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Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. VI. Apparent Molar Volumes, Expansibilities, and Compressibilities of Divalent Transition Metal Ions in Methanol and Dimethylsulfoxide

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The temperature dependence of the density of divalent transition metal perchlorates in dimethylsulfoxide as well as cobalt(II), nickel(II) perchlorates, and copper(II) trifluoromethanesulfonate in methanol was determined. Moreover, sound velocities for solutions of cobalt(II), nickel(II) perchlorates, and copper(II) trifluoromethanesulfonate in methanol have been measured at 298.15 K. From these data, the partial molar volumes, partial molar expansibilities, and partial molar isentropic compressibilities have been estimated. The results obtained are discussed in terms of ion−solvent interactions.

1. Introduction

The divalent transition metal perchlorates and trifluoromethanesulfonates are known to occur in strongly coordinating donor solvents in well-defined coordination forms, i.e., as the solvates $\mathrm{M(solvent)}_6^{2+}\cdot 2\mathrm{X}^-$ or $\mathrm{M(solvent)}_5^{2+}\cdot 2\mathrm{X}^-$ and $\mathrm{M(solvent)}_4^{2+}\cdot 2\mathrm{X}^-$.[1−4] It has been established that the solvation number of the metal ion is determined by keeping a balance among the increasing contribution due to higher charge of the metal ion, the decreasing contribution due to bulkiness of the solvent molecule, and the ligand field stabilization on the metal ion.[1,4] Moreover, in some solvents, e.g., *N*,*N*-dimethylacetamide and water, the coordination of solvent molecules to the divalent transition metal cations is controlled by the equilibrium between octahedral hexasolvates and tetrahedral tetrasolvates.[2,5] In less bulky solvents such as dimethylsulfoxide (DMSO) and methanol, the solvation structures of the transition metal ions are six-coordinate octahedral.[4]

Detailed analysis of conductometric, volumetric, and acoustic data shows that the properties of the solvated divalent cations exhibit small, but distinct, variation within the Mn(II)−Zn(II) series, obviously related to the electronic structure of the metal cation.[6,7]

The present study is the continuation of our earlier investigations.[8−10] So far, we have studied volumetric and acoustic properties of divalent transition metal ions in DMSO at 298.15 K and Mn(II) and Zn(II) in methanol. The main aim of this work is to explore the temperature influence on investigated properties as well as to complete the data for ions which have not been investigated earlier.

In our paper, we report data on the densities of methanolic solutions of cobalt(II), nickel(II) perchlorates, and copper(II) trifluoromethanesulfonate at (283.15, 288.15, 293.15, 298.15, 303.15, 308.15, and 313.15) K and DMSO solutions of transition metal perchlorates within the Mn(II)−Zn(II) series at (293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K. Moreover, we present experimental values of sound velocities of cobalt(II), nickel(II) perchlorates, and copper(II) trifluoromethanesulfonate in methanol at 298.15 K.

2. Experimental Section

Materials. Copper(II) trifluoromethanesulfonate (Alfa Aesar 99 % min., CAS no. 34946-82-2) was dried in a vacuum oven for several hours at $T = 378$ K. The solution of the salt in methanol was filtered before use.

Anhydrous solutions of metal(II) perchlorates in methanol have been prepared using 2,2-dimethoxypropane as a dehydration agent in the way described in our earlier work.[8]

Solid DMSO-solvated metal perchlorates were obtained from the corresponding hydrates by dissolving them in 2,2-dimethoxypropane (Fluka) followed by an addition of dimethylsulfoxide. The precipitated solids were filtered off and dissolved in anhydrous dimethylsulfoxide. This step was followed by removing any excess of the solvent as well as products of dehydratation under reduced pressure (1000 Pa) at about 343 K. During cooling, the crystalline solids were obtained and recrystallized twice from anhydrous DMSO.

The stock solutions of metal salts were standardized by EDTA titration. At least ten determinations were carried out for each of the solutions, and the uncertainties in the solution composition were smaller than 0.1 %. Solutions for density and speed of sound measurements were prepared by weighed dilutions.

Dimethylsulfoxide (Fluka - puriss, $H_2O < 0.01$ %) and methanol (Sigma-Aldrich, for HPLC, ≥ 99.9 %) were dried and stored over 4 Å and 3 Å molecular sieves, respectively. Methanol was distilled using a Vigreux column immediately before use. DMSO was used without further purification. The density values of $(1095.196 \pm 0.009)\ \mathrm{kg\cdot m^{-3}}$ at 298.15 K for DMSO and $(786.458 \pm 0.006)\ \mathrm{kg\cdot m^{-3}}$ for methanol were found in the present study, while literature values vary from $1095.271\ \mathrm{kg\cdot m^{-3}}$ to $1097.2\ \mathrm{kg\cdot m^{-3}}$ for DMSO and from $786.36\ \mathrm{kg\cdot m^{-3}}$ to $786.64\ \mathrm{kg\cdot m^{-3}}$ for methanol.[11−18]

Sound velocity in pure methanol was found to be between $(1101.14 \text{ and } 1101.34)\ \mathrm{m\cdot s^{-1}}$. The range compares reasonably well with values of $1098.64\ \mathrm{m\cdot s^{-1}}$ and $1101.9\ \mathrm{m\cdot s^{-1}}$ published by Lankford and Resa and the value obtained by our laboratory in previous studies.[19−21]

Measurements. Densities of the solutions were measured using an Anton Paar DMA 5000 densimeter equipped with a thermostate system based on a Peltier unit with a repeat-

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ability 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 between (283.15 and 333.15) K with a precision of 0.001 K according to the manufacturer's 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 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 return to the same transducer (*pulse-echo*). The cell was thermostatted 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.[22]

3. Results and Discussion

3.1. Apparent Molar Volumes. The density data obtained for solutions of the transition metal perchlorates in dimethylsulfoxide and cobalt(II), nickel(II) perchlorates, and copper(II) trifluoromethanesulfonate in methanol are presented in Tables 1 and 2. The concentration dependencies of the density can be described by the following polynomial

$$d = d_\mathrm{o} + A_1 \cdot c^{1/2} + A_2 \cdot c \qquad (1)$$

The polynomial coefficients and respective values of the standard deviations σ are given in Tables 3 and 4. It is obvious that d_o corresponds to the density of pure DMSO or methanol at the respective temperature.

The values of the apparent molar volumes Φ_V of solutions with different electrolyte concentration were calculated from the usual relationship

$$\Phi_\mathrm{v} = (d_\mathrm{o} - d)/(m_\mathrm{s} d d_\mathrm{o}) + M_2/d_\mathrm{o} \qquad (2)$$

where m_s denotes the number of moles of solute per kilogram of solution (molonity); d and d_o are the densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. The direct calculation of the molar concentration is possible using the equation: $c = m_\mathrm{s} \cdot d$.

The apparent molar volumes at infinite dilution were determined by treating the Φ_V versus $c^{1/2}$ data according to the Masson-type equation:

$$\Phi_\mathrm{v} = \Phi_\mathrm{v}^\mathrm{o} + S_\mathrm{v} \cdot c^{1/2} \qquad (3)$$

The necessity of extrapolating the data using the empirical Masson equation results from the lack of physical property data for DMSO and MeOH over the temperature range studied required for calculating the limiting slope involved in the relationship proposed on the basis of the Debye–Hückel equation. Plots of apparent molar volume against the square root of concentration for nickel(II) perchlorate in methanol at temperatures between (283.15 and 313.15) K are given in Figure 1. As seen, plots of Φ_V against $c^{1/2}$ are found to be linear over the concentration as well as temperature range studied. The coefficients of the Masson-type equation and standard deviations σ are presented in Tables 5 and 6. It should be added that the values of the limiting apparent molar volumes of transition metal perchlorates in DMSO at 298.15 K compare reasonably well with those obtained by Bobicz et al.[9]

An inspection of the data reveals that an increase in concentration causes an increase in the limiting apparent molar volumes for all electrolytes in methanol as well as in dimethylsulfoxide. However, the value of the experimental slope S_V in methanol is about ten times higher than that in DMSO.

Table 1. Densities of the Solutions of $Mn(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ in Dimethylsulfoxide at Temperatures Between (293.15 and 333.15) K

m_s	d/(kg·m^{-3})					
(mol·kg^{-1})	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
$Mn(ClO_4)_2$						
0.01626	1103.515	1098.496	1093.487	1083.460	1073.442	1063.422
0.02110	1104.499	1099.482	1094.474	1084.454	1074.445	1064.433
0.02843	1105.988	1100.977	1095.975	1085.962	1075.964	1065.962
0.03700	1107.738	1102.731	1097.733	1087.73	1077.742	1067.752
0.04758	1109.899	1104.898	1099.909	1089.918	1079.945	1069.971
0.05763	1111.960	1106.966	1101.980	1092.006	1082.049	1072.090
0.07358	1115.242	1110.261	1105.282	1095.326	1085.389	1075.452
0.09456	1119.588	1114.615	1109.650	1099.732	1089.817	1079.911
0.1139	1123.616	1118.653	1113.697	1103.802	1093.919	1084.037
0.1337	1127.767	1122.816	1117.873	1107.998	1098.14	1088.288
0.1569	1132.594	1127.655	1122.728	1112.885	1103.056	1093.239
0.1754	1136.601	1131.673	1126.754	1116.936	1107.135	1097.340
DMSO	1100.222	1095.193	1090.171	1080.123	1070.084	1060.039
$Co(ClO_4)_2$						
0.01481	1103.365	1098.345	1093.341	1083.306	1073.289	1063.264
0.02150	1104.791	1099.775	1094.773	1084.746	1074.739	1064.726
0.03236	1107.104	1102.100	1097.100	1087.090	1077.095	1067.100
0.04309	1109.405	1104.405	1099.406	1089.417	1079.437	1069.457
0.05528	1112.024	1107.026	1102.038	1092.062	1082.100	1072.139
0.06505	1114.126	1109.136	1104.152	1094.204	1084.251	1074.300
0.08726	1118.943	1113.971	1109.000	1099.074	1089.148	1079.219
0.1069	1123.236	1118.267	1113.305	1103.395	1093.506	1083.613
0.1285	1127.981	1123.025	1118.080	1108.194	1098.326	1088.466
0.1480	1132.320	1127.381	1122.441	1112.574	1102.732	1092.900
0.1695	1137.117	1132.180	1127.257	1117.416	1107.602	1097.797
0.1911	1141.973	1137.050	1132.136	1122.329	1112.534	1102.759
0.2111	1146.482	1141.572	1136.670	1126.882	1117.125	1107.378
DMSO	1100.222	1095.193	1090.179	1080.123	1070.082	1060.034
$Ni(ClO_4)_2$						
0.01259	1102.915	1097.895	1092.878	1082.847	1072.824	1062.800
0.01738	1103.941	1098.923	1093.911	1083.884	1073.868	1063.850
0.02515	1105.610	1100.595	1095.589	1085.570	1075.562	1065.557
0.03153	1106.980	1101.970	1096.964	1086.956	1076.960	1066.960
0.03816	1108.410	1103.403	1098.398	1088.402	1078.408	1068.425
0.05100	1111.180	1106.185	1101.185	1091.205	1081.235	1071.270
0.06341	1113.877	1108.878	1103.890	1093.920	1083.968	1074.013
0.07675	1116.779	1111.785	1106.807	1096.857	1086.922	1076.993
0.08797	1119.230	1114.242	1109.272	1099.336	1089.416	1079.500
0.1004	1121.965	1116.985	1112.015	1102.100	1092.195	1082.295
0.1126	1124.633	1119.667	1114.704	1104.799	1094.910	1085.028
0.1251	1127.400	1122.433	1117.495	1107.600	1097.730	1087.864
DMSO	1100.222	1095.194	1090.171	1080.123	1070.084	1060.039
$Cu(ClO_4)_2$						
0.01424	1103.320	1098.306	1093.291	1083.263	1073.235	1063.214
0.01956	1104.480	1099.473	1094.456	1084.437	1074.416	1064.399
0.02779	1106.270	1101.264	1096.262	1086.251	1076.240	1066.236
0.03497	1107.843	1102.831	1097.830	1087.833	1077.832	1067.840
0.04190	1109.353	1104.347	1099.358	1089.367	1079.364	1069.385
0.05636	1112.527	1107.535	1102.539	1092.566	1082.596	1072.636
0.07067	1115.686	1110.703	1105.706	1095.756	1085.800	1075.851
0.08366	1118.565	1113.582	1108.608	1098.652	1088.719	1078.786
0.09783	1121.712	1116.735	1111.754	1101.825	1091.912	1082.001
0.1114	1124.760	1119.784	1114.820	1104.899	1095.003	1085.101
0.1251	1127.826	1122.854	1117.894	1107.998	1098.111	1088.230
0.1384	1130.816	1125.854	1120.903	1111.017	1101.145	1091.275
DMSO	1100.226	1095.200	1090.179	1080.125	1070.084	1060.039
$Zn(ClO_4)_2$						
0.01680	1103.883	1098.864	1093.853	1083.822	1073.810	1063.780
0.02409	1105.475	1100.460	1095.454	1085.433	1075.430	1065.410
0.02918	1106.588	1101.575	1096.564	1086.558	1076.560	1066.549
0.03465	1107.788	1102.776	1097.775	1087.767	1077.772	1067.774
0.05104	1111.385	1106.390	1101.387	1091.404	1081.428	1071.449
0.06794	1115.124	1110.133	1105.138	1095.176	1085.216	1075.260
0.08574	1119.081	1114.099	1109.118	1099.166	1089.230	1079.296
0.1022	1122.778	1117.795	1112.833	1102.908	1092.994	1083.082
0.1190	1126.551	1121.580	1116.618	1106.699	1096.799	1086.905
0.1435	1132.092	1127.136	1122.186	1112.301	1102.431	1092.566
0.1684	1137.796	1132.850	1127.909	1118.046	1108.210	1098.365
DMSO	1100.226	1095.198	1090.179	1080.125	1070.084	1060.039

Table 2. Densities of the Solutions of $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Cu(CF_3SO_3)_2$ in Methanol at Temperatures Between (283.15 and 313.15) K

	$d/(kg \cdot m^{-3})$						
$m_s/(mol \cdot kg^{-1})$	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
				$Co(ClO_4)_2$			
0.04954	810.666	806.009	801.334	796.648	791.945	787.216	782.455
0.06520	813.871	809.222	804.551	799.871	795.174	790.456	785.712
0.08043	816.972	812.325	807.661	802.983	798.285	793.568	788.838
0.09601	820.184	815.542	810.881	806.210	801.517	796.812	792.084
0.1106	823.205	818.568	813.913	809.247	804.564	799.855	795.128
0.1255	826.259	821.625	816.975	812.313	807.634	802.929	798.211
0.1570	832.839	828.214	823.572	818.918	814.251	809.557	804.844
0.1876	839.345	834.726	830.096	825.452	820.793	816.116	811.415
0.2171	845.636	841.028	836.402	831.765	827.115	822.438	817.746
0.2464	851.879	847.275	842.656	838.024	833.388	828.730	824.046
0.2747	858.053	853.458	848.847	844.226	839.592	834.938	830.254
0.3036	864.446	859.854	855.253	850.642	846.019	841.375	836.709
MeOH	800.550	795.872	791.172	786.464	781.742	776.992	772.214
				$Ni(ClO_4)_2$			
0.04976	810.894	806.238	801.564	796.875	792.174	787.453	782.702
0.06138	813.322	808.669	804.000	799.318	794.619	789.897	785.142
0.07317	815.812	811.165	806.497	801.821	797.126	792.410	787.658
0.08448	818.152	813.508	808.845	804.169	799.474	794.767	790.033
0.09669	820.699	816.056	811.401	806.731	802.044	797.340	792.608
0.1085	823.230	818.592	813.937	809.271	804.589	799.878	795.147
0.1208	825.801	821.168	816.518	811.856	807.179	802.481	797.759
0.1447	830.859	826.231	821.586	816.930	812.261	807.568	802.853
0.1676	835.774	831.151	826.515	821.865	817.198	812.514	807.813
0.1901	840.657	836.042	831.412	826.771	822.114	817.440	812.739
0.2123	845.469	840.858	836.233	831.599	826.950	822.280	817.588
0.2356	850.636	846.033	841.413	836.783	832.140	827.476	822.785
MeOH	800.541	795.866	791.169	786.460	781.733	776.979	772.189
				$Cu(CF_3SO_3)_2$			
0.1213	829.484	824.791	820.094	815.380	810.649	805.885	801.107
0.1418	834.535	829.841	825.141	820.428	815.692	810.942	806.159
0.1772	843.312	838.612	833.908	829.190	824.450	819.682	814.901
0.2047	850.214	845.512	840.803	836.081	831.338	826.565	821.777
0.2310	856.972	852.265	847.554	842.828	838.081	833.302	828.513
0.2571	863.707	858.996	854.279	849.545	844.805	840.033	835.231
0.2847	871.006	866.292	861.570	856.839	852.088	847.311	842.504
MeOH	800.548	795.857	791.162	786.452	781.722	776.978	772.200

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

		d_0	A_1	A_2	σ
salt		$kg \cdot m^{-3}$	$(kg^2 \cdot m^{-3} \cdot mol^{-1})^{1/2}$	$kg \cdot mol^{-1}$	$kg \cdot m^{-3}$
$Mn(ClO_4)_2$	293.15 K	1100.222	0.012 ± 0.0064	0.1816 ± 0.00055	0.023
	298.15 K	1095.193	0.013 ± 0.0067	0.1828 ± 0.00057	0.024
	303.15 K	1090.171	0.015 ± 0.0067	0.1840 ± 0.00056	0.023
	313.15 K	1080.123	0.015 ± 0.0072	0.1868 ± 0.00060	0.025
	323.15 K	1070.084	0.017 ± 0.0074	0.1895 ± 0.00064	0.026
	333.15 K	1060.039	0.019 ± 0.0074	0.1924 ± 0.00066	0.026
$Co(ClO_4)_2$	293.15 K	1100.222	0.011 ± 0.0036	0.1906 ± 0.00033	0.015
	298.15 K	1095.193	0.013 ± 0.0042	0.1918 ± 0.00034	0.016
	303.15 K	1090.179	0.013 ± 0.0042	0.1931 ± 0.00035	0.016
	313.15 K	1080.123	0.017 ± 0.0054	0.1956 ± 0.00040	0.020
	323.15 K	1070.082	0.020 ± 0.0057	0.1983 ± 0.00043	0.022
	333.15 K	1060.034	0.024 ± 0.0063	0.2012 ± 0.00047	0.024
$Ni(ClO_4)_2$	293.15 K	1100.222	0.011 ± 0.0038	0.1919 ± 0.00036	0.011
	298.15 K	1095.194	0.012 ± 0.0036	0.1931 ± 0.00034	0.010
	303.15 K	1090.171	0.011 ± 0.0027	0.1946 ± 0.00030	0.010
	313.15 K	1080.123	0.012 ± 0.0037	0.1973 ± 0.00037	0.010
	323.15 K	1070.084	0.013 ± 0.0040	0.2003 ± 0.00039	0.011
	333.15 K	1060.039	0.015 ± 0.0043	0.2033 ± 0.00048	0.013
$Cu(ClO_4)_2$	293.15 K	1100.226	0.012 ± 0.0035	0.1946 ± 0.00033	0.010
	298.15 K	1095.200	0.015 ± 0.0040	0.1957 ± 0.00039	0.010
	303.15 K	1090.179	0.015 ± 0.0039	0.1969 ± 0.00037	0.011
	313.15 K	1080.125	0.020 ± 0.0036	0.1994 ± 0.00036	0.011
	323.15 K	1070.084	0.020 ± 0.0049	0.2024 ± 0.00049	0.014
	333.15 K	1060.039	0.024 ± 0.0058	0.2051 ± 0.00054	0.016
$Zn(ClO_4)_2$	293.15 K	1100.226	0.010 ± 0.0035	0.1954 ± 0.00030	0.011
	298.15 K	1095.198	0.011 ± 0.0036	0.1966 ± 0.00030	0.010
	303.15 K	1090.179	0.011 ± 0.0041	0.1979 ± 0.00036	0.013
	313.15 K	1080.125	0.015 ± 0.0047	0.2004 ± 0.00043	0.016
	323.15 K	1070.084	0.018 ± 0.0051	0.2030 ± 0.00046	0.015
	333.15 K	1060.039	0.020 ± 0.0067	0.2059 ± 0.00062	0.021

Table 4. Coefficients of Equation 1 for Density of the Solutions of the Transition Metal Salts in Methanol at Different Temperatures

		d_0	A_1	A_2	σ
salt		$kg \cdot m^{-3}$	$(kg^2 \cdot m^{-3} \cdot mol^{-1})^{1/2}$	$kg \cdot mol^{-1}$	$kg \cdot m^{-3}$
$Co(ClO_4)_2$	283.15 K	800.550	0.11 ± 0.017	0.237 ± 0.0013	0.068
	288.15 K	795.872	0.11 ± 0.018	0.238 ± 0.0014	0.070
	293.15 K	791.172	0.12 ± 0.018	0.240 ± 0.0014	0.072
	298.15 K	786.464	0.12 ± 0.019	0.241 ± 0.0014	0.073
	303.15 K	781.742	0.13 ± 0.020	0.243 ± 0.0015	0.076
	308.15 K	776.992	0.13 ± 0.020	0.244 ± 0.0015	0.077
	313.15 K	772.214	0.14 ± 0.021	0.246 ± 0.0016	0.081
$Ni(ClO_4)_2$	283.15 K	800.541	0.094 ± 0.011	0.2435 ± 0.00093	0.035
	288.15 K	795.866	0.10 ± 0.011	0.2450 ± 0.00097	0.036
	293.15 K	791.169	0.10 ± 0.011	0.246 ± 0.0010	0.037
	298.15 K	786.460	0.10 ± 0.012	0.248 ± 0.0011	0.039
	303.15 K	781.733	0.11 ± 0.012	0.250 ± 0.0011	0.039
	308.15 K	776.979	0.11 ± 0.012	0.251 ± 0.0011	0.039
	313.15 K	772.189	0.12 ± 0.013	0.253 ± 0.0011	0.041
$Cu(CF_3SO_3)_2$	283.15 K	800.548	0.103 ± 0.0080	0.2776 ± 0.00059	0.015
	288.15 K	795.857	0.107 ± 0.0083	0.2788 ± 0.00061	0.015
	293.15 K	791.162	0.112 ± 0.0087	0.2799 ± 0.00064	0.016
	298.15 K	786.452	0.117 ± 0.0099	0.2811 ± 0.00073	0.018
	303.15 K	781.722	0.120 ± 0.0086	0.2824 ± 0.00064	0.015
	308.15 K	776.978	0.12 ± 0.010	0.2837 ± 0.00077	0.019
	313.15 K	772.200	0.13 ± 0.011	0.2848 ± 0.00082	0.020

To discuss ion−solvent interaction effectively, the partial molar volumes of the salts were divided into the respective ionic contributions using the relation

$$\Phi_V^o(M^{2+}) = \Phi_V^o(MX_2) - 2\Phi_V^o(X^-) \qquad (4)$$

The literature values for limiting apparent molar volumes of perchlorate and trifluoromethanesulfonate ions obtained by the reference electrolyte method were employed in the calculation.[21,23,24] The partial molar volumes of the transition metal ions in DMSO and methanol calculated from eq 4 are listed in Table 7. Figure 2 shows the variation of their values at temperature 298.15 K. To complete the discussion, in Table 7 as well as Figure 2 we

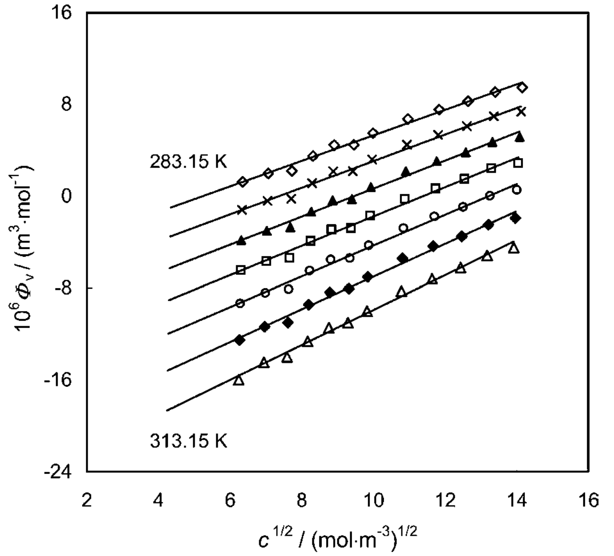

Figure 1. Apparent molar volumes Φ_V against the square root of molarity $c^{1/2}$ of the $Ni(ClO_4)_2$ in methanol at temperatures between (283.15 and 313.15) K.

Table 5. Coefficients of Masson's Equation for Apparent Molar Volume of the Solutions of $Mn(ClO_4)_2$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, and $Zn(ClO_4)_2$ in Dimethylsulfoxide at Temperatures Between (293.15 and 333.15) K

		$10^6\Phi_V^0$	10^6S_V	$10^6\sigma$
salt		(m^3·mol^{-1})	(m^9·mol^{-3})$^{1/2}$	(m^3·mol^{-1})
$Mn(ClO_4)_2$	293.15 K	63.38 ± 0.048	0.098 ± 0.0049	0.025
	298.15 K	62.36 ± 0.063 (62.4)[a]	0.107 ± 0.0067	0.034
	303.15 K	61.19 ± 0.056	0.126 ± 0.0059	0.030
	313.15 K	59.10 ± 0.076	0.135 ± 0.0076	0.038
	323.15 K	56.67 ± 0.073	0.154 ± 0.0078	0.039
	333.15 K	54.02 ± 0.080	0.181 ± 0.0086	0.042
$Co(ClO_4)_2$	293.15 K	59.13 ± 0.064	0.092 ± 0.0063	0.037
	298.15 K	57.98 ± 0.075 (58.2)[a]	0.107 ± 0.0071	0.043
	303.15 K	57.0 ± 0.14	0.11 ± 0.017	0.071
	313.15 K	54.4 ± 0.14	0.14 ± 0.016	0.061
	323.15 K	51.7 ± 0.14	0.18 ± 0.010	0.058
	333.15 K	48.87 ± 0.075	0.215 ± 0.0073	0.043
$Ni(ClO_4)_2$	293.15 K	57.35 ± 0.065	0.134 ± 0.0078	0.032
	298.15 K	56.24 ± 0.074 (55.0)[a]	0.153 ± 0.0089	0.036
	303.15 K	55.22 ± 0.082	0.155 ± 0.0096	0.040
	313.15 K	52.91 ± 0.051	0.169 ± 0.0062	0.025
	323.15 K	50.53 ± 0.085	0.18 ± 0.015	0.042
	333.15 K	47.6 ± 0.16	0.21 ± 0.017	0.058
$Cu(ClO_4)_2$	293.15 K	58.9 ± 0.14	0.16 ± 0.018	0.056
	298.15 K	57.8 ± 0.16 (57)[a]	0.18 ± 0.015	0.063
	303.15 K	56.6 ± 0.20	0.20 ± 0 0.024	0.076
	313.15 K	53.6 ± 0.21	0.28 ± 0.023	0.086
	323.15 K	51.5 ± 0.16	0.27 ± 0.021	0.074
	333.15 K	48.6 ± 0.17	0.32 ± 0.014	0.059
$Zn(ClO_4)_2$	293.15 K	60.4 ± 0.16	0.11 ± 0.016	0.053
	298.15 K	59.41 ± 0.076 (59.8)[a]	0.125 ± 0.0084	0.037
	303.15 K	58.5 ± 0.21	0.13 ± 0.023	0.090
	313.15 K	55.87 ± 0.016	0.17 ± 0.099	0.072
	323.15 K	53.1 ± 0.30	0.23 ± 0.028	0.12
	333.15 K	50.7 ± 0.22	0.23 ± 0.021	0.092

[a] Ref 9.

included the literature values of the partial molar volumes of the manganese(II) and zinc(II) ions in methanol.[8] As is seen, the sequences of the values of the limiting apparent molar volumes of the six-coordinated divalent metal ions are in methanol $Mn^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} > Zn^{2+}$ and in dimethylsulfoxide $Mn^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} < Zn^{2+}$ and are the same irrespective of temperature. Obviously, the orders reflect the effects related to the electronic structure and the ionic radii of metal cations. The high stability of the octahedral $Ni(L)_6^{2+}$ solvate resulting from the highest ligand field stabilization typical for the $3d^8$ ion is responsible for the lowest values of the partial molar volume observed for the nickel(II) ion in both solvents. The highest values of the limiting partial molar volumes were obtained for the $Mn(L)_6^{2+}$ solvate for which the ligand field stabilization effect is absent. The relative high value of the partial molar volume obtained for the Cu(II) ion in methanol may result from a tetragonal distortion of the octahedral complex due to the Jahn–Teller effect.[4] The fact that the values of Φ_V^0 obtained for metal ions in methanol are considerably more negative than in dimethylsulfoxide at a given temperature is the result of the much higher compressibility of MeOH.[25]

Table 6. Coefficients of Masson's Equation for Apparent Molar Volume of the Solutions of $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Cu(CF_3SO_3)_2$ in Methanol at Temperatures Between (283.15 and 313.15) K

		$10^6\Phi_V^0$	10^6S_V	$10^6\sigma$
salt		(m^3·mol^{-1})	(m^9·mol^{-3})$^{1/2}$	(m^3·mol^{-1})
$Co(ClO_4)_2$	283.15 K	1.0 ± 0.65	1.06 ± 0.056	0.27
	288.15 K	−1.7 ± 0.69	1.12 ± 0.059	0.29
	293.15 K	−4.7 ± 0.72	1.18 ± 0.063	0.30
	298.15 K	−7.6 ± 0.78	1.23 ± 0.067	0.33
	303.15 K	−10.4 ± 0.83	1.28 ± 0.072	0.35
	308.15 K	−13.4 ± 0.88	1.33 ± 0.077	0.37
	313.15 K	−16.7 ± 0.79	1.40 ± 0.070	0.33
$Ni(ClO_4)_2$	283.15 K	−5.8 ± 0.84	1.11 ± 0.081	0.31
	288.15 K	−8.5 ± 0.87	1.16 ± 0.084	0.32
	293.15 K	−11.5 ± 0.85	1.22 ± 0.083	0.31
	298.15 K	−14.5 ± 0.90	1.27 ± 0.087	0.33
	303.15 K	−17.7 ± 0.92	1.34 ± 0.090	0.34
	308.15 K	−21.3 ± 0.93	1.42 ± 0.091	0.34
	313.15 K	−25.1 ± 0.89	1.52 ± 0.087	0.33
$Cu(CF_3SO_3)_2$	283.15 K	85 ± 1.2	0.80 ± 0.093	0.19
	288.15 K	83 ± 1.3	0.84 ± 0.096	0.19
	293.15 K	81 ± 1.3	0.89 ± 0.099	0.20
	298.15 K	79 ± 1.4	0.9 ± 0.10	0.21
	303.15 K	77 ± 1.4	1.0 ± 0.11	0.21
	308.15 K	75 ± 1.6	1.0 ± 0.13	0.25
	313.15 K	73 ± 1.6	1.1 ± 0.12	0.24

Figure 3 shows the limiting values of the apparent molar volumes of the metal ions against temperature. As is seen, the plots are linear in methanol and not linear in dimethylsulfoxide. Therefore, different equations were used to describe the temperature dependence of Φ_V^0 in solvents studied

$$\Phi_V^0 = A_T + B_T(T/\mathrm{K} - 298.15) + C_T(T/\mathrm{K} - 298.15)^2 \quad \text{for dimethylsulfoxide} \quad (5)$$

$$\Phi_V^0 = A_T + B_T(T/\mathrm{K} - 298.15) \quad \text{for methanol} \quad (6)$$

Coefficients of eqs 5 and 6 are listed in Tables 8 and 9. It is evident that the first of the coefficients can be considered as a value of the limiting molar volume of the metal ions at 298.15 K.

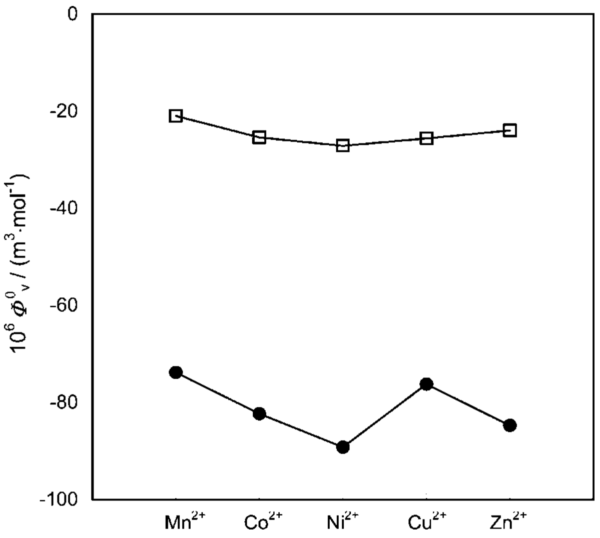

Figure 2. Partial molar volumes of the transition metal ions in □, DMSO and ●, methanol at 298.15 K.

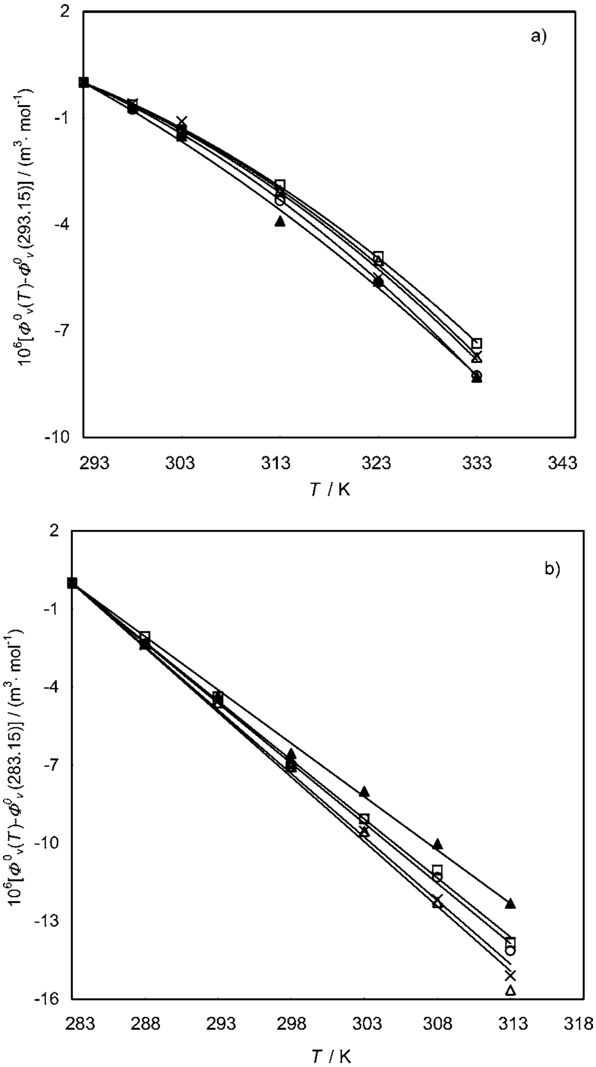

Figure 3. Plots of the difference $\Phi^o_V(T) - \Phi^o_V$ (293.15 or 283.15) of the ions against the temperature in (a) DMSO and (b) methanol: □, Mn^{2+}; ○, Co^{2+}; △, Ni^{2+}; ▲, Cu^{2+}; ×, Zn^{2+}.

The volume expansibilities, for the limiting values of the apparent molar volumes of the transition metal ions, were calculated using the equation

$$\alpha^o_V = (d\Phi^o_V/dT)_P/|\Phi^o_V| \tag{7}$$

The parameters of eq 7 are given in Tables 8 and 9.

Table 8. Parameters of Equation 5 and the Volume Expansibility for Ions in DMSO

ion	10^6A_T (m^3·mol^{-1})	10^6B_T (m^3·mol^{-1})	10^6C_T (m^3·mol^{-1})	$10^6\sigma$ (m^3·mol^{-1})	$\alpha^o_V\cdot10^3$ K^{-1}
Mn^{2+}	−21 ± 2.3	−0.13 ± 0.017	−1.9 ± 0.54	0.074	−6.0 ± 0.12
Co^{2+}	−25 ± 2.7	−0.14 ± 0.022	−2.2 ± 0.71	0.094	−5.4 ± 0.24
Ni^{2+}	−27 ± 2.4	−0.12 ± 0.025	−2.2 ± 0.78	0.10	−4.5 ± 0.42
Cu^{2+}	−26 ± 2.6	−0.17 ± 0.051	−1.2 ± 1.6	0.22	−6.8 ± 1.5
Zn^{2+}	−24 ± 2.3	−0.15 ± 0.045	−1.7 ± 1.4	0.19	−6.1 ± 1.4

Table 9. Parameters of Equation 6 and the Volume Expansibility for Ions in Methanol

ion	10^6A_T (m^3·mol^{-1})	10^6B_T (m^3·mol^{-1})	$10^6\sigma$ (m^3·mol^{-1})	$\alpha^o_V\cdot10^3$ K^{-1}
Mn^{2+a}	−74 ± 1.9	−0.46 ± 0.036	0.39	−6.2 ± 0.64
Co^{2+}	−82 ± 1.6	−0.46 ± 0.016	0.17	−5.6 ± 0.31
Ni^{2+}	−89 ± 1.8	−0.51 ± 0.045	0.49	−5.7 ± 0.62
Cu^{2+}	−76 ± 2.7	−0.40 ± 0.038	0.41	−5.2 ± 0.68
$Zn^{2}+^{a}$	−85 ± 1.4	−0.50 ± 0.028	0.31	−5.9 ± 0.43

[a] Ref 8.

Analysis of the obtained values reveals the temperature dependence of the partial molar volumes of ions. Because of the electrostatic effects, the Φ^o_V values become more negative with increasing temperature in both DMSO and MeOH. As the temperature is increased and the dielectric constant decreases, more and more solvent molecules are influenced by ionic charge. The differences in the values of temperature coefficients for the Φ^o_V of ions in investigated solvents can be connected with lower isobaric expansibility of dimethylsulfoxide. Furthermore, temperature coefficients and volume expansibilities for the partial molar volumes of the divalent transition metal ions belonging to the Mn(II)−Zn(II) series in methanol as well as in dimethylsulfoxide, within the experimental error, are practically the same, that is, independent of the nature of the metal ion.

3.2. Apparent Molar Isentropic Compressibilities. The experimental data for sound velocity obtained at 298.15 K for nickel(II) and cobalt(II) perchlorate and copper(II) trifluoromethanesulfonate in methanol together with the apparent molar compressibilities and the isentropic compressibilities are presented in Table 10. As can be seen, the sound velocity of all solutions always increases with the salt concentration. The same behavior was observed for density, so the behavior of the isentropic compressibility is also very regular and logical: it decreases with concentration. The

Table 7. Limiting Values of the Apparent Molar Volumes of the Ions in DMSO (at *T* = (293.15 and 333.15) K) and Methanol (at *T* = (283.15 and 313.15) K)

	$10^6\Phi^o_V$/(m^3·mol^{-1})						
T/K	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	$CF_3SO_3^{-b}$	ClO_4^{-a}
				DMSO			
293.15 K	−20 ± 2.9	−25 ± 2.8	−26 ± 2.9	−25 ± 2.1	−23 ± 2.8	-	41.9 ± 1.2
298.15 K	−21 ± 2.3	−25 ± 2.7	−27 ± 2.4	−26 ± 2.6	−24 ± 2.3	-	41.7 ± 1.1
303.15 K	−22 ± 2.5	−26 ± 22	−28 ± 2.5	−26 ± 2.6	−24 ± 2.7	-	41.5 ± 1.1
313.15 K	−23 ± 2.8	−28 ± 2.4	−29 ± 2.9	−29 ± 2.6	−27 ± 2.9	-	41.2 ± 1.2
323.15 K	−25 ± 2.7	−30 ± 2.8	−31 ± 2.7	−31 ± 2.7	−29 ± 2.3	-	41.0 ± 1.1
333.15 K	−28 ± 2.5	−33 ± 2.3	−34 ± 2.4	−33 ± 2.6	−31 ± 2.3	-	40.9 ± 1.1
				Methanol			
283.15 K	−67 ± 1.8[c]	−75 ± 1.6	−82 ± 1.7	−70 ± 2.5	−78 ± 1.3[c]	77.1 ± 0.64	38.2 ± 0.45
288.15 K	−69 ± 1.9[c]	−78 ± 1.6	−85 ± 1.8	−72 ± 2.6	−80 ± 1.3[c]	77.3 ± 0.66	38.0 ± 0.45
293.15 K	−71 ± 1.9[c]	−80 ± 1.7	−87 ± 1.8	−74 ± 2.7	−82 ± 1.4[c]	77.4 ± 0.70	37.7 ± 0.47
298.15 K	−74 ± 1.9[c]	−82 ± 1.6	−89 ± 1.8	−76 ± 2.7	−85 ± 1.4[c]	77.5 ± 0.67	37.4 ± 0.43
303.15 K	−76 ± 1.8[c]	−84 ± 1.6	−92 ± 1.7	−78 ± 2.9	−87 ± 1.4[c]	77.2 ± 0.74	37.0 ± 0.40
308.15 K	−78 ± 1.8[c]	−87 ± 1.8	−94 ± 1.8	−80 ± 3.3	−90 ± 1.5[c]	77.3 ± 0.85	36.6 ± 0.44
313.15 K	−81 ± 1.8[c]	−90 ± 1.7	−98 ± 1.8	−82 ± 3.2	−93 ± 1.6[c]	77.3 ± 0.80	36.4 ± 0.47

[a] For DMSO, ref 23; for methanol, ref 21. [b] Ref 23. [c] Ref 8.

Table 10. Sound Velocity, Isentropic Compressibility, and the Apparent Molar Isentropic Compressibility of the Solutions of $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Cu(CF_3SO_3)_2$ in Methanol at 298.15 K

salt	m_s / $mol \cdot kg^{-1}$	u / $m \cdot s^{-1}$	10^{10} K_s / $m^2 \cdot N^{-1}$	$10^{14}\Phi_{KS}$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
$Co(ClO_4)_2$	0.04954	1108.25	10.22	−67.55
	0.06520	1110.50	10.14	−66.80
	0.08043	1112.56	10.06	−65.61
	0.09601	1114.62	9.984	−64.60
	0.1106	1116.90	9.906	−64.48
	0.1255	1118.56	9.839	−62.99
	0.1570	1122.74	9.687	−61.46
	0.1876	1126.96	9.539	−60.41
	0.2171	1130.99	9.399	−59.30
	0.2464	1135.05	9.262	−58.23
	0.2747	1138.92	9.132	−57.24
	0.3036	1143.04	8.998	−56.41
$Ni(ClO_4)_2$	0.04976	1108.66	10.21	−69.56
	0.06138	1110.29	10.15	−68.74
	0.07317	1111.94	10.09	−68.05
	0.08448	1113.38	10.03	−66.85
	0.09669	1115.24	9.966	−66.53
	0.1085	1116.69	9.909	−65.63
	0.1208	1118.35	9.848	−64.88
	0.1447	1121.70	9.729	−63.82
	0.1676	1124.85	9.616	−62.84
	0.1901	1127.80	9.509	−61.78
	0.2123	1130.56	9.408	−60.63
	0.2356	1134.19	9.290	−60.22
$Cu(CF_3SO_3)_2$	0.1213	1106.00	10.03	−37.39
	0.1418	1106.61	9.953	−36.57
	0.1772	1107.43	9.834	−35.00
	0.2047	1108.25	9.738	−34.19
	0.2310	1109.06	9.646	−33.55
	0.2571	1109.68	9.559	−32.77
	0.2847	1110.50	9.464	−32.19

Table 11. Coefficients of Equation 8 for Speed of Sound in the Solutions of the Transition Metal Salts in Methanol at 298.15 K

salt	B_0 / $m \cdot s^{-1}$	B_1 / $(m^5 \cdot s^{-2} \cdot mol^{-1})^{1/2}$	B_2 / $m^4 \cdot s^{-2} \cdot mol^{-1}$	σ / $m \cdot s^{-1}$
$Co(ClO_4)_2$	1101.14	0.24 ± 0.032	0.148 ± 0.0024	0.12
$Ni(ClO_4)_2$	1101.34	0.24 ± 0.040	0.149 ± 0.0036	0.13
$Cu(CF_3SO_3)_2$	1101.14	0.29 ± 0.040	0.020 ± 0.0029	0.072

Table 12. Coefficients of Equation 8 for Isentropic Compressibility of the Solutions of the Transition Metal Salts in Methanol at 298.15 K

salt	$10^{10}B_0$ / $m^2 \cdot N^{-1}$	$10^{13}B_1$ / $(m^7 \cdot N^{-2} \cdot mol^{-1})^{1/2}$	$10^{13}B_2$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{13}\sigma$ / $m^2 \cdot N^{-1}$
$Co(ClO_4)_2$	10.49	−14 ± 2.3	−5.0 ± 0.17	8.8
$Ni(ClO_4)_2$	10.48	−12 ± 1.7	−5.2 ± 0.15	5.6
$Cu(CF_3SO_3)_2$	10.49	−13 ± 1.1	−3.36 ± 0.083	2.0

Table 13. Coefficients of Masson's Equation for Apparent Molar Isentropic Compressibility of the Solutions of $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Cu(CF_3SO_3)_2$ in Methanol at 298.15 K

salt	$10^{14}\Phi^0_{KS}$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{16}S_{KS}$ / $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{14}\sigma$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
	Methanol		
$Co(ClO_4)_2$	−75.0 ± 0.55	117 ± 4.8	0.23
$Ni(ClO_4)_2$	−77.3 ± 0.49	124 ± 4.8	0.18
$Cu(CF_3SO_3)_2$	−46 ± 1.1	92 ± 8.7	0.17

concentration variation of sound velocity and isentropic compressibility can be represented by the following polynomial

$$y = B_0 + B_1 \cdot c^{1/2} + B_2 \cdot c \tag{8}$$

where y and B_0 denote the sound velocity (or the isentropic compressibility) of the solution and pure methanol, respectively. Parameters of eq 8 are presented in Tables 11 and 12.

The apparent molar compressibilities Φ_{KS} were calculated from the following equation

$$\Phi_{KS} = (K_S d_o - K_{S0} d)/(m_s d d_o) + M_2 K_{S0}/d_o \tag{9}$$

where K_S and K_{S0} are isentropic compressibilities of solution and solvent, respectively. The isentropic compressibilities of the solutions were obtained from the respective values of density and sound velocity according to the Laplace relation

$$K_S = 1/(u^2 \cdot d) \tag{10}$$

The concentration dependence of the apparent molar compressibility in a given system was determined by the least-squares method and was fitted to a Masson-type equation

$$\Phi_{KS} = \Phi^0_{KS} + S_{KS} \cdot c^{1/2} \tag{11}$$

where Φ^0_{KS} is the apparent molar compressibility at infinite dilution and S_K is an empirical constant. The parameters of the plots and their standard deviations σ are collected in Table 13. Figure 4 presents the concentration dependence of the apparent molar compressibility of nickel(II) and cobalt(II) perchlorates in methanol together with literature data for respective metal perchlorates in DMSO.[26] As is seen, the apparent molar compressibilities of metal perchlorates in methanol increase with concentration considerably faster than in DMSO. Moreover, the limiting values of Φ^0_{KS} of the respective electrolytes are distinctly smaller in methanol.

The limiting apparent molar compressibilities of the nickel(II), cobalt(II), and copper(II) ions in methanol were calculated using the analogous equation to eq 4. In calculations, the literature data for the partial molar compressibility of trifluoromethanesulfonate and perchlorate ions in methanol were used.[21,24] The obtained values together with the literature values for the manganese(II) and zinc(II) ions are presented in Table 14 and Figure 5.[8]

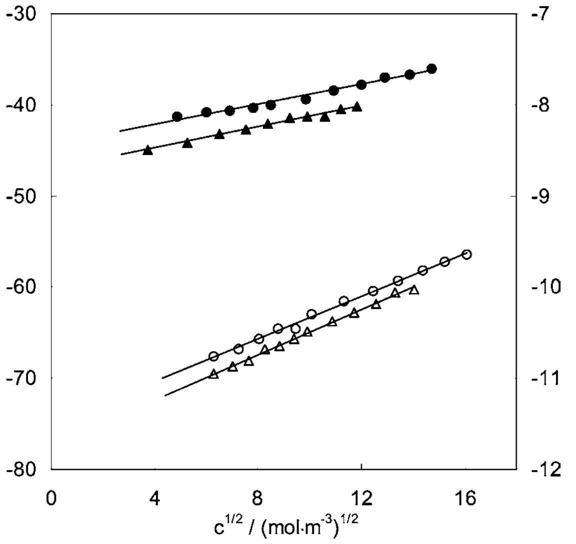

Figure 4. Apparent molar compressibilities Φ_{KS} of the solutions of ○, $Co(ClO_4)_2$ and △, $Ni(ClO_4)_2$ in methanol (left scale, open symbols) and DMSO (right scale, full symbols) against the square root of molarity at 298.15 K.

Table 14. Ionic Standard Partial Molar Compressibilities in Methanol at 298.15 K

$10^{14}\Phi^0_{KS}/(m^5 \cdot N^{-1} \cdot mol^{-1})$						
Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	$CF_3SO_3^{-}$[a]	ClO_4^{-}[b]
−48 ± 5.3[c]	−47 ± 3.2	−49 ± 3.2	−42 ± 4.1	−48 ± 3.5[c]	−2.2 ± 1.5	−14 ± 1.4

[a] Ref 24. [b] Ref 21. [c] Ref 8.

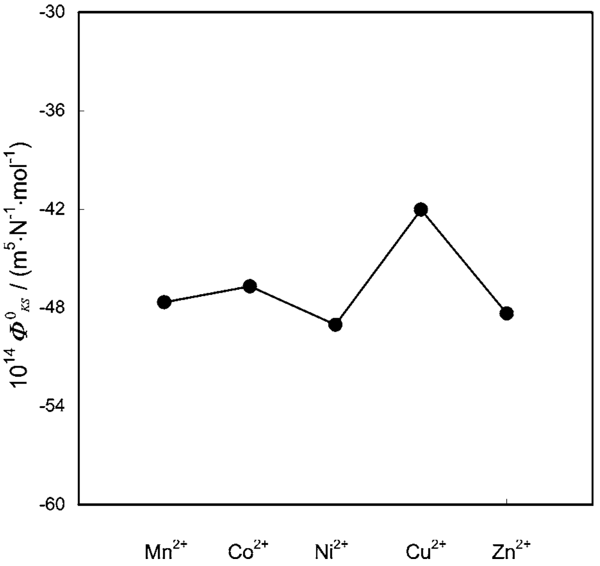

Figure 5. Limiting apparent molar compressibilities Φ^0_{KS} of the transition metal ions in methanol at 298.15 K.

An examination of the obtained results leads to the general conclusion that the values of the limiting apparent molar compressibilities of the transition metal ion within the Mn(II)−Zn(II) series vary in accordance with the same sequence as the limiting apparent molar volumes, and the size and nature of the ions are responsible for differentiation in values.

Literature Cited

(1) Inada, Y.; Sugimoto, K.; Ozutsumi, K.; Funahashi, S. Solvation Structures of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II), and Indium(III) Ions in 1,1,3,3-Tetramethylurea As Studied by EXAFS and Electronic Spectroscopy. Variation of Coordination Number. *Inorg. Chem.* **1994**, *33*, 1875–1880.

(2) Ozutsumi, K.; Koide, M.; Suzuki, H.; Ishiguro, S. Solvation Structure of Divalent Transition-Metal Ions in N,N-Dimethylformamide and N, N-Dimethylacetamide. *J. Phys. Chem.* **1993**, *97*, 500–502.

(3) Libuś, W.; Chachulski, B.; Grzybkowski, W.; Pilarczyk, M.; Puchalska, D. Mobilities of Complex Forming Cations in Nonaqueos Donor Solvents. *J. Solution Chem.* **1981**, *10*, 631–648.

(4) Inada, Y.; Hayashi, H.; Sugimoto, K.; Funahashi, S. Solvation Structures of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Gallium(III) Ions in Methanol, Ethanol, Dimethyl Sulfoxide, and Trimethyl Phosphate As Studied by EXAFS and Electronic Spectroscopies. *J. Phys. Chem. A* **1999**, *103*, 1401–1406.

(5) Diaz, N.; Suarez, D.; Merz, K., Jr. Hydratation of Zinc Ions: Theoretical Study of $[Zn(H_2O)_4](H_2O)_8^{2+}$ and $[Zn(H_2O)_6](H_2O)_6^{2+}$. *Chem. Phys. Lett.* **2000**, *326*, 288–292.

(6) Warmińska, D.; Krakowiak, J.; Grzybkowski, W. Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. I. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Perchlorates in N,N-Dimethylformamide. *J. Chem. Eng. Data* **2005**, *50* (1), 221–225.

(7) Krakowiak, J.; Koziel, H.; Grzybkowski, W. Apparent Molar Volumes of Divalent Transition Metal Perchlorates and Chlorides in N,N-Dimethylacetamide. *J. Mol. Liq.* **2005**, *118*, 57–65.

(8) Wawer, J.; Krakowiak, J.; Płaczek, A.; Grzybkowski, W. Solvation Numbers of Manganese (II) and Zinc (II) Perchlorates in Methanol Obtained from Volumetric and Compressibilty Properties. *J. Mol. Liq.* **2008**, *143*, 95–99.

(9) Bobicz, D.; Grzybkowski, W.; Lewandowski, A. Apparent Molar Volumes of Divalent Transition Metal Chlorides and Perchlorates in Dimethyl Sulfoxide Solutions. *J. Mol. Liq.* **2003**, *105* (1), 93–104.

(10) Bobicz, D.; Grzybkowski, W. Apparent Molar Volumes of Divalent Transition Metal Cations in Dimethyl Sulfoxide Solutions. *J. Solution Chem.* **1998**, *27*, 817–826.

(11) De Visser, C.; Heuvelsland, W. J. M.; Dunn, L. A.; Somsen, G. Some Properties of Binary Aqueous Liquid Mixtures. Apparent Molar Volumes and Heat Capacities at 298.15 K Over the Whole Mole Fraction Range. *J. Chem. Soc., Faraday Trans.* **1978**, *74* (5), 1159–1169.

(12) Bakshi, M. S.; Singh, J.; Ahmad, S. T.; Kaur, G. Thermodynamic Behavior of Mixtures. 3. Mixtures of Acetonitrile with Dimethylacetamide, Dimethyl Sulfoxide, Nitrobenzene, and Methanol at 25 °C. *J. Chem. Eng. Data* **1996**, *41*, 1459–1461.

(13) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and Compressibility Behaviour of Ionic Liquid, 1-n-Butyl-3-methylimidazolium Hexafluorophosphate and Tetrabutylammonium Hexafluorophosphate in Organic Solvents at T = 298.15 K. *J. Chem. Thermodyn.* **2006**, *38*, 624–633.

(14) Syal, V. K.; Chauhan, S.; Gautam, R. Ultrasonic Velocity Measurements of Carbohydrates in Binary Mixtures of DMSO + H2O at 25°C. *Ultrasonics* **1998**, *36*, 619–623.

(15) Jolicoeur, C.; Philip, P. R.; Perron, G.; Leduc, P. A.; Desnoyers, J. E. A Comparative Study of Bu_4NBr, $NaBPh_4$, Ph_4PCl, and Ph_4AsCl in Water and Methanol at 25 °C: Partial Molal Volumes, Heat Capacities, and Viscosities. *Can. J. Chem.* **1972**, *50*, 3167–3178.

(16) Tominaga, T. Solute-Solvent Interactions of Metal Chelate and Onium Electrolytes by Study of Viscosity and Apparent Molar Volume in Methanol, Acetone, and Nitrobenzene. *J. Phys. Chem.* **1975**, *79*, 1664–1670.

(17) Cornelli, F.; Fracesconi, R. Isothermal Vapor−Liquid Equilibria Measurements, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + Methanol, + Ethanol, and + Propan-1-ol at 313.15K. *J. Chem. Eng. Data* **1997**, *42*, 705–709.

(18) Shin, C.; Criss, C. M. Effect of Temperature on Ionic Volumes and Heat Capacities in Methanol. *J. Solution Chem.* **1986**, *15*, 307–321.

(19) Lankford, J. I.; Holladay, C. M.; Criss, C. M. Isentropic Compressibilities of Univalent Electrolytes in Methanol at 25 °C. *J. Solution Chem.* **1984**, *13*, 699–719.

(20) Resa, J. M.; Gonzaqlez, C.; Landaluce, S. O. (Vapour + Liquid) Equilibria, Densities, Excess Molar Volumes, Refractive Indices, Speed of Sound for (Methanol + Allyl Acetate) and (Vinyl Acetate + Allyl Acetate). *J. Chem. Thermodyn.* **2002**, *34*, 1013–1027.

(21) Wawer, J.; Krakowiak, J.; Grzybkowski, W. Apparent Molar Volumes, Expansibilities, and Isentropic Compressibilities of Selected Electrolytes in Methanol. *J. Chem. Thermodyn.* **2008**, *40* (8), 1193–1199.

(22) Del Grosso, V. A.; Mader, C. W. Speed of Sound in Pure Water. *J. Acoust. Soc.Am.* **1972**, *52*, 1442–1446.

(23) Warmińska, D.; Stangret, J.; Grzybkowski, W. Apparent Molar Volumes and Compressibilities of Selected Electrolytes in Dimethylsulfoxide. *J. Chem. Thermodyn.*, submitted.

(24) Warmińska, D.; Wawer, J.; Grzybkowski, W. Apparent Molar Volumes and Compressibilities of Alkaline Earth Metal Ions in Methanol and Dimethylsulfoxide. *J. Chem. Thermodyn.*, submitted.

(25) Marcus, Y. *The Properties of Solvents*; John Wiley & Sons: London, 1998.

(26) Warmińska, D.; Placzek, A.; Koziel, H.; Grzybkowski, W. Adiabatic Compressibilities of Divalent Transition - Metal Perchlorates and Chlorides in N,N-Dimethylacetamide and Dimethylsulfoxide. *J. Chem. Eng. Data* **2009**, *54*, 745–751.

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