

Viscosity Coefficients of NaSCN, KSCN, NH₄SCN and MnSO₄, CoSO₄, NiSO₄, CdSO₄ in Aqueous Binary Mixtures of *N,N*-Dimethylformamide at 20 °C

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Viscosities of sodium, potassium, ammonium thiocyanates and manganese, cobalt, nickel, cadmium sulfates have been measured in water + *N,N*-dimethylformamide (DMF) mixtures at 20 °C. The experimental data have been analyzed using the Jones–Dole equation and the *B* coefficients have been calculated. The results have been discussed in terms of ion-solvent and solvent-solvent interactions.

1. Introduction

It has already been known the important role played by mixed solvents in the study of the solvation behaviour of various ions. The change of solvent properties (*e.g.* dielectric constant, viscosity) with the solvent composition enables the study of the interactions that appear between the species of the solution.

During the last years a large number of viscosity measurements in electrolyte solutions in mixed solvents appear in the literature [1–5], but such studies in water + DMF are still scarce.

DMF is an aprotic polar solvent with a large dipole moment ($\mu = 3.8$ D), a strong electron-pair donating capacity ($DN = 26.6$ kcal mol⁻¹) and a low dielectric constant ($\epsilon = 36.7$) [6]. DMF has a peptide group with the two basic centers, the oxygen of carbonyl and the nitrogen, which are in the same

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plane [7]. For that reason the study of the properties of electrolyte solutions in DMF is interesting since it may lead to information concerning the binding of the salts to the peptide groups in proteins [8].

In the pure state it shows self association which is due to dipole-dipole interactions by creating open and cyclic dimers [9–11], whereas in aqueous solutions are formed, through hydrogen bonding, two- or three-dimensional networks [12]. NMR studies showed [13] that the oxygen of the carbonyl group and not the nitrogen, is that which forms hydrogen bonds with the water molecules and that these bonds are stronger even than the hydrogen bonds between the water molecules.

We have recently reported viscometric measurements of CuSO_4 in water + ethylene glycol mixtures [14] and of LiBr in water + DMSO mixtures [15]. Extending our investigation we present in this work viscosity measurements of NaSCN , KSCN , NH_4SCN , NiSO_4 , CdSO_4 , CoSO_4 and MnSO_4 in water + DMF mixtures at 20°C . The viscosity data have been analyzed using the Jones–Dole equation and the B coefficients have been derived.

2. Experimental section

Materials: DMF (Fluka, 99.8%) was used without further purification. 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 salts, $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ (Fluka, > 99.0%), $\text{CdSO}_4\cdot \text{H}_2\text{O}$ (Fluka, > 99.5%), $\text{MnSO}_4\cdot \text{H}_2\text{O}$ (Fluka, > 99.0%), $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (Fluka, > 97.5%), NaSCN (Fluka, > 98.0%), KSCN (Merck, > 98.5%), NH_4SCN (Fluka, > 99%), were used without further purification.

Apparatus and Procedures: Densities were measured with an Anton Paar (DMA 58) micro-computer controlled precision densimeter, with build-in solid state thermostat. The precision of the sample thermostat was $\pm 0.01^\circ\text{C}$. The DMA cell was calibrated with air and doubly distilled water at atmospheric pressure. The precision in the density was $\pm 0.00001\ \text{g cm}^{-3}$.

The viscosities have been measured in the concentration range 0.0010 – $0.1500\ \text{mol dm}^{-3}$ with a viscosity measuring unit (Schott Geräte AVS 310) equipped with an Ubbelohde capillary viscometer. The viscometer was calibrated with doubly distilled water. The time measurement tolerance was $\pm 0.005\%$ and the display accuracy $\pm 0.01\ \text{s}$. The temperature was maintained constant within $\pm 0.03^\circ\text{C}$. The viscosities were averaged from four readings. The accuracy in the viscosity measurements was $\pm 0.1\%$.

All solutions were prepared by weight from a stock solution. The weighings were accurate up to $\pm 0.0001\ \text{g}$ (salts) and $\pm 0.01\ \text{g}$ (solvent mixtures). Molar concentrations were obtained from molality and density values with an accuracy of $\pm 0.0001\ \text{mol dm}^{-3}$.

3. Results and discussion

The viscosity data were analyzed using the empirical equation of Jones–Dole

$$\eta_r = 1 + Ac^{1/2} + Bc \quad (1)$$

where η_r is the relative viscosity of the solution, c the concentration (mol dm⁻³), and A , B adjustable coefficients.

The A coefficient is a measure of the interactions between the ions and is always positive. It depends on the solvent properties (dielectric constant, viscosity), the charge and the mobilities of the ions and on the temperature.

The B coefficient reflects the ion-solvent interactions and is a measure of the effect of the ion in the structure of the solvent in the secondary solvation region. The B coefficient can have positive or negative values depending on the surface charge density of the ion and consequently on its capability in exerting long-range order at the solvent molecules [16–18].

The A and B coefficients have been calculated as the intercept and the slope respectively, from plots of $[(\eta/\eta_o) - 1]/c^{1/2}$ against $c^{1/2}$. The derived A and B values are given with their standard deviations in the Tables 1 and 2. The B coefficients are plotted versus the DMF composition in Figs. 1 and 2.

The B coefficients for the sulfate salts are positive throughout all solvent mixtures and increase as the DMF content increases (Fig. 1), indicating the structure making behaviour of these salts. This behaviour can be mainly attributed to the cations, which cause long-range ordering of the solvent molecules, due to their large surface potential (the SO₄²⁻ ions are weak structure breakers). This remark is in agreement with our previous work [17] concerning conductivity measurements of the same systems.

The B coefficients for NaSCN are positive throughout all solvent mixtures, whereas for KSCN and NH₄SCN, negative values are exhibited at the water rich solvent region.

Thus it is indicated the structure making behaviour of the NaSCN (due to the small radius of the Na⁺) which results to long range ordering of the solvent molecules. KSCN behave as structure breaker because of the low surface potential of the K⁺, whereas the structure breaking behaviour of the NH₄SCN can be attributed to the steric influences produced by the NH₄⁺. (The SCN⁻ ions are weak structure breakers).

The B coefficients for the thiocyanate salts diminish in the order NaSCN > NH₄SCN > KSCN and pass through minima at ca. 50% *w/w* DMF.

The minima indicate weaker tendency of the Na⁺, K⁺, NH₄⁺ ions to orientate the solvent molecules. This is in accordance with the observation that at the same mole fraction of DMF, predominate the interactions between the unlike molecules, which result to the formation of clusters of water and DMF molecules [12, 17, 19]. Thus the ion-solvent interactions are not favored. This remark is in agreement with the results obtained in our previous work [19] where it was observed, stronger ion association and higher values of partial

Table 1. Viscosity A and B coefficients of NaSCN, KSCN and NH_4SCN in water + DMF mixtures at 20 °C.

% w/w DMF	$10^2 A$ $\text{dm}^{3/2} \text{mol}^{-1/2}$	B $\text{dm}^3 \text{mol}^{-1}$	% w/w DMF	$10^2 A$ $\text{dm}^{3/2} \text{mol}^{-1/2}$	B $\text{dm}^3 \text{mol}^{-1}$
NaSCN					
0.00	0.030 ± 0.003	0.032 ± 0.001	60.00	0.07 ± 0.01	0.132 ± 0.003
10.00	0.06 ± 0.01	0.024 ± 0.001	70.00	0.33 ± 0.03	0.242 ± 0.005
20.00	0.33 ± 0.03	0.020 ± 0.001	80.00	0.04 ± 0.01	0.429 ± 0.009
30.00	0.14 ± 0.01	0.014 ± 0.001	90.00	0.20 ± 0.02	0.605 ± 0.012
40.00	0.16 ± 0.02	0.014 ± 0.001	100.00	0.09 ± 0.01	0.683 ± 0.014
50.00	0.04 ± 0.01	0.038 ± 0.001			
KSCN					
0.00	0.010 ± 0.001	-0.063 ± 0.001	60.00	0.08 ± 0.01	-0.028 ± 0.001
10.00	0.34 ± 0.03	-0.090 ± 0.002	70.00	0.05 ± 0.01	0.110 ± 0.002
20.00	0.32 ± 0.03	-0.103 ± 0.002	80.00	0.33 ± 0.03	0.280 ± 0.006
30.00	0.23 ± 0.02	-0.120 ± 0.002	90.00	0.96 ± 0.10	0.460 ± 0.009
40.00	0.56 ± 0.06	-0.122 ± 0.002	100.00	3.98 ± 0.40	0.534 ± 0.011
50.00	0.04 ± 0.01	-0.090 ± 0.002			
NH_4SCN					
0.00	0.28 ± 0.03	-0.026 ± 0.001	60.00	0.02 ± 0.002	0.0090 ± 0.0002
10.00	0.010 ± 0.001	-0.065 ± 0.001	70.00	0.010 ± 0.001	0.146 ± 0.003
20.00	0.020 ± 0.002	-0.089 ± 0.002	80.00	0.19 ± 0.02	0.322 ± 0.006
30.00	0.45 ± 0.04	-0.098 ± 0.002	90.00	0.04 ± 0.01	0.491 ± 0.010
40.00	0.20 ± 0.02	-0.101 ± 0.002	100.00	0.05 ± 0.01	0.564 ± 0.011
50.00	0.08 ± 0.01	-0.070 ± 0.001			

Table 2. Viscosity A and B coefficients of NiSO_4 , CoSO_4 , MnSO_4 , CdSO_4 in water + DMF mixtures at 20 °C.

% w/w DMF	A $\text{dm}^{3/2} \text{mol}^{-1/2}$	B $\text{dm}^3 \text{mol}^{-1}$	A $\text{dm}^{3/2} \text{mol}^{-1/2}$	B $\text{dm}^3 \text{mol}^{-1}$
NiSO_4		CoSO_4		
0.00	0.203 ± 0.020	0.490 ± 0.010	0.214 ± 0.021	0.498 ± 0.010
10.00	0.102 ± 0.010	0.511 ± 0.010	0.152 ± 0.015	0.520 ± 0.010
20.00	0.091 ± 0.009	0.537 ± 0.011	0.107 ± 0.011	0.585 ± 0.012
30.00	0.0020 ± 0.0002	0.651 ± 0.013	0.013 ± 0.001	0.840 ± 0.017
40.00	0.0010 ± 0.0001	0.731 ± 0.015	0.0020 ± 0.0002	0.935 ± 0.019
50.00	0.036 ± 0.004	0.841 ± 0.017	0.021 ± 0.002	1.043 ± 0.021
MnSO_4		CdSO_4		
0.00	0.244 ± 0.024	0.492 ± 0.010	0.175 ± 0.017	0.457 ± 0.009
10.00	0.152 ± 0.015	0.530 ± 0.011	0.061 ± 0.006	0.478 ± 0.010
20.00	0.096 ± 0.010	0.601 ± 0.012	0.0010 ± 0.0001	0.539 ± 0.011
30.00	0.017 ± 0.002	0.776 ± 0.016	0.013 ± 0.001	0.701 ± 0.014
40.00	0.0002	0.873 ± 0.017	0.0030 ± 0.0003	0.819 ± 0.016
50.00	0.0001	0.955 ± 0.019	0.0010 ± 0.0001	0.903 ± 0.018

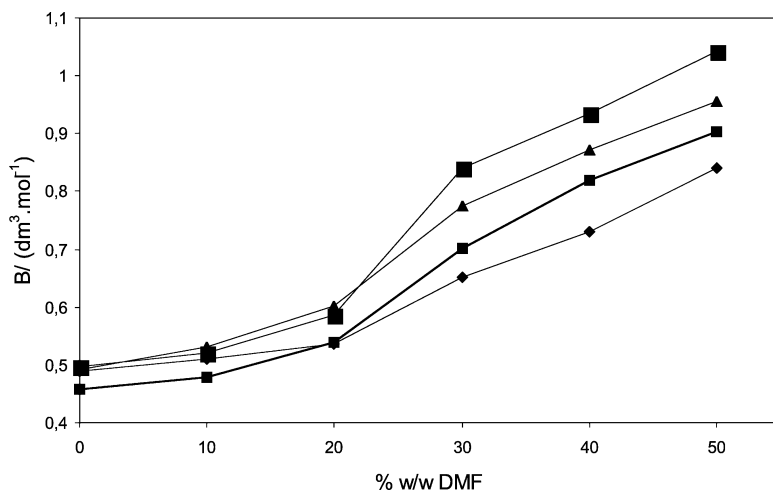


Fig. 1. B coefficients of the Jones–Dole equation for NiSO₄ (◆), CdSO₄ (■), MnSO₄ (▲), CoSO₄ (■), in water + DMF mixtures at 20 °C.

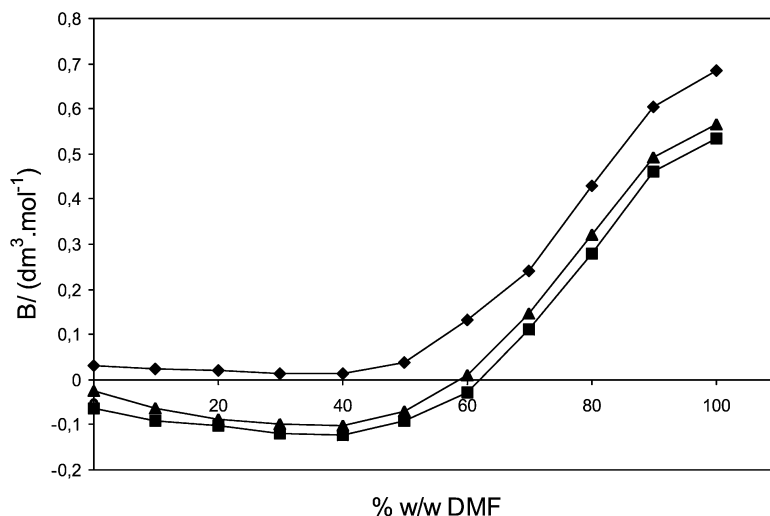


Fig. 2. B coefficients of the Jones–Dole equation for NaSCN (◆), NH₄SCN (■), KSCN (▲), in water + DMF mixtures at 20 °C.

molar volumes and isentropic compressibilities of the thiocyanates in the same solvent mixtures.

In the DMF-rich region the B coefficient progressively increases, due to the solvation of the cations by the DMF molecules and their resulting larger effect-

ive size. In this case it is assumed that, because of steric hindrance, the anions do not interact with the positive pole of the DMF molecule.

4. Conclusions

In this study have been obtained the viscosity coefficients B of the salts of NaSCN, KSCN, NH_4SCN , NiSO_4 , CdSO_4 , CoSO_4 and MnSO_4 in water + DMF mixtures and have been discussed the ion-solvent interactions.

The Na^+ , K^+ , and NH_4^+ show structure breaking ability at the composition *ca.* 40% *w/w* DMF. At this region the interactions between H_2O – DMF are stronger and are stabilized by the creation of clusters. Consequently, the ion-solvent interactions are not favored and the B coefficients tend to minimum values.

The B coefficients for the 2:2 salts are positive throughout all solvent composition range, indicating that the Ni^{+2} , Mn^{+2} , Co^{+2} and Cd^{+2} ions cause long range ordering. This behaviour is due to the large surface potential of the bivalent cations, which are characterized as structure makers.

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