

Conductance Studies on Manganese(II), Cobalt(II), Nickel(II), and Cadmium(II) Sulfates in Water + *N,N*-Dimethylformamide Mixtures at 293.15 K

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Molar conductances of manganese(II), cobalt(II), nickel(II), and cadmium(II) sulfate in water + *N,N*-dimethylformamide mixtures have been measured at 293.15 K. The limiting molar conductances (Λ_0) and association constants (K_A) have been derived from the Lee–Wheaton conductivity equation. The ion–ion and ion–solvent interactions have been discussed.

Introduction

Studies on the transport properties (conductance, viscosity, transference numbers) of electrolytes in different solvent media are of great importance for obtaining information concerning the behavior of electrolyte solutions. The use of mixed solvents enables the variation of properties such as dielectric constant or viscosity, and therefore the ion–solvent interactions can be better studied.

Conductance measurements of 1:1 electrolytes in mixed solvents are now plentiful, but such studies for 2:2 electrolytes are still very rare and demand further investigation.^{1–3}

We have recently reported conductance measurements of 2:2 electrolytes in water + methanol mixtures.⁴ Extending our study, we present conductance measurements of MnSO_4 , CoSO_4 , NiSO_4 , and CdSO_4 in water + *N,N*-dimethylformamide (DMF) mixtures in the composition range from 0 to 80 mass % DMF at 293.15 K. The concentration range was 0.0001–0.0010 mol·dm⁻³. The limiting molar conductivities (Λ_0) and the association constants (K_A) of the electrolytes have been derived.

DMF is an aprotic polar solvent with a large dipole moment ($\mu = 3.8$ D).⁵ In the liquid state, it shows low self-association which is due to dipole–dipole interactions,⁶ and in aqueous mixtures, it creates a two- or three-dimensional network through hydrogen bonding between the negative carbonyl oxygen and the water molecules.^{7–10}

Experimental Section

N,N-Dimethylformamide (Fluka, 99.8%) was used without further purification. The purity was checked by measuring the density (0.948 81 g·cm⁻³), the refractive index (1.4308), and the relative permittivity (38.5) at 293.15 K. These values are in agreement with the literature values $\rho = 0.9500$ g·cm⁻³, $n_D = 1.4305$, and $\epsilon = 38.48$ at 293.15 K.^{11–13} The water was doubly distilled, and the specific conductivity was found to be better than 0.40 $\mu\text{S}\cdot\text{cm}^{-1}$ at 293.15 K.

Nickel sulfate hexahydrate ($\text{NiSO}_4\cdot 6\text{H}_2\text{O}$) (Merck, 99.0%), cadmium sulfate monohydrate ($\text{CdSO}_4\cdot\text{H}_2\text{O}$) (Fluka, 99.0%), manganese sulfate monohydrate ($\text{MnSO}_4\cdot\text{H}_2\text{O}$) (Fluka,

Table 1. Densities (ρ), Viscosities (η), and Relative Permittivities (ϵ) of Water, DMF, and Water + DMF Mixtures at 293.15 K

mass % DMF	$\rho/\text{g}\cdot\text{cm}^3$	$\eta/\text{mPa}\cdot\text{s}$	ϵ
0.00	0.998 22	1.002	79.9
10.00	0.997 85	1.301	79.0
20.00	0.998 61	1.636	75.8
30.00	0.999 64	2.036	72.3
40.00	1.000 34	2.455	69.6
50.00	1.001 26	2.827	65.8
60.00	0.997 11	2.976	58.8
70.00	0.991 13	2.771	54.5
80.00	0.980 96	2.159	47.7
90.00	0.966 47	1.416	44.2
100.00	0.948 81	0.862	38.5

99.0%), and cobalt sulfate heptahydrate ($\text{CoSO}_4\cdot 7\text{H}_2\text{O}$) (Fluka, 99.0%) were used without further purification.

The water + DMF mixtures were prepared by mass. The mole fractions were known from ± 0.0001 to ± 0.0005 in all cases. All solutions were prepared by mass from a stock solution. Molar concentrations were obtained from the salt and solution masses as well as the density values. The uncertainty of the molar concentrations was $\pm 0.000 01$ mol·dm⁻³.

Densities were measured with an Anton Paar (DMA 58) microcomputer-controlled precision densimeter with a built-in solid-state thermostat at (293.15 \pm 0.01) K. The estimated uncertainty of the measured densities was $\pm 0.000 01$ g·cm⁻³.

The flow times of the solvent mixtures were measured with a viscosity-measuring unit (Schott Geräte AVS 310), equipped with an Ubbelohde capillary viscometer. The temperature was maintained constant within ± 0.03 K. The uncertainty in the viscosity measurements was ± 0.001 mPa·s.

Relative permittivities (ϵ), for water, DMF, and water + DMF mixtures, were measured with a Hewlett-Packard impedance analyzer (HP 4291A RF). The frequency range was 1 MHz to 1.8 GHz, and the precision in the ϵ values was 1%. The sample capacitor was used as the termination of the extension line. The complex reflection factor (the ratio of voltages or electrical fields of the reflected wave to the incoming wave on the line) at the analyzer end of the line is dependent on sample impedance and was measured

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Table 2. Continued

$10^2 c^a$	ρ^b	$10^6 \kappa^c$	Λ^d	$10^2 c$	ρ	$10^6 \kappa$	Λ	$10^2 c$	ρ	$10^6 \kappa$	Λ	$10^2 c$	ρ	$10^6 \kappa$	Λ
Cobalt(II) Sulfate				Manganese(II) Sulfate				Nickel(II) Sulfate				Cadmium(II) Sulfate			
70 mass % DMF				70 mass % DMF				70 mass % DMF				70 mass % DMF			
0.009	0.991 19	2.11	22.76	0.017	0.991 13	2.76	16.43	0.021	0.991 12	3.79	18.05	0.016	0.992 56	1.89	12.06
0.019	0.991 20	3.50	18.84	0.029	0.991 15	3.89	13.52	0.040	0.991 18	5.76	14.29	0.026	0.992 58	2.65	10.22
0.024	0.991 24	4.38	18.14	0.039	0.991 17	4.70	12.18	0.054	0.991 18	6.94	12.80	0.036	0.992 59	3.22	8.97
0.031	0.991 24	5.13	16.34	0.050	0.991 17	5.57	11.15	0.067	0.991 19	7.93	11.86	0.046	0.992 61	3.71	8.10
0.039	0.991 26	5.91	15.08	0.060	0.991 17	6.18	10.37	0.081	0.991 21	8.89	10.98	0.057	0.992 63	4.22	7.43
0.047	0.991 27	6.62	14.12	0.072	0.991 20	6.94	9.65	0.088	0.991 22	9.33	10.66	0.066	0.992 65	4.63	6.96
0.058	0.991 29	7.54	13.01	0.083	0.991 21	7.46	8.99	0.101	0.991 24	10.18	10.06	0.082	0.992 67	5.26	6.37
0.071	0.991 31	8.49	12.03	0.101	0.991 23	8.42	8.36	0.114	0.991 26	10.94	9.58	0.096	0.992 70	5.75	5.96
0.078	0.991 34	9.02	11.56									0.103	0.992 71	6.01	5.82
80 mass % DMF				80 mass % DMF				80 mass % DMF				80 mass % DMF			
0.020	0.981 03	1.50	7.47	0.016	0.980 99	0.99	6.24	0.007	0.980 97	0.79	10.70	0.011	0.981 01	0.53	5.00
0.025	0.981 05	1.77	7.00	0.021	0.981 00	1.15	5.46	0.015	0.980 99	1.26	8.50	0.015	0.981 02	0.69	4.65
0.036	0.981 05	2.18	6.05	0.031	0.981 01	1.46	4.64	0.026	0.981 01	1.79	7.01	0.024	0.981 03	0.97	3.96
0.041	0.981 06	2.35	5.77	0.042	0.981 03	1.74	4.09	0.035	0.981 02	2.15	6.10	0.033	0.981 05	1.14	3.44
0.051	0.981 08	2.70	5.26	0.053	0.981 04	1.96	3.71	0.045	0.981 04	2.44	5.49	0.040	0.981 06	1.26	3.13
0.061	0.981 10	3.02	4.92	0.060	0.981 05	2.13	3.52	0.055	0.981 05	2.78	5.06	0.048	0.981 07	1.38	2.90
0.076	0.981 12	3.44	4.55	0.075	0.981 06	2.42	3.22	0.071	0.981 07	3.24	4.57	0.057	0.981 09	1.50	2.64
0.091	0.981 15	3.84	4.24	0.088	0.981 09	2.65	2.99	0.085	0.981 09	3.60	4.23	0.071	0.981 11	1.73	2.45
0.101	0.981 17	4.14	4.08	0.101	0.981 12	2.94	2.92	0.095	0.981 11	3.90	4.10	0.090	0.981 14	1.97	2.19

a mol·dm⁻³, b g·cm⁻³, c S·cm⁻¹, d S·cm²·mol⁻¹.

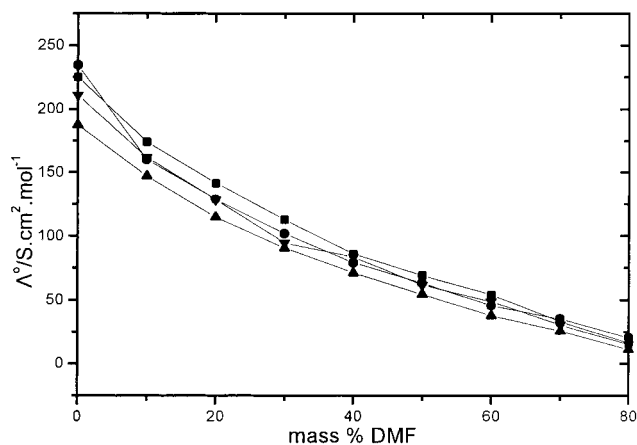


Figure 1. Variation of limiting molar conductivities with mass % DMF for CoSO₄ (■), NiSO₄ (●), CdSO₄ (▲), and MnSO₄ (▼) in water + DMF mixtures at 293.15 K.

with the aforementioned analyzer. Because lines are not ideal, calibration procedures should be applied. The calibration was carried out by capacitors of standard values (0 S, 0 Ω, and 50 Ω) supplied by the manufacturer.

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 ±0.01 K. The specific conductivities were measured in a 30 min period of time. The values that are provided in the text are the average of the measurements of the last 15 min. The specific conductivity of each solvent mixture has been subtracted from the corresponding values of the electrolyte solutions. The uncertainty of the specific conductance was ±0.3%. The experimental details of such measurements were the same as those reported earlier.⁴

Results and Discussion

Densities, viscosities, and relative permittivities of water, DMF, and water + DMF mixtures are reported in Table 1, and the densities, specific conductivities, and molar conductivities of each electrolyte in the water + DMF mixtures,

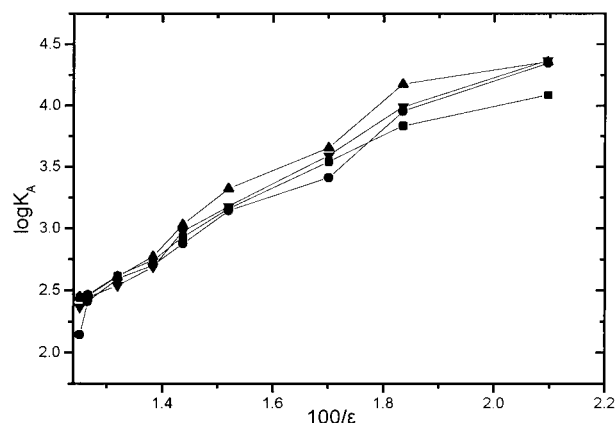


Figure 2. Variation of association constants with the inverse dielectric constant for CoSO₄ (■), NiSO₄ (●), CdSO₄ (▲), and MnSO₄ (▼) in water + DMF mixtures at 293.15 K.

in Table 2 (the reported Λ values are evaluated from the round concentrations and the round specific conductivities).

A maximum has been found in both density and viscosity values. These maxima have been observed in all aqueous mixtures of *N,N*-disubstituted amides¹⁴ and can be attributed to the stronger hydrogen bonding, which is stronger between the carbonyl oxygen and water molecules than between the water molecules.^{9,15}

The experimental data (Λ , c)_T were analyzed using the Lee–Wheaton^{16,17} conductivity equation in the form suggested by Pethybridge and Taba,¹⁸ and the following set of equations was used:

$$\Lambda = \gamma \left[\Lambda_0 \left(1 + \frac{\Delta x}{x} \right) - \Delta \Lambda_e \right] \quad (1)$$

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

$$-\ln f_{\pm} = \frac{\beta \kappa}{2(1 + \kappa R)} \quad (3)$$

where $\Delta x/x$ and $\Delta \Lambda_e$ are the relaxation and electrophoretic term, respectively, β is twice the Bjerrum's distance, γ is

Table 3. Limiting Molar Conductances (Λ_0) and Association Constants (K_A) for Cobalt(II), Manganese(II), Nickel(II), and Cadmium(II) Sulfates in Water + DMF Mixtures at 293.15 K

mass % DMF	$\Lambda_0/\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$	$K_A/\text{dm}^3\cdot\text{mol}^{-1}$	σ_A
CoSO ₄			
0.00	225.1 ± 0.9	276 ± 1	0.2988
10.00	173.9 ± 0.9	290 ± 1	0.2155
20.00	141.4 ± 0.7	414 ± 1	0.1733
30.00	112.6 ± 0.6	551 ± 1	0.1035
40.00	85.8 ± 0.4	847 ± 2	0.0397
50.00	69.2 ± 0.3	1443 ± 3	0.0188
60.00	54.0 ± 0.3	3479 ± 7	0.0071
70.00	33.0 ± 0.2	6830 ± 14	0.0034
80.00	16.03 ± 0.08	12202 ± 24	0.0004
NiSO ₄			
0.00	234.4 ± 0.9	139 ± 1	0.5580
10.00	159.8 ± 0.8	256 ± 1	0.3395
20.00	128.7 ± 0.6	390 ± 1	0.1149
30.00	101.6 ± 0.5	502 ± 1	0.0693
40.00	78.8 ± 0.4	750 ± 2	0.0465
50.00	63.2 ± 0.3	1385 ± 3	0.0117
60.00	45.5 ± 0.2	2573 ± 5	0.0272
70.00	35.2 ± 0.2	8987 ± 18	0.0005
80.00	20.3 ± 0.1	22166 ± 44	0.0002
CdSO ₄			
0.00	187.3 ± 0.9	280 ± 1	0.3482
10.00	147.0 ± 0.7	287 ± 1	0.1494
20.00	114.6 ± 0.6	406 ± 1	0.1615
30.00	90.4 ± 0.5	591 ± 1	0.0431
40.00	71.1 ± 0.4	1066 ± 2	0.0203
50.00	54.4 ± 0.3	2097 ± 4	0.0068
60.00	37.6 ± 0.2	4511 ± 9	0.0022
70.00	25.5 ± 0.1	14934 ± 30	0.0003
80.00	11.00 ± 0.06	22681 ± 45	0.0004
MnSO ₄			
0.00	210.9 ± 0.9	231 ± 1	0.1736
	267.08 ^a	146 ^a	
	265.48 ± 0.04 ^b	181 ± 0.4 ^b	
10.00	161.8 ± 0.8	276 ± 1	0.2295
20.00	128.4 ± 0.6	344 ± 1	0.1269
30.00	94.4 ± 0.5	486 ± 1	0.0591
40.00	83.4 ± 0.4	941 ± 2	0.0190
50.00	61.7 ± 0.3	1501 ± 3	0.0080
60.00	48.7 ± 0.2	3902 ± 8	0.0034
70.00	30.3 ± 0.2	9744 ± 19	0.0006
80.00	15.00 ± 0.08	23346 ± 47	0.0002

^a At 298.15 K (ref 23). ^b At 298.15 K (ref 3).

the degree of dissociation, f_{\pm} is the mean ion activity coefficient, and κ^{-1} is the Debye length. The values of R were actually equal to Bjerrum's critical distance,¹⁹ a procedure which is mentioned by other researchers.^{20,21} The other symbols have the usual meanings.

The Λ_0 and K_A values were obtained as the best fit parameters which minimize the standard deviation (σ_A) and are given in Table 3, together with values given in the literature.

The values of Λ_0 are represented graphically in Figure 1, and the dependence of $\log K_A$ on the inverse of the dielectric constant of the binary solvent is given in Figure 2.

As is shown in Figure 1, the Λ_0 values of MnSO₄, CoSO₄, NiSO₄, and CdSO₄ are relatively similar. The solvation that predominates is that of the cation-solvent type because the sulfate anions, due to their tetrahedral symmetry, exhibit restricted solvation. Therefore, it is indicated that the solvation of the cations ranges to the same extent and leads to similar effective volumes.

The K_A values indicate that ionic association occurs in all solvent mixtures tested. The K_A values increase in the DMF-rich region where the water molecules are replaced by DMF. The DMF molecules, due to steric hindrance²² and lower polarizability compared to that of water molecules, do not align around the cation. Hence, ion pair formation occurs.

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