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Articles

Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. III. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Chlorides in *N*,*N*-Dimethylformamide

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The densities of divalent transition-metal chlorides in *N*,*N*-dimethylformamide have been measured over the whole composition range at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K. From these densities, apparent molar volumes and partial molar volumes of the salts at infinite dilution as well as the expansibilities have been evaluated. The apparent molar isentropic compressibilities of transition-metal chlorides in DMF have been determined from sound velocity data obtained at 298.15 K. The results have been discussed in terms of complex formation.

Introduction

The volumetric and ultrasonic properties of divalent transition-metal perchlorates in *N*,*N*-dimethylformamide and acetonitrile were the subject of our previous papers.[1,2] The obtained sequences of limiting apparent molar volumes and the limiting apparent molar isentropic compressibilities of the transition-metal perchlorates within the manganese(II)−zinc(II) series

$$Mn(ClO_4)_2 > Co(ClO_4)_2 > Ni(ClO_4)_2 < Cu(ClO_4)_2 > Zn(ClO_4)_2$$

reflect effects related to the electronic structure and the ionic radii of metal cations. The results indicate that the structural factors controlling the properties of divalent transition-metal cations are related to the ligand field stabilization effect. It should be noted that the values of limiting apparent molar isentropic compressibility of the manganese(II)−zinc(II) perchlorates in DMF are practically, within experimental error, constant.

The present work was undertaken to study an influence of complex formation on the apparent molar volumes at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K and the apparent molar isentropic compressibilities at 298.15 K for DMF solutions of chlorides of the divalent metal cations belonging to the Mn(II) to Zn(II) series. Moreover, an influence of temperature on the limiting values of the apparent molar volume of the metal chlorides is studied.

The transition-metal halides dissolved in strongly polar solvents which behave like electrolytes. It seems to be obvious that the most important factor controlling the electrolytic properties of their solutions is the relative stability of the tetrahedral and octahedral complexes. The coordination geometry around the metal ion changes upon complexation.

Formation of chloro complexes of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) in DMF was studied by calorimetry and spectrophotometry.[3−8] The authors demonstrated that all the monochloro complexes of transition-metal(II) ions have an octahedral structure, and almost all di-, tri-, and tetrachloro complexes appear as tetrahedral species. The spectrophotometric results confirm the high tendency of the Ni^{2+} cation toward an octahedral structure, resulting in the formation of six-coordinated mono- and dichloro complexes of nickel(II) in DMF solutions of $NiCl_2$ in the whole range of concentrations, and the tetrahedral complexes are formed in more concentrated solutions only. The presence of the $NiCl(DMF)_5^+\cdot NiCl_3DMF^-$ complex electrolyte has been established in a more concentrated solution of $NiCl_2$ in DMF.[9] The properties of $CoCl_2$ in DMF solution are determined by high stability of pseudotetrahedral trichloro complexes of cobalt $CoCl_3DMF^-$ accompanied by the octahedral cationic species $CoCl(DMF)_5^+$ and $Co(DMF)_6^{2+}$.[10,11] Almost in the whole concentration range, $CoCl_2$ appears in DMF as a complex electrolyte $Co(DMF)_6^{2+}\cdot 2CoCl_3DMF^-$ type.

Experimental Section

The solid DMF-solvated metal chlorides were prepared in a way similar to that for the perchlorates reported previously.[1] The temperature during the removal of an excess of solvent was 343 K. The stock solutions of the metal chlorides were standardized by titration with EDTA. At least ten determinations were carried out for each of the solutions, and the relative errors were smaller than 0.1 %. Solutions for density and speed of sound measurements were prepared by weighed dilutions. Details of measurement procedures and their errors are identical to those described previously.[1,2] The densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with a thermostate system based on a Peltier unit with a repeatability of $1.0\cdot 10^{-3}$ kg·m^{-3} and an uncertainty of $5.0\cdot 10^{-3}$ kg·m^{-3}. The temperature was kept constant at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K with an accuracy of 0.001

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Table 1. Densities *d* of the Solutions of the Metal Chlorides in DMF at Different Temperatures

	d/kg·m^{-3}						
m_s/mol·kg^{-1}	T = 283.15 K	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 313.15 K	T = 323.15 K	T = 333.15 K
$MnCl_2$							
0.04624	962.590	953.076	948.310	943.542	933.965	924.343	914.669
0.06428	964.332	954.820	950.056	945.286	935.713	926.096	916.423
0.09217	967.038	957.528	952.763	947.988	938.421	928.811	919.148
0.1143	969.210	959.696	954.925	950.152	940.583	930.979	921.318
0.1371	971.425	961.910	957.146	952.375	942.812	933.206	923.554
0.1848	976.113	966.588	961.824	957.054	947.495	937.898	928.260
0.2303	980.630	971.096	966.324	961.561	952.000	942.403	932.768
0.2759	985.198	975.658	970.889	966.113	956.562	946.978	937.350
0.3186	989.506	979.952	975.177	970.405	960.846	951.260	941.644
0.3621	993.925	984.354	979.577	974.803	965.244	955.662	946.053
0.4066	998.488	988.910	984.128	979.352	969.792	960.216	950.606
0.4492	1002.850	993.259	988.473	983.694	974.133	964.558	954.960
DMF	958.124	948.611	943.840	939.073	929.490	919.855	910.162
$CoCl_2$							
0.03256	961.446	951.934	947.164	942.391	932.806	923.170	913.477
0.04604	962.841	953.329	948.560	943.786	934.200	924.564	914.868
0.06503	964.805	955.294	950.526	945.751	936.166	926.532	916.836
0.08297	966.667	957.154	952.386	947.613	938.030	928.392	918.698
0.09936	968.358	958.847	954.078	949.306	939.723	930.090	920.490
0.1327	971.824	962.310	957.545	952.770	943.191	933.558	923.862
0.1626	974.954	965.440	960.675	955.901	946.325	936.697	927.006
0.1950	978.345	968.837	964.070	959.300	949.724	940.096	930.410
0.2258	981.574	972.065	967.300	962.531	952.954	943.336	933.650
0.2584	985.027	975.520	970.757	965.988	956.417	946.793	937.112
0.2910	988.485	978.977	974.216	969.447	959.880	950.263	940.589
0.3225	991.882	982.380	977.612	972.845	963.280	953.675	944.000
DMF	958.077	948.565	943.797	939.025	929.440	919.807	910.120
$NiCl_2$							
0.03259	962.082	952.450	947.629	942.808	933.149	923.470	913.752
0.04688	963.743	954.073	949.237	944.400	934.728	925.034	915.307
0.06402	965.693	955.984	951.134	946.288	936.602	926.900	917.168
0.08077	967.611	957.870	953.012	948.154	938.450	928.739	919.009
0.09656	969.403	959.631	954.763	949.895	940.183	930.465	920.731
0.1290	973.099	963.284	958.396	953.517	943.780	934.047	924.300
0.1602	976.640	966.785	961.878	956.984	947.224	937.476	927.718
0.1936	980.460	970.565	965.641	960.734	950.949	941.185	931.418
0.2240	984.004	974.071	969.128	964.209	954.393	944.614	934.841
0.2553	987.592	977.628	972.675	967.740	957.911	948.115	938.325
0.2849	991.072	981.075	976.108	971.156	961.300	951.488	941.688
0.3174	994.846	984.819	979.836	974.874	964.990	955.164	945.357
DMF	958.077	948.565	943.797	939.025	929.440	919.807	910.120
$CuCl_2$							
0.04589	963.051	953.520	948.740	943.959	934.353	924.694	914.982
0.06604	965.227	955.686	950.901	946.116	936.500	926.833	917.110
0.08998	967.814	958.263	953.474	948.680	939.052	929.374	919.635
0.1154	970.570	961.008	956.214	951.414	941.773	932.082	922.330
0.1355	972.774	963.200	958.403	953.593	943.944	934.243	924.480
0.1828	977.958	968.365	963.553	958.739	949.069	939.344	929.554
0.2256	982.714	973.103	968.285	963.455	953.763	944.016	934.205
0.2659	987.200	977.571	972.743	967.913	958.201	948.438	938.610
0.3096	992.122	982.473	977.637	972.786	963.062	953.275	943.422
0.3541	997.168	987.500	982.657	977.793	968.041	958.230	948.350
0.3961	1001.957	992.272	987.415	982.551	972.780	962.949	953.050
0.4388	1006.900	997.196	992.327	987.456	977.662	967.814	957.890
DMF	958.124	948.611	943.840	939.073	929.490	919.855	910.162
$ZnCl_2$							
0.04462	962.503	952.966	948.188	943.406	933.803	924.158	914.465
0.06243	964.265	954.715	949.933	945.146	935.547	925.902	916.200
0.08859	966.878	957.313	952.524	947.727	938.110	928.450	918.744
0.1331	971.364	961.766	956.965	952.155	942.518	932.850	923.130
0.1783	975.981	966.350	961.530	956.713	947.055	937.368	927.640
0.2208	980.357	970.694	965.856	961.028	951.335	941.642	931.908
0.2664	985.118	975.422	970.574	965.724	956.018	946.289	936.527
0.3080	989.513	979.781	974.918	970.059	960.330	950.590	940.821
0.3501	993.990	981.226	979.352	974.481	964.728	954.963	945.176
0.4350	1003.136	993.308	988.400	983.499	973.697	963.890	954.072
DMF	958.124	948.611	943.840	939.073	929.490	919.855	910.162

K according to the manufacturer declaration. Before each measurement series, the accuracy of the density measurements and the purity of the solvent were verified by measuring its density at 298.15 K. The density value of (943.82 ± 0.069) kg·m^{-3} for *N*,*N*-dimethylformamide was found in the present study, whereas literature values vary from 944.03 kg·m^{-3} to

Table 2. Speed of Sound u, Adiabatic Compressibility K_S, and Apparent Molar Compressibility Φ_{KS} of the Metal Chlorides in DMF at 298.15 K

salt	m_s mol·kg^{-1}	u m·s^{-1}	$10^{10}K_S$ m^2·N^{-1}	$10^{14}\Phi_{KS}$ m^5·N^{-1}·mol^{-1}
$MnCl_2$	0.09217	1460.90	4.918	−6.94
	0.1371	1462.81	4.882	−6.90
	0.1848	1464.89	4.845	−6.85
	0.2303	1466.82	4.810	−6.79
	0.2759	1468.89	4.774	−6.76
	0.3186	1470.78	4.741	−6.71
	0.3621	1472.85	4.706	−6.68
	0.4066	1475.02	4.670	−6.66
	0.4492	1477.10	4.637	−6.62
$CoCl_2$	0.06503	1458.95	4.943	−6.60
	0.09936	1460.07	4.917	−6.64
	0.1327	1461.38	4.890	−6.68
	0.1626	1462.35	4.868	−6.70
	0.1950	1463.62	4.842	−6.72
	0.2258	1464.95	4.817	−6.75
	0.2584	1466.38	4.791	−6.77
	0.2910	1467.81	4.764	−6.78
	0.3225	1469.25	4.738	−6.79
$NiCl_2$	0.06402	1459.61	4.935	−8.60
	0.09656	1461.03	4.907	−8.51
	0.1290	1462.45	4.879	−8.42
	0.1602	1463.88	4.851	−8.36
	0.1936	1465.30	4.823	−8.27
	0.2240	1466.38	4.799	−8.14
	0.2553	1467.81	4.772	−8.09
	0.2849	1469.00	4.747	−8.02
	0.3174	1470.32	4.721	−7.93
$CuCl_2$	0.04589	1458.20	4.957	−6.43
	0.08998	1459.26	4.925	−6.38
	0.1355	1460.32	4.893	−6.32
	0.1828	1461.44	4.859	−6.24
	0.2256	1462.45	4.829	−6.19
	0.2659	1463.52	4.800	−6.16
	0.3096	1464.55	4.769	−6.10
	0.3541	1465.66	4.737	−6.05
	0.3961	1466.73	4.708	−6.00
	0.4388	1467.81	4.677	−5.96
$ZnCl_2$	0.04462	1457.49	4.965	−4.22
	0.08859	1457.93	4.939	−4.27
	0.1331	1458.45	4.913	−4.31
	0.1783	1459.00	4.886	−4.34
	0.2208	1459.61	4.860	−4.36
	0.2664	1460.32	4.831	−4.40
	0.3080	1461.03	4.805	−4.42
	0.3501	1461.77	4.779	−4.44
	0.3894	1462.45	4.754	−4.45
	0.4350	1463.52	4.724	−4.47

943.82 kg·m^{-3}.[12,13] DMF was purchased from two different companies (Fluka, puriss, H_2O < 0.01 %; and Aldrich, puriss, H_2O < 0.005 %). This might explain the differences in the values of densities of DMF obtained from two series of measurements. The speed of sound was measured using the sound analyzer OPTIME 1.0 from OPTEL (Poland) with an uncertainty of 0.05 m·s^{-1} by measuring the time it takes for a pulse of ultrasound to travel from one transducer to another (*pitch-catch*) or to return to the same transducer (*pulse-echo*). The cell was thermostated at (298.15 ± 0.005) K and calibrated with double distilled water, where the value 1496.69 m·s^{-1} of the sound velocity in pure water has been used. The speed of sound obtained for DMF was 1457.13 m·s^{-1}, whereas the corresponding literature values are (1468.0 and 1448.55) m·s^{-1}.[14,15]

Measurement Results And Calculations

Speed of Sound and Density. The density and speed of sound data together with respective values of the adiabatic compressibility coefficients, as well as apparent molar adiabatic compressibilities obtained for the solutions of the transition-metal chlorides in DMF, are collected in Tables 1 and 2. It has been found that for all the solutions studied the relation

$$y = A_0 + A_1 \cdot c^{1/2} + A_2 \cdot c \tag{1}$$

where y denotes density d or speed of sound u is valid. The coefficients of the polynomials and respective values of the residual variance σ are given in Tables 3 and 4. It is obvious that A_0 denotes density or speed of sound for pure DMF.

Table 3. Coefficients of Equation 1 for Density of the Solutions of the Metal Chlorides in DMF at Different Temperatures

salt		A_0 kg·m^{-3}	A_1 (kg^2·m^{-3}·mol^{-1})$^{1/2}$	A_2 kg·mol^{-1}	σ_d kg·m^{-3}
$MnCl_2$	283.15	958.124	0.013 ± 0.0034	0.099 ± 0.00020	0.018
	293.15	948.611	0.017 ± 0.0043	0.0994 ± 0.00026	0.021
	298.15	943.840	0.019 ± 0.0045	0.0997 ± 0.00027	0.022
	303.15	939.073	0.019 ± 0.0047	0.1002 ± 0.00027	0.024
	313.15	929.490	0.022 ± 0.0056	0.1011 ± 0.00032	0.028
	323.15	919.855	0.025 ± 0.0062	0.1021 ± 0.00036	0.031
	333.15	910.162	0.028 ± 0.0069	0.1032 ± 0.00040	0.033
$CoCl_2$	283.15	958.077	0.024 ± 0.0047	0.1044 ± 0.00032	0.020
	293.15	948.565	0.024 ± 0.0051	0.1054 ± 0.00033	0.020
	298.15	943.797	0.024 ± 0.0049	0.1059 ± 0.00034	0.021
	303.15	939.025	0.024 ± 0.0048	0.1065 ± 0.00033	0.021
	313.15	929.440	0.024 ± 0.0051	0.1076 ± 0.00037	0.022
	323.15	919.807	0.022 ± 0.0053	0.1089 ± 0.00037	0.021
	333.15	910.120	0.024 ± 0.0085	0.1099 ± 0.00059	0.036
$NiCl_2$	283.15	958.077	0.095 ± 0.0036	0.1111 ± 0.00025	0.016
	293.15	948.565	0.074 ± 0.0040	0.1118 ± 0.00028	0.015
	298.15	943.797	0.065 ± 0.0034	0.1122 ± 0.00024	0.015
	303.15	939.025	0.057 ± 0.0032	0.1126 ± 0.00023	0.014
	313.15	929.440	0.047 ± 0.0031	0.1134 ± 0.00018	0.011
	323.15	919.807	0.041 ± 0.0029	0.1143 ± 0.00021	0.012
	333.15	910.120	0.038 ± 0.0036	0.1153 ± 0.00025	0.015
$CuCl_2$	283.15	958.124	0.016 ± 0.0046	0.1097 ± 0.00026	0.022
	293.15	948.611	0.024 ± 0.0038	0.1101 ± 0.00022	0.018
	298.15	943.840	0.017 ± 0.0044	0.1106 ± 0.00026	0.023
	303.15	939.073	0.017 ± 0.0043	0.1109 ± 0.00024	0.021
	313.15	929.490	0.016 ± 0.0043	0.1116 ± 0.00026	0.022
	323.15	919.855	0.016 ± 0.0045	0.1122 ± 0.00026	0.022
	333.15	910.162	0.017 ± 0.0045	0.1128 ± 0.00027	0.022
$ZnCl_2$	283.15	958.124	−0.016 ± 0.0038	0.1039 ± 0.00019	0.015
	293.15	948.611	−0.015 ± 0.0033	0.1041 ± 0.00018	0.014
	298.15	943.840	−0.013 ± 0.0032	0.1042 ± 0.00023	0.014
	303.15	939.073	−0.013 ± 0.0033	0.1045 ± 0.00019	0.014
	313.15	929.490	−0.011 ± 0.0034	0.1049 ± 0.00019	0.015
	323.15	919.855	−0.013 ± 0.0040	0.1056 ± 0.0063	0.017
	333.15	910.162	−0.0051 ± 0.0027	0.1061 ± 0.00014	0.010

Table 4. Coefficients of Equation 1 for Speed of Sound in the Solutions of the Metal Chlorides in DMF at 298.15 K (A_0 = 1457.13 m·s^{-1})

salt	A_1 (m^5·s^{-2}·mol^{-1})$^{1/2}$	A_2 m^4·s^{-1}·mol^{-1}	σ_u m·s^{-1}
$MnCl_2$	−0.046 ± 0.021	0.047 ± 0.0013	0.082
$CoCl_2$	−0.16 ± 0.038	0.047 ± 0.0026	0.13
$NiCl_2$	0.007 ± 0.037	0.042 ± 0.0025	0.12
$CuCl_2$	0.0008 ± 0.0055	0.0245 ± 0.00032	0.024
$ZnCl_2$	−0.10 ± 0.036	0.019 ± 0.0021	0.15

Adiabatic Compressibility. The adiabatic (isentropic) compressibility of solution is defined by the thermodynamic relation

$$K_S = -(\partial V/\partial P)_S/V \tag{2}$$

It was calculated with the help of ultrasonic velocity and density data using the Laplace equation

$$K_S = 1/(u^2 \cdot d) \tag{3}$$

In the concentration range studied, the adiabatic compressibility values decrease nonlinearly; that is

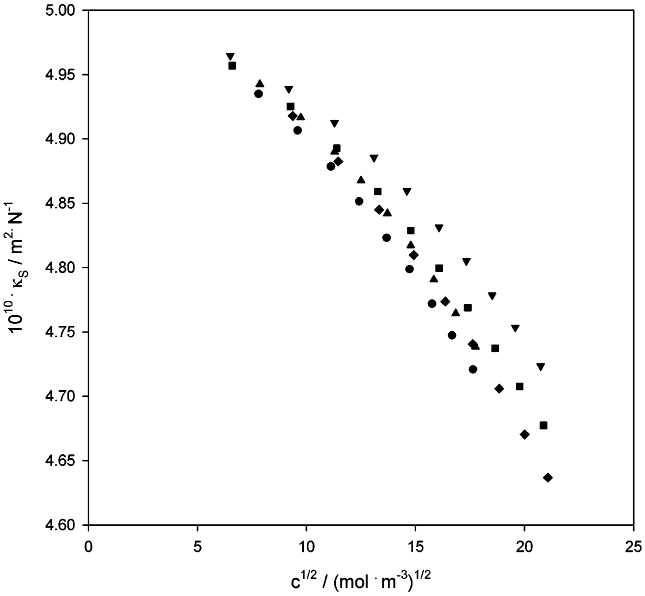

Figure 1. Adiabatic compressibility coefficient K_S against the square root of molarity c of the divalent transition-metal chlorides in DMF at T = 298.15 K: ◆, $MnCl_2$; ▲, $CoCl_2$; ●, $NiCl_2$; ■, $CuCl_2$; ▼, $ZnCl_2$.

Table 5. Coefficients of Equation 4 for Adiabatic Compressibility of the Solutions of the Metal Chlorides in DMF at 298.15 K and Their Standard Deviations σ

salt	$10^{13}B_1$ $(m^7 \cdot N^{-2} \cdot mol^{-1})^{1/2}$	$10^{13}B_2$ $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{12}\sigma$ $m^2 \cdot N^{-1}$
$MnCl_2$	-0.60 ± 0.15	-0.769 ± 0.0083	0.055
$CoCl_2$	0.46 ± 0.091	-0.824 ± 0.0059	0.029
$NiCl_2$	-0.94 ± 0.38	-0.82 ± 0.028	0.12
$CuCl_2$	-0.73 ± 0.25	-0.69 ± 0.018	0.11
$ZnCl_2$	0.30 ± 0.080	-0.633 ± 0.0045	0.033

$$K_S = B_0 + B_1 \cdot c^{1/2} + B_2 \cdot c \qquad (4)$$

where $4.99 \cdot 10^{-10}$ $N \cdot m^{-2}$ is the adiabatic compressibility of pure DMF, K_{S0}, at 298.15 K, calculated using the values of density and speed of sound reported in the present study. The coefficients B_1 and B_2 of the polynomials and values of the residual variance σ are given in Table 5. Figure 1 shows the adiabatic compressibility coefficients of manganese(II)−zinc(II) chlorides in DMF against the square root of concentration. Inspection of the presented data shows that the highest impact on solution compressibility was nickel(II) chloride, whereas the lowest influence on solution compressibility is observed for zinc(II) chloride. It is evident that the observed differences are related to the complex formation. Pilarczyk and Kliszporn reported that dissolution of $NiCl_2$ in DMF results in the formation of a $NiCl(DMF)_5^+ \cdot NiCl_3DMF^-$ complex electrolyte.[9] The same process for $ZnCl_2$ is probably associated with formation of the $Zn(DMF)_2Cl_2$ coordination form.[5]

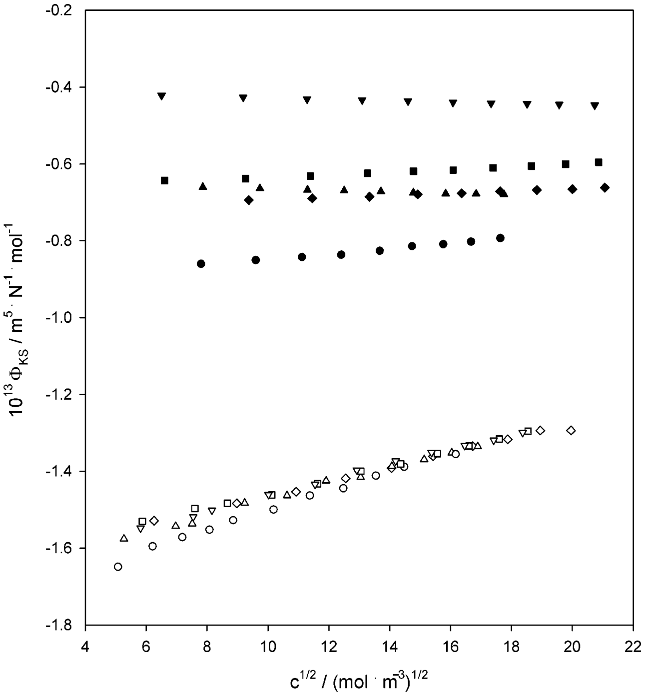

Figure 2. Apparent molar compressibility Φ_{KS} against the square root of molarity c of the divalent transition-metal chlorides and perchlorates in DMF at T = 298.15 K: solid symbols as in Figure 1, this work; ◇, $Mn(ClO_4)_2$; △, $Co(ClO_4)_2$; ○, $Ni(ClO_4)_2$; □, $Cu(ClO_4)_2$; ▽, $Zn(ClO_4)_2$, Warmińska et al.[1]

Table 6. Coefficients of Equation 6 for Apparent Molar Compressibility of the Solutions of the Metal Chlorides in DMF at 298.15 K

salt	$10^{13}A_0$ $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{16}A_1$ $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{14}\sigma$ $m^5 \cdot N^{-1} \cdot mol^{-1}$
$MnCl_2$	-0.72 ± 0.0030	2.8 ± 0.19	0.0086
$CoCl_2$	-0.645 ± 0.0024	-2.0 ± 0.20	0.0071
$NiCl_2$	-0.92 ± 0.013	6.9 ± 0.73	0.029
$CuCl_2$	-0.669 ± 0.0043	3.4 ± 0.29	0.018
$ZnCl_2$	-0.410 ± 0.0017	-1.8 ± 0.10	0.0046

Apparent and Partial Quantities. Apparent Molar Isentropic Compressibility. The apparent molar isentropic compressibility, Φ_{KS}, of the electrolyte solutions was calculated from the equation

$$\Phi_{KS} = (K_S d_0 - K_{S0} d)/(m_S d d_0) + M_2 K_S / d_0 \qquad (5)$$

where m_s denotes the number of moles of the solute per kilogram of solution (molonity); d and d_0 are the densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. The terms K_S and K_{S0} refer to the adiabatic compressibility of the solution and the solvent, respectively, and were calculated using eq 3. The obtained values of K_S and Φ_{KS} are presented in Table 2. Figure 2 shows the apparent molar adiabatic compressibility of manganese(II)−zinc(II) chlorides in DMF against the square root of concentration. As is seen, the plots are linear, and Masson's type equation

$$\Phi_{KS} = A_0 + A_1 \cdot c^{1/2} \qquad (6)$$

can been used for extrapolation. The coefficients A_0 and A_1 of the plots and values of the residual variance σ are given in Table 6. In the figure, there are data for metal perchlorates from our previous paper along with the data for metal chlorides.[1] Once again, inspection of the data presented shows that complex formation has an essential influence on solution compressibility. Because of the variety of structural forms of metal chloro complexes in DMF solutions, the values of the apparent molar isentropic compressibilities of metal chlorides at infinite dilution vary within wide limits. The highest value of the apparent molar isentropic compressibility is with $ZnCl_2$, and the lowest is with $NiCl_2$. The limiting apparent molar isentropic compressibilities Φ_{KS}^0 for metal perchlorates, which exist in DMF as the $M(DMF)_6^{2+} \cdot 2ClO_4^-$ type solvates, are practically constant.

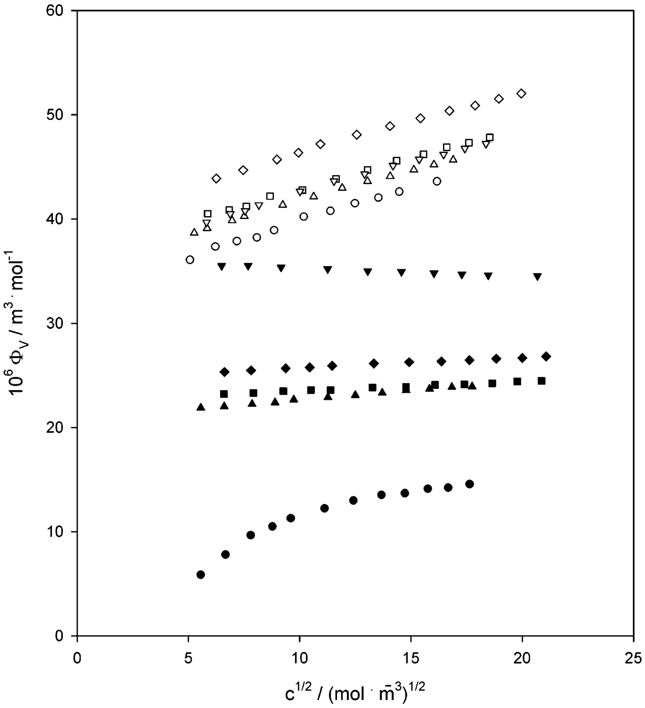

Figure 3. Apparent molar volumes Φ_V against the square root of molarity c of the divalent transition-metal chlorides and perchlorates in DMF at $T = 298.15$ K: solid symbols as in Figure 1, this work; ◇, $Mn(ClO_4)_2$; △, $Co(ClO_4)_2$; ○, $Ni(ClO_4)_2$; □, $Cu(ClO_4)_2$; ▽, $Zn(ClO_4)_2$, Warmiska et al.[1]

Apparent Molar Volume. The apparent molar volume Φ_V of the electrolyte solutions was calculated according to

$$\Phi_V = (d_0 - d)/(m_S d d_0) + M_2/d_0 \tag{7}$$

where the symbols have the same meanings as in eq 5. Figure 3 shows the apparent molar volumes of metal chlorides Φ_V plotted against the square root of concentration $c^{1/2}$. For solutions of manganese(II), cobalt(II), copper(II), and zinc(II) chlorides, the plots of Φ_V against $c^{1/2}$ are found to be linear over the concentration range studied at all measured temperatures. Therefore, the equation

$$\Phi_V = A_0 + A_1 \cdot c^{1/2} \tag{8}$$

was valid. The coefficients of the equation and their standard deviations, δ, are given in Table 7. Further inspection of Figure 3 shows that the apparent molar volumes of $NiCl_2$ with concentration are not a linear function of $c^{1/2}$. The concentration dependencies of the apparent molar volume of the $NiCl_2$ solution can be satisfactorily described by the equation

$$\Phi_V = A_0 + A_1 \cdot c^{1/2} + A_2 \cdot c \tag{9}$$

The proper extrapolation of apparent molar volumes to infinite dilution has been discussed by Marcus and Hefter.[16] We know that the use of both the purely empirical Masson and the extended Masson equations for obtaining the standard molar volumes is at best a crude approximation. However, there are data available for the theoretical slope estimation for DMF for $T = 298.15$ K only, whereas our data cover the temperature range between $T = 283.15$ K and $T = 333.15$ K.[17]

The coefficients of eq 9 and their standard deviations, δ, are given in Table 8. It should be noted that coefficients A_0 in eqs 6, 8, and 9 cannot be considered as the values of the limiting molar adiabatic compressibilities or apparent molar volumes of the salts. At infinite dilution, ions are surrounded only by the solvent, with other ions being infinitely distant. Therefore, both Φ_V^o and Φ_{KS}^o are a good measure of ion−solvent interactions with ion−ion interactions being negligible. Unfortunately, in DMF as well as in other nonaqueous solvents, in which the dielectric constant is significantly lower than the dielectric constant of water, apparent molar volumes can be affected by ion pairing. This phenomenon takes place in solutions of chlorides and bromides of transition metals. Therefore, both apparent molar volumes and molar compressibilities at infinite dilution should not be considered as the limiting values of both quantities.

Table 7. Coefficients of Equation 8 for Apparent Molar Volume of the Solutions of the Metal Chlorides in DMF at Different Temperatures

salt	T/K	$10^6 A_0$ / $m^3 \cdot mol^{-1}$	$10^8 A_1$ / $(m^9 \cdot mol^{-3})^{1/2}$	$10^6 \sigma$ / $m^3 \cdot mol^{-1}$
$MnCl_2$	283.15	26.28 ± 0.048	6.7 ± 0.83	0.060
	293.15	25.34 ± 0.040	8.6 ± 0.69	0.050
	298.15	24.74 ± 0.039	9.9 ± 0.70	0.048
	303.15	24.37 ± 0.041	9.9 ± 0.68	0.049
	313.15	23.22 ± 0.032	11.4 ± 0.54	0.036
	323.15	21.82 ± 0.035	13.4 ± 0.62	0.041
	333.15	20.27 ± 0.043	15.6 ± 0.72	0.049
$CoCl_2$	283.15	22.2 ± 0.15	17.2 ± 0.84	0.052
	293.15	21.3 ± 0.14	17.7 ± 0.91	0.056
	298.15	20.9 ± 0.12	17.6 ± 0.83	0.050
	303.15	20.5 ± 0.13	17.5 ± 0.75	0.046
	313.15	19.5 ± 0.13	17.6 ± 0.77	0.047
	323.15	18.6 ± 0.10	16.9 ± 0.81	0.048
	333.15	17.7 ± 0.17	15.3 ± 0.15	0.060
$CuCl_2$	283.15	23.41 ± 0.069	8.1 ± 0.49	0.034
	293.15	22.91 ± 0.060	8.6 ± 0.44	0.029
	298.15	22.63 ± 0.067	8.8 ± 0.49	0.032
	303.15	22.51 ± 0.059	8.5 ± 0.41	0.027
	313.15	22.07 ± 0.068	8.5 ± 0.49	0.031
	323.15	21.59 ± 0.071	8.8 ± 0.51	0.034
	333.15	21.01 ± 0.097	9.6 ± 0.70	0.046
$ZnCl_2$	283.15	36.4 ± 0.13	−9.3 ± 0.94	0.056
	293.15	36.3 ± 0.14	−8.3 ± 0.86	0.051
	298.15	36.0 ± 0.14	−7.2 ± 0.75	0.046
	303.15	36.0 ± 0.17	−7.6 ± 0.79	0.049
	313.15	35.6 ± 0.14	−6.6 ± 0.79	0.049
	323.15	35.0 ± 0.22	−5.0 ± 1.20	0.072
	333.15	34.1 ± 0.17	−3.0 ± 0.10	0.060

Table 8. Coefficients of Equation 9 for Apparent Molar Volume of the Solutions of Nickel Chloride in DMF at Different Temperatures

T/K	$10^6 A_0$ / $m^3 \cdot mol^{-1}$	$10^6 A_1$ / $(m^9 \cdot mol^{-3})^{1/2}$	$10^8 A_2$ / $m^6 \cdot mol^{-2}$	$10^6 \sigma$ / $m^3 \cdot mol^{-1}$
283.15	−10 ± 0.94	2.7 ± 0.22	−7.8 ± 0.73	0.32
293.15	−5.6 ± 0.95	2.4 ± 0.23	−7.0 ± 0.74	0.32
298.15	−3.3 ± 0.86	2.1 ± 0.17	−6.3 ± 0.68	0.30
303.15	−1.5 ± 0.83	1.9 ± 0.20	−5.8 ± 0.70	0.30
310.15	1.9 ± 0.68	1.5 ± 0.14	−4.4 ± 0.52	0.22
320.15	3.3 ± 0.62	1.2 ± 0.17	−3.7 ± 0.49	0.21
330.15	4.8 ± 0.85	0.93 ± 0.53	−2.3 ± 0.66	0.28

An inspection of Figure 3 shows that the points obtained for metal chlorides run below the points for metal perchlorates.[1] The highest values of the apparent molar volumes are observed for the zinc(II) chloride solution. The lowest values of the apparent molar volume were obtained for the nickel(II) chloride solution.

As one can see, the apparent molar volumes are less sensitive to structural effects in solutions than the compressibilities. Whereas the volumes of the metal perchlorates and chlorides are close, the difference in values of compressibility for both salt types is quite large.

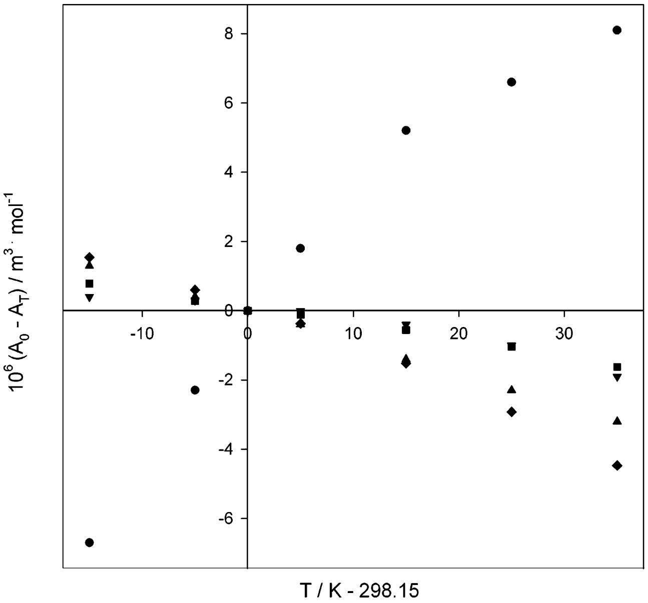

Figure 4. Apparent molar volumes at infinite dilution against the temperature of the divalent transition-metal chlorides in DMF: ◆, $MnCl_2$; ▲, $CoCl_2$; ●, $NiCl_2$; ■, $CuCl_2$; ▼, $ZnCl_2$.

Table 9. Parameters of Equation $A_0 - A_T = B_T(T/K - 298.15) + C_T(T/K - 298.15)^2$ for Metal Chlorides in DMF

salt	$10^6 B_T$ $m^3 \cdot mol^{-1}$	$10^6 C_T$ $m^3 \cdot mol^{-1}$	$10^6 \sigma$ $m^3 \cdot mol^{-1}$
$MnCl_2$	-0.11 ± 0.019	-0.0006 ± 0.00049	0.14
$CoCl_2$	-0.089 ± 0.0043	-0.0009 ± 0.00014	0.038
$NiCl_2$	0.39 ± 0.029	-0.0045 ± 0.00035	0.26
$CuCl_2$	-0.046 ± 0.099	-0.000052 ± 0.00034	0.096
$ZnCl_2$	-0.029 ± 0.016	-0.00062 ± 0.00056	0.16

Volume Expansibility. In Figure 4, the values of the difference $A_0 - A_T$, where A_T is equal to the apparent molar volume at infinite dilution at 298.15 K, are plotted against the difference $(T - 298.15)$ K. Inspection of the data shows that only for the solution of nickel(II) chloride an increase in temperature causes an increase of the apparent molar volume at infinite dilution. For other salts, more associated, a decrease was observed.[18] Moreover, the apparent molar volumes at infinite dilution of nickel(II) chloride are the most sensitiveto-ward temperature change. As seen, the plots are not linear, and the best description was obtained using the equation

$$A_0 - A_T = B_T(T/\mathrm{K} - 298.15) + C_T(T/\mathrm{K} - 298.15)^2 \quad (10)$$

Coefficients of eq 10 are listed in Table 9 along with the respective values of the residual variance. The influence of temperature on the apparent molar volumes can be discussed in terms of coordination disproportionation equilibria between the tetra- and hexacomplexes. The changes of molar volumes of octahedral chloro complexes in $NiCl_2$ solution with temperature result mainly from the expansibility of bulk solvent molecules. As far as the other salts are concerned, a decrease of the molar volume with temperature results from both the change in coordination sphere of the metal ion and a decrease in association.

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