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

Ioanna E. Molinou* and Nikos G. Tsierkezos

Laboratory of Physical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, P.O. Box 64004, 157 10 Zografou, Athens, Greece

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 μS·cm^{-1} at 293.15 K.

Nickel sulfate hexahydrate ($NiSO_4$·$6H_2O$) (Merck, 99.0%), cadmium sulfate monohydrate ($CdSO_4$·H_2O) (Fluka, 99.0%), manganese sulfate monohydrate ($MnSO_4$·H_2O) (Fluka, 99.0%), and cobalt sulfate heptahydrate ($CoSO_4$·$7H_2O$) (Fluka, 99.0%) were used without further purification.

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

mass % DMF	ρ/g·cm^3	η/mPa·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

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 ±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 ± 0.01) K. The estimated uncertainty of the measured densities was ±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

* To whom correspondence should be addressed. E-mail: imolinou@cc.uoa.gr.

10.1021/je0101101 CCC: $20.00 © 2001 American Chemical Society
Published on Web 09/12/2001

Table 2. Densities (ρ), Specific Conductivities (κ), and Molar Conductivities (Λ) for Cobalt(II), Manganese(II), Nickel(II), and Cadmium(II) Sulfates in Water + DMF Mixtures at 293.15 K

10^2c^a	ρ^b	$10^6\kappa^c$	Λ^d	10^2c	ρ	$10^6\kappa$	Λ	10^2c	ρ	$10^6\kappa$	Λ	10^2c	ρ	$10^6\kappa$	Λ
Cobalt(II) Sulfate				Manganese(II) Sulfate				Nickel(II) Sulfate				Cadmium(II) Sulfate			
0 mass % DMF				0 mass % DMF				0 mass % DMF				0 mass % DMF			
0.016	0.999 60	35.68	216.10	0.017	0.998 20	34.80	202.71	0.025	0.998 23	56.84	227.36	0.014	0.998 22	25.33	181.41
0.027	0.999 64	56.64	210.73	0.031	0.998 23	62.08	197.64	0.037	0.998 25	82.52	223.02	0.023	0.998 23	39.73	176.11
0.036	0.999 65	74.32	205.06	0.041	0.998 24	79.84	193.34	0.050	0.998 27	109.44	218.88	0.033	0.998 26	56.77	171.50
0.047	0.999 67	94.40	200.26	0.052	0.998 26	98.96	190.63	0.062	0.998 30	134.29	216.59	0.042	0.998 29	70.53	168.35
0.056	0.999 70	111.52	197.40	0.062	0.998 28	116.00	187.06	0.074	0.998 31	158.10	213.65	0.051	0.998 30	83.73	165.58
0.067	0.999 71	130.88	194.13	0.068	0.998 29	125.68	185.33	0.087	0.998 33	183.43	210.84	0.060	0.998 32	97.89	163.07
0.084	0.999 72	158.72	189.82	0.077	0.998 30	141.44	183.15	0.098	0.998 35	205.96	210.16	0.069	0.998 33	110.77	160.57
0.094	0.999 76	174.96	185.18	0.089	0.998 33	158.96	179.14	0.125	0.998 39	254.81	203.85	0.082	0.998 35	129.81	158.61
0.104	0.999 78	190.96	182.77												
10 mass % DMF				10 mass % DMF				10 mass % DMF				10 mass % DMF			
0.019	0.997 88	30.80	165.79	0.018	0.997 86	27.86	155.17	0.013	0.997 98	20.64	155.59	0.022	0.997 89	30.26	139.23
0.031	0.997 88	49.28	161.06	0.035	0.997 89	51.06	147.72	0.040	0.998 02	58.24	144.78	0.038	0.997 92	51.30	133.20
0.043	0.997 90	66.56	155.85	0.046	0.997 90	66.58	144.61	0.053	0.998 04	74.80	141.57	0.050	0.997 94	64.66	130.27
0.054	0.997 92	82.00	151.91	0.057	0.997 92	80.90	141.59	0.067	0.998 06	92.72	138.96	0.064	0.997 96	80.90	126.54
0.067	0.997 95	98.88	148.52	0.069	0.997 94	95.78	138.90	0.080	0.998 08	108.80	136.10	0.081	0.997 99	99.14	122.84
0.078	0.997 96	114.00	145.88	0.077	0.997 95	106.18	137.14	0.093	0.998 10	123.68	133.45	0.099	0.998 02	117.78	119.31
0.097	0.998 00	137.52	141.65	0.087	0.997 97	117.14	135.12	0.106	0.998 12	139.04	131.09	0.112	0.998 04	131.46	117.45
0.109	0.998 03	152.48	139.58	0.101	0.997 99	133.46	132.57	0.119	0.998 14	154.64	129.48	0.126	0.998 07	145.78	115.36
0.122	0.998 04	166.64	136.95												
20 mass % DMF				20 mass % DMF				20 mass % DMF				20 mass % DMF			
0.018	0.998 61	23.24	132.83	0.016	0.998 61	19.13	121.32	0.005	0.998 62	6.66	134.30	0.012	0.998 59	13.54	109.89
0.027	0.998 62	34.44	128.89	0.030	0.998 63	35.77	117.93	0.016	0.998 63	18.99	121.96	0.024	0.998 61	25.37	105.36
0.038	0.998 64	46.68	123.04	0.041	0.998 64	46.81	114.06	0.040	0.998 68	45.07	112.49	0.037	0.998 63	37.29	100.49
0.047	0.998 66	56.52	120.40	0.050	0.998 66	55.93	111.58	0.050	0.998 69	54.99	110.10	0.047	0.998 65	46.17	97.35
0.060	0.998 68	69.56	116.94	0.060	0.998 68	65.77	109.23	0.057	0.998 70	61.23	108.10	0.060	0.998 67	56.97	94.68
0.069	0.998 70	79.32	114.48	0.066	0.998 69	71.05	107.55	0.067	0.998 72	71.31	105.91	0.070	0.998 69	65.37	92.87
0.080	0.998 72	90.12	111.90	0.076	0.998 70	80.01	105.87	0.077	0.998 73	79.79	104.04	0.095	0.998 73	83.77	88.56
0.097	0.998 75	105.72	108.55	0.086	0.998 71	89.45	103.53	0.088	0.998 75	89.31	101.98	0.106	0.998 75	92.09	87.19
0.108	0.998 76	115.72	106.91									0.120	0.998 78	102.17	85.33
30 mass % DMF				30 mass % DMF				30 mass % DMF				30 mass % DMF			
0.018	0.999 66	18.35	103.79	0.016	0.999 68	14.47	88.00	0.017	0.999 68	16.06	94.25	0.016	0.999 66	13.44	83.21
0.030	0.999 69	29.15	98.69	0.033	0.999 70	27.36	82.80	0.031	0.999 71	27.90	89.35	0.026	0.999 68	20.71	79.73
0.040	0.999 72	38.11	94.24	0.043	0.999 72	34.48	79.85	0.045	0.999 73	38.22	85.16	0.035	0.999 70	27.11	76.72
0.053	0.999 74	47.55	90.37	0.054	0.999 73	41.92	77.78	0.055	0.999 75	45.34	82.30	0.046	0.999 72	34.07	73.68
0.064	0.999 77	55.95	87.90	0.063	0.999 74	47.76	75.56	0.066	0.999 77	53.26	80.45	0.058	0.999 74	40.95	70.97
0.076	0.999 78	64.67	85.37	0.069	0.999 76	51.36	74.50	0.072	0.999 78	57.34	79.56	0.067	0.999 75	46.63	69.35
0.087	0.999 81	72.67	83.42	0.080	0.999 77	58.08	73.01	0.083	0.999 80	64.30	77.26	0.078	0.999 77	52.31	67.48
0.105	0.999 84	84.35	80.68	0.089	0.999 78	64.00	71.78	0.094	0.999 81	71.34	75.83	0.088	0.999 79	58.23	66.24
0.117	0.999 86	91.87	78.69									0.103	0.999 82	65.59	63.71
40 mass % DMF				40 mass % DMF				40 mass % DMF				40 mass % DMF			
0.018	1.000 41	13.52	75.28	0.017	1.000 42	12.19	73.35	0.020	1.000 37	14.06	69.94	0.016	1.000 38	9.83	61.76
0.028	1.000 43	20.22	72.29	0.032	1.000 44	21.78	67.20	0.040	1.000 41	24.91	63.14	0.026	1.000 40	15.38	58.27
0.039	1.000 45	26.46	68.26	0.042	1.000 45	27.22	64.06	0.053	1.000 43	31.95	60.18	0.037	1.000 42	20.18	54.57
0.050	1.000 46	32.30	64.66	0.053	1.000 46	32.26	60.95	0.066	1.000 46	38.11	57.75	0.047	1.000 44	24.42	51.93
0.061	1.000 48	38.06	62.41	0.064	1.000 48	37.38	58.72	0.079	1.000 47	44.11	55.71	0.057	1.000 45	28.58	49.88
0.072	1.000 50	43.26	60.30	0.069	1.000 48	40.02	57.76	0.086	1.000 49	47.07	54.81	0.068	1.000 46	32.42	47.71
0.083	1.000 52	48.46	58.39	0.079	1.000 50	44.26	55.95	0.100	1.000 51	52.83	52.88	0.086	1.000 49	38.90	45.27
0.100	1.000 55	55.98	55.81	0.096	1.000 52	51.14	53.55	0.112	1.000 52	57.87	51.65	0.098	1.000 52	43.06	43.73
0.111	1.000 57	60.30	54.31									0.105	1.000 53	44.98	42.80
50 mass % DMF				50 mass % DMF				50 mass % DMF				50 mass % DMF			
0.012	0.999 99	7.10	59.84	0.094	1.000 02	32.74	34.69	0.019	0.999 88	9.99	51.83	0.015	1.001 30	6.51	43.30
0.022	1.000 02	12.27	55.67	0.078	0.999 99	28.66	36.55	0.036	0.999 91	16.94	46.45	0.024	1.001 31	9.60	40.08
0.033	1.000 03	16.84	51.62	0.068	0.999 98	26.02	38.19	0.049	0.999 93	21.26	43.03	0.035	1.001 32	12.78	36.56
0.043	1.000 05	21.00	48.51	0.058	0.999 97	22.90	39.83	0.062	0.999 95	25.18	40.61	0.043	1.001 35	14.84	34.76
0.055	1.000 07	24.76	45.38	0.048	0.999 96	19.86	41.63	0.075	0.999 97	29.10	38.89	0.053	1.001 37	17.36	32.82
0.068	1.000 10	29.48	43.21	0.037	0.999 94	16.26	44.10	0.080	0.999 98	30.62	38.24	0.062	1.001 38	19.44	31.10
0.087	1.000 14	35.08	40.17	0.027	0.999 93	12.78	47.34	0.092	1.000 00	33.82	36.67	0.076	1.001 40	22.40	29.29
0.099	1.000 16	38.44	38.74	0.016	0.999 91	8.26	51.34	0.104	1.000 02	36.94	35.35	0.090	1.001 43	25.04	27.96
0.109	1.000 18	41.16	37.74									0.096	1.001 44	26.24	27.45
60 mass % DMF				60 mass % DMF				60 mass % DMF				60 mass % DMF			
0.012	0.997 19	5.06	40.40	0.017	0.997 19	5.66	33.45	0.010	0.997 12	3.73	35.90	0.014	0.997 18	3.70	25.91
0.023	0.997 21	8.18	36.04	0.028	0.997 20	8.31	29.39	0.018	0.997 15	6.12	34.89	0.019	0.997 19	4.56	24.56
0.034	0.997 23	11.02	32.19	0.032	0.997 21	9.26	28.48	0.027	0.997 17	8.62	31.42	0.028	0.997 19	6.12	22.02
0.045	0.997 24	13.30	29.67	0.043	0.997 22	11.26	26.03	0.036	0.997 20	10.50	29.29	0.037	0.997 19	7.45	20.11
0.056	0.997 25	15.20	27.29	0.054	0.997 23	12.98	24.22	0.045	0.997 21	12.33	27.33	0.047	0.997 23	8.67	18.56
0.066	0.997 28	17.20	25.88	0.066	0.997 25	14.90	22.63	0.052	0.997 21	13.70	26.17	0.057	0.997 25	9.93	17.36
0.082	0.997 31	19.84	24.04	0.081	0.997 27	16.97	20.87	0.066	0.997 24	15.84	23.97	0.070	0.997 28	11.28	16.21
0.099	0.997 35	22.32	22.48	0.091	0.997 29	18.17	19.92	0.074	0.997 25	17.12	23.07	0.079	0.997 30	12.18	15.42
0.111	0.997 38	24.00	21.56	0.108	0.997 32	20.41	18.84	0.088	0.997 29	19.12	21.66	0.089	0.997 32	13.21	14.84

Table 2. Continued

10^2c^a	ρ^b	$10^6\kappa^c$	Λ^d	10^2c	ρ	$10^6\kappa$	Λ	10^2c	ρ	$10^6\kappa$	Λ	10^2c	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·cm^2·mol^{-1}.

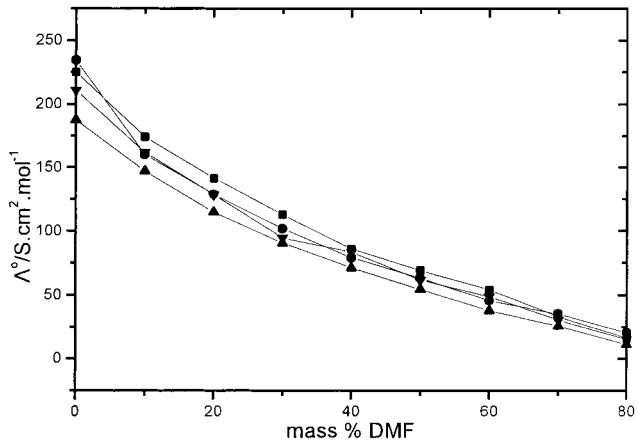

Figure 1. Variation of limiting molar conductivities with mass % DMF for $CoSO_4$ (■), $NiSO_4$ (●), $CdSO_4$ (▲), and $MnSO_4$ (▼) in water + DMF mixtures at 293.15 K.

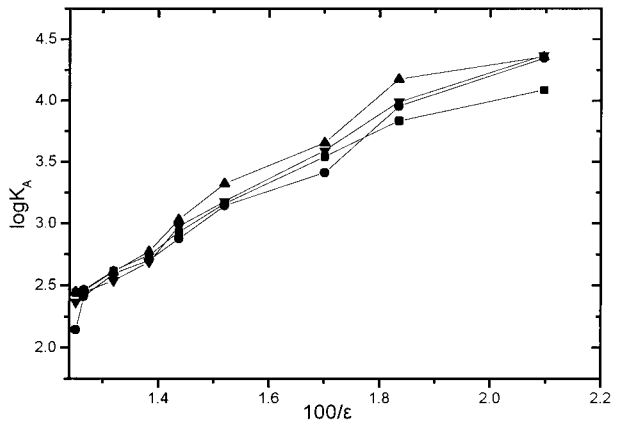

Figure 2. Variation of association constants with the inverse dielectric constant for $CoSO_4$ (■), $NiSO_4$ (●), $CdSO_4$ (▲), and $MnSO_4$ (▼) in water + DMF mixtures at 293.15 K.

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 conductances of each electrolyte in the water + DMF mixtures, 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 amides[14] 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 $(\Lambda, c)_T$ 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	Λ_0/S·cm^2·mol^{-1}	K_A/dm^3·mol^{-1}	σ_Λ
	$CoSO_4$		
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_Λ) 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 $MnSO_4$, $CoSO_4$, $NiSO_4$, and $CdSO_4$ 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 hindrance[22] and lower polarizability compared to that of water molecules, do not align around the cation. Hence, ion pair formation occurs.

Acknowledgment

The authors wish to thank Mr. G. A. Polizos, Ph.D. student, Department of Physics, National and Technical University of Athens, for his help in the measurement of the relative permittivities of the solvent mixtures.

Literature Cited

(1) Pethybridge, A. D.; Taba, S. S. Precise Conductometric Studies on Aqueous Solutions of 2:2 Electrolytes. *Discuss. Faraday Soc.* **1977**, *64*, 274−284.

(2) Quintana, C.; Llorente, M. L.; Sanchez, M.; Vivo, A. Viscosity of Na_2SO_4 and $MgSO_4$ Solutions in Ethanol−Water Mixtures at 15, 25 and 35 °C. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 3307−3314.

(3) Niazi, M. S. K.; Hussain, M. Conductivities and Ionic Association of Copper(II) and Manganese(II) Sulfates in Ethanol + Water at 298.15 K. *J. Chem. Eng. Data* **1994**, *39*, 48−49.

(4) Tsierkezos, N. G.; Molinou, I. E. Limiting Molar Conductances andThermodynamic Association Constants for Nickel(II), Cadmium(II), Magnesium(II), and Copper(II) Sulfates in Mixtures of Methanol and Water at 293.15 K. *J. Chem. Eng. Data* **2000**, *45*, 819−822.

(5) Shelley, V. M.; Talintyre, A.; Yarwood, J.; Buchner, R. Spectroscopic Studies of Solute−Solute and Solute−Solvent Interactions in Solutions Containing *N*,*N*-Dimethylformamide. *Discuss. Faraday Trans.* **1988**, *85*, 211−224.

(6) Krishnan, C. V.; Friedman, H. L. Solvation Enthalpies of Electrolytes in Methanol and Dimethylformamide. *J. Phys. Chem.* **1971**, *75* (23), 3606−3612.

(7) Garcia, B.; Alcalde, R.; Leal, J. M.; Matos, J. S. Shear viscosities of the *N*-methylformamide- and *N*,*N*-dimethylformamide- (C_1−C_{10}) alkan-1-ol solvent systems. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (6), 1115−1118.

(8) Visser, C.; Somsen, G. Hydrophobic Interactions in Mixtures of *N*,*N*-Dimethylformamide and Water. Model Calculations and Enthalpies of Solution. *J. Phys. Chem.* **1974**, *78* (17), 1719−1722.

(9) Rajasekhar, P.; Reddy, K. S. Excess Thermodynamic properties for Mixtures of Water and *N*,*N*-Dimethylformamide at 303.15 K. *Thermochim. Acta* **1987**, *17*, 379−383.

(10) Guarino, G.; Ortona, O.; Sartorio, R.; Vitagllano, V. Diffusion, Viscosity, and Refractivity Data on the Systems Dimethylformamide-Water and *N*-Methylpyrrolidone-Water at 5 °C. *J. Chem. Eng. Data* **1985**, *30*, 366−368.

(11) Kalugin, O. N.; Gorobetz, M. A.; Jalah, R. M. N.; Vjunnik, I. N.; Zavgorodnij, Y. N. Structure and Dynamics of Ion-Molecular Interactions in 1−1 Electrolyte Solutions in Dimethylformamide on the Temperature Range 25−70 °C from Viscosity and Density Data. *Z. Phys. Chem.* **1997**, *199*, 145−164.

(12) Corradini, F.; Marchetti, A.; Tagliazucchi, M.; Tassi, L.; Tosi, G. Dielectric Behaviour of the *N*,*N*-Dimethylformamide−2-Methoxyethanol−1,2-Dimethoxyethane Ternary Solvent System from −10 to +20 °C. *J. Chem. Soc., Faraday Trans.* **1994**, *90* (8), 1089−1094.

(13) Ramadevi, R. S.; Prabhakara Rao, M. V. Excess Volumes of Substituted Benzenes with *N*,*N*-Dimethylformamide. *J. Chem. Eng. Data* **1995**, *40*, 65−67.

(14) Assarsson, P.; Eirich, F. R. Properties of Amides in Aqueous Solution. *J. Phys. Chem.* **1968**, *72* (8), 2710−2719.

(15) Petersen, R. C. Interactions in the Binary Liquid System *N*,*N*-Dimethylacetamide−Water: Viscosity and Density. *J. Phys. Chem.* **1960**, *64*, 184−185.

(16) Lee, W. H.; Wheaton, R. J. Conductance of Symmetrical, Unsymmetrical and Mixed Electrolytes. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 743−766.

(17) Lee, W. H.; Wheaton, R. J. Conductance of Symmetrical, Unsymmetrical and Mixed Electrolytes. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1456−1482.

(18) Pethybridge, A.D.; Taba, S. S. Precise Conductometric Studies on Aqueous Solutions of 2:2 Electrolytes. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 368−376.

(19) Justice, J. C. An Interpretation for the Distance Parameter of the Fuoss-Onsager Conductance Equation in the Case of Ionic Association. *Electrochim. Acta* **1971**, *16*, 701−711.

(20) Gill, S.; Sekhri, M. B. New Approach to the Evaluation of Single-ion Conductances in Pure and Mixed Nonaqueous Solvents. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 119−125.
(21) Barczynska, J.; Bald, A.; Szejgis, A. Viscometric and Conductometric Studies for $CaCl_2$ Solutions in Water−Propan-1-ol Mixtures at 25 °C. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (19), 2887−2890.
(22) Garcia-Paneda, E.; Yanes, C.; Calvente, J. J.; Maestre, A. Limiting Partial Molar Volumes of Electrolytes in Dimethylformamide−Water Mixtures at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1994**, *90* (4), 575−577.
(23) Petrucci, S.; Hemmes, P.; Battistini, M. Electrical Conductance and Viscosity of the Solvent System $MnSO_4$ in Water−Glycol at 25 °C. *J. Am. Chem. Soc.* **1967**, *89*, 5552−5555.

Received for review March 29, 2001. Accepted June 26, 2001. This work was financially supported by the National and Kapodistrian University of Athens through its Special Research Account.

JE0101101