.7	35.5 ± 0.1	0.9406
$\text{NH}_4\text{SCN}$			
0.00	139.9 ± 1.1	37.2 ± 0.1	1.1696
10.00	110.9 ± 0.9	37.9 ± 0.1	1.5980
20.00	92.0 ± 0.7	42.8 ± 0.1	0.9586
30.00	69.3 ± 0.6	43.4 ± 0.1	0.6415
40.00	59.5 ± 0.5	54.9 ± 0.1	0.4878
50.00	51.2 ± 0.4	67.7 ± 0.1	0.2778
60.00	45.1 ± 0.4	72.4 ± 0.1	0.1575
70.00	41.6 ± 0.3	63.1 ± 0.1	0.2109
80.00	44.3 ± 0.4	55.8 ± 0.1	0.2539
90.00	56.1 ± 0.4	53.9 ± 0.1	0.1400
100.00	90.1 ± 0.7	49.2 ± 0.1	0.2875

the derivation of viscosity  $B$  coefficient. Therefore the limiting molar conductances for NaBr,  $\text{Bu}_4\text{NBr}$  and  $\text{NaBPh}_4$ , have been also derived and are listed in Table 2. The calculated  $\Lambda_{\circ}$  values for  $\text{Bu}_4\text{NBPh}_4$  are also listed in Table 2.



**Fig. 1.** Association constants ( $K_A$ ) as a function of DMF content for NaSCN (■), KSCN (●), and NH<sub>4</sub>SCN (▲) in water + DMF mixtures at 20 °C.

**Table 2.** Limiting molar conductances ( $\Lambda_\circ$ ) for NaBPh<sub>4</sub>, Bu<sub>4</sub>NBr, NaBr and Bu<sub>4</sub>NBPh<sub>4</sub> in water + DMF mixtures at 20 °C.

% w/w DMF	$\Lambda_\circ$ /S cm <sup>2</sup> mol <sup>-1</sup>			
	NaBPh <sub>4</sub>	Bu <sub>4</sub> NBr	NaBr	Bu <sub>4</sub> NBPh <sub>4</sub>
0.00	61.4 ± 0.5	89.7 ± 0.7	132.3 ± 1.1	18.8 ± 0.1
10.00	53.4 ± 0.4	72.0 ± 0.6	108.8 ± 0.9	16.6 ± 0.1
20.00	45.8 ± 0.4	59.1 ± 0.5	88.6 ± 0.7	16.3 ± 0.2
30.00	40.3 ± 0.3	49.6 ± 0.4	73.7 ± 0.6	16.2 ± 0.1
40.00	34.5 ± 0.3	41.1 ± 0.3	60.2 ± 0.5	15.4 ± 0.1
50.00	31.5 ± 0.3	37.4 ± 0.3	53.6 ± 0.4	15.3 ± 0.2
60.00	29.9 ± 0.2	34.3 ± 0.3	49.6 ± 0.4	14.6 ± 0.1
70.00	29.0 ± 0.2	34.5 ± 0.3	46.8 ± 0.4	16.7 ± 0.1
80.00	28.5 ± 0.2	35.0 ± 0.3	42.5 ± 0.3	21.0 ± 0.2
90.00	35.8 ± 0.3	45.4 ± 0.4	49.2 ± 0.4	32.0 ± 0.3
100.00	48.1 ± 0.4	70.1 ± 0.6	75.1 ± 0.6	43.1 ± 0.4

The single ion conductivities were evaluated on the basis of the fundamental assumption,  $\lambda_\circ(\text{Bu}_4\text{N}^+) = \lambda_\circ(\text{BPh}_4^-) = \frac{1}{2}\Lambda_\circ(\text{Bu}_4\text{NBPh}_4)$  [19, 20]. The  $\lambda_\pm$  values are listed in Table 3.

**Table 3.** Limiting ion conductances ( $\lambda_{\pm}^{\circ}$ ) for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{SCN}^-$ ,  $\text{Bu}_4\text{N}^+$  and  $\text{Ph}_4\text{B}^-$  in water + DMF mixtures at 20 °C.

% w/w DMF	$\lambda_{\pm}^{\circ}/\text{S cm}^2 \text{ mol}^{-1}$				
	$\text{Na}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{SCN}^-$	$\text{Bu}_4\text{N}^+/\text{Ph}_4\text{B}^-$
0.00	52.0 ± 0.4	78.9 ± 0.6	82.2 ± 0.6	57.7 ± 0.5	9.4 ± 0.1
10.00	45.1 ± 0.3	53.7 ± 0.3	60.6 ± 0.4	50.3 ± 0.5	8.3 ± 0.1
20.00	37.7 ± 0.3	45.5 ± 0.3	48.2 ± 0.3	43.8 ± 0.4	8.2 ± 0.1
30.00	32.2 ± 0.2	34.6 ± 0.2	26.8 ± 0.2	42.5 ± 0.4	8.1 ± 0.1
40.00	26.8 ± 0.2	30.3 ± 0.2	23.1 ± 0.2	36.4 ± 0.3	7.7 ± 0.1
50.00	23.9 ± 0.2	29.2 ± 0.3	23.1 ± 0.2	28.1 ± 0.2	7.6 ± 0.1
60.00	22.6 ± 0.1	24.9 ± 0.1	20.3 ± 0.1	24.8 ± 0.3	7.3 ± 0.1
70.00	20.7 ± 0.1	20.9 ± 0.1	21.9 ± 0.1	19.8 ± 0.2	8.4 ± 0.1
80.00	18.0 ± 0.1	22.2 ± 0.1	23.5 ± 0.2	20.8 ± 0.2	10.5 ± 0.1
90.00	19.8 ± 0.2	24.2 ± 0.3	23.9 ± 0.2	32.2 ± 0.2	16.0 ± 0.1
100.00	26.6 ± 0.3	27.3 ± 0.3	28.5 ± 0.3	61.7 ± 0.4	21.6 ± 0.1

### 3.3 Apparent molar volumes and isentropic compressibilities

The apparent molar volumes ( $V_{\varphi}$ ) have been calculated from the equation [21]:

$$V_{\varphi} = \frac{M}{\rho} - \frac{1000(\rho - \rho_{\circ})}{m\rho\rho_{\circ}} \quad (4)$$

where  $m$ : molality,  $M$ : molar mass of the electrolyte,  $\rho$ ,  $\rho_{\circ}$ : densities of the solution and pure solvent respectively.

The isentropic compressibility ( $k_s$ ) is defined by the equation:

$$k_s = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_s \quad (5)$$

where  $V$ : is the volume of the mixture. The  $k_s$  values were calculated from density ( $\rho$ ) and ultrasonic velocity ( $u$ ) data according to the relation,  $k_s = 1/(u^2\rho)$ .

The apparent isentropic compressibilities ( $k_{\varphi}$ ) of the electrolytes have been evaluated using the equation [22, 23]:

$$k_{\varphi} = V_{\varphi}k_s + \frac{1000(k_s - k_s^{\circ})}{m\rho_{\circ}} \quad (6)$$

where  $m$ : molality,  $\rho_{\circ}$ : density of the solvent,  $k_s^{\circ}$ : isentropic compressibility of the pure solvent.

The limiting apparent molar volumes and apparent isentropic compressibilities were obtained by fitting the calculated values to the equation  $Y = Y^{\circ} +$

**Table 4.** Limiting partial molar volumes ( $V^\circ$ ) and limiting apparent isentropic compressibilities ( $k_\varphi^\circ$ ) for NaSCN, KSCN and  $\text{NH}_4\text{SCN}$  in water + DMF mixtures at 20 °C.

% w/w DMF	$V^\circ/\text{cm}^3 \text{mol}^{-1}$		
	NaSCN	KSCN	$\text{NH}_4\text{SCN}$
0.00	$38.8 \pm 0.4$	$49.3 \pm 0.5$	$58.1 \pm 0.6$
10.00	$40.6 \pm 0.4$	$50.2 \pm 0.5$	$60.0 \pm 0.6$
20.00	$42.8 \pm 0.4$	$52.9 \pm 0.5$	$62.1 \pm 0.6$
30.00	$44.6 \pm 0.4$	$54.2 \pm 0.5$	$63.6 \pm 0.6$
40.00	$47.3 \pm 0.5$	$55.5 \pm 0.6$	$64.7 \pm 0.6$
50.00	$57.4 \pm 0.6$	$59.4 \pm 0.6$	$75.1 \pm 0.8$
60.00	$47.0 \pm 0.5$	$57.2 \pm 0.6$	$63.8 \pm 0.6$
70.00	$46.4 \pm 0.5$	$55.0 \pm 0.6$	$61.7 \pm 0.6$
80.00	$41.9 \pm 0.4$	$50.8 \pm 0.5$	$57.8 \pm 0.6$
90.00	$36.8 \pm 0.4$	$45.0 \pm 0.4$	$51.3 \pm 0.5$
100.00	$30.7 \pm 0.3$	$36.8 \pm 0.4$	$43.3 \pm 0.4$

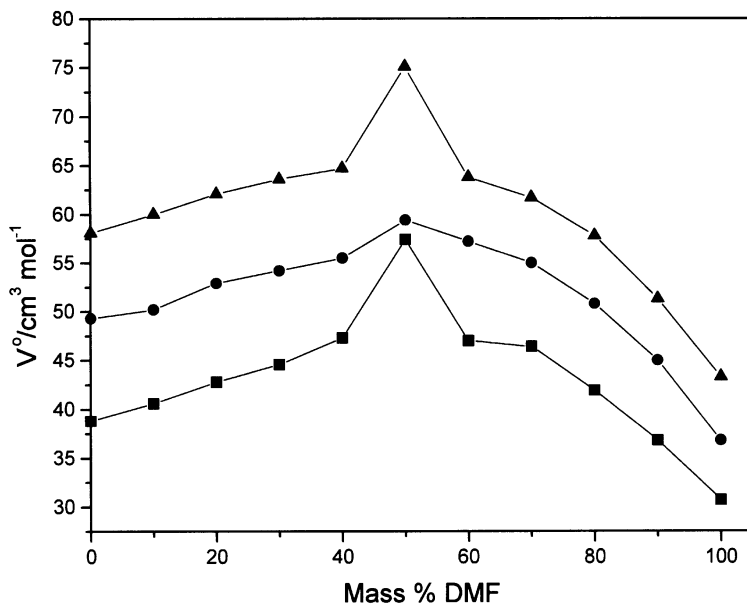
  

% w/w DMF	$10^3 k_\varphi^\circ/\text{TPa}^{-1} \text{mol}^{-1} \text{m}^3$		
	NaSCN	KSCN	$\text{NH}_4\text{SCN}$
0.00	$-32.7 \pm 0.1$	$-27.2 \pm 0.1$	$-0.100 \pm 0.001$
10.00	$-9.2 \pm 0.1$	$-10.9 \pm 0.1$	$21.0 \pm 0.1$
20.00	$-5.8 \pm 0.1$	$0.140 \pm 0.001$	$23.0 \pm 0.1$
30.00	$0.940 \pm 0.003$	$6.8 \pm 0.1$	$27.2 \pm 0.1$
40.00	$5.8 \pm 0.1$	$8.9 \pm 0.1$	$27.7 \pm 0.1$
50.00	$11.8 \pm 0.1$	$11.8 \pm 0.1$	$31.6 \pm 0.1$
60.00	$1.9 \pm 0.1$	$7.7 \pm 0.1$	$19.3 \pm 0.1$
70.00	$-4.9 \pm 0.1$	$-3.6 \pm 0.1$	$10.0 \pm 0.1$
80.00	$-18.1 \pm 0.1$	$-15.8 \pm 0.1$	$-0.390 \pm 0.001$
90.00	$-44.5 \pm 0.2$	$-46.9 \pm 0.2$	$-24.3 \pm 0.1$
100.00	$-66.7 \pm 0.2$	$-73.4 \pm 0.3$	$-53.1 \pm 0.2$

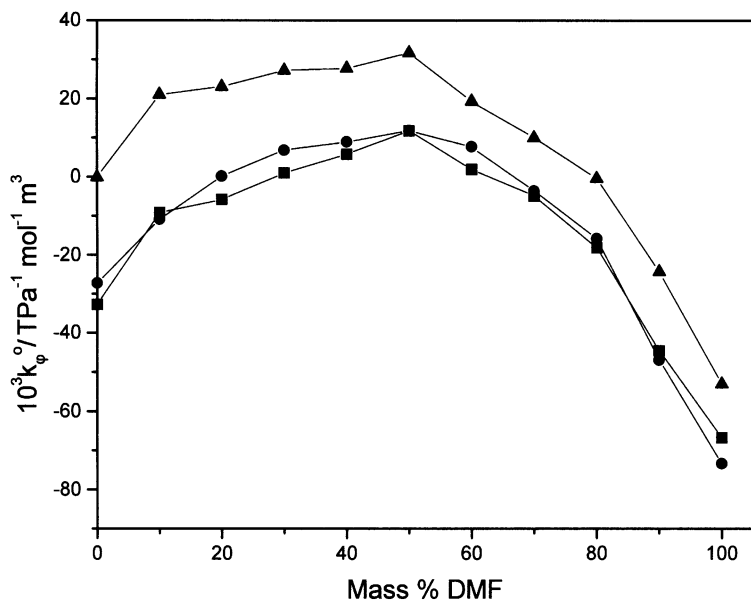
$Am^{1/2}$ , where  $Y = V_\varphi$  or  $k_\varphi$  and are plotted, as a function of the DMF content, in Figs. 2 and 3 respectively.

The limiting apparent isentropic compressibility and molar volume curves show the same behaviour as the association constants. The values pass through a maximum at the same solvent region which can be attributed to the predominance of the interactions between the unlike solvent molecules. In this region, electrostriction is limited.

The solvent molecules around the ions become more structured and lead to lower values of the sound velocities which result in higher isentropic compressibilities. The curves tend to higher values with the increase of the ionic radii of the ions, as it is expected.



**Fig. 2.** Limiting partial molar volumes ( $V^\circ$ ) as a function of DMF content for NaSCN (■), KSCN (●), and  $\text{NH}_4\text{SCN}$  (▲) in water + DMF mixtures at 20 °C.



**Fig. 3.** Limiting apparent isentropic compressibilities ( $k_\phi^\circ$ ) as a function of DMF content for NaSCN (■), KSCN (●), and  $\text{NH}_4\text{SCN}$  (▲) in water + DMF mixtures at 20 °C.



## 4. Conclusion

This work has provided information on the solvation behaviour NaSCN, KSCN and NH<sub>4</sub>SCN in DMF–water solvent mixtures. The association constants, the apparent molar volumes and the isoentropic compressibilities obtained showed the same qualitative behaviour for all salts tested. The values exhibited a maximum in the 40–50% DMF w/w region. In this region, as has been showed in previous investigation, predominate the interactions between the unlike solvent molecules. As a consequence the ion solvation is restricted and this leads to stronger ion association and to higher values of the molar volumes and the isoentropic compressibilities.

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