Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. V. Apparent Molar Volumes and Compressibilities of Divalent Transition Metal Bromides in *N*,*N*-Dimethylformamide[†]

Dorota Warmińska,* Anna Płaczek, and Wacław Grzybkowski

Department of Physical Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12, 80-952 Gdańsk, Poland

Densities at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K and sound velocities at 298.15 K of divalent transition metal bromides in *N*,*N*-dimethylformamide have been measured. From these data, apparent molar volumes and apparent molar isentropic compressibilities have been evaluated. The results have been discussed in terms of complex formation.

1. Introduction

Our research group has recently been involved in studies on thermodynamic properties of divalent transition metal salts in acetonitrile and *N*,*N*-dimethylformamide.[1−4] The studies enabled us to understand the solute−solvent interactions and effects occurring due to complex formation. The obtained sequences of limiting apparent molar volumes and the limiting apparent molar isentropic compressibilities of the transition metal perchlorates within the Mn(II)−Zn(II) series reflect effects related to the electronic structure and the ionic radii of metal cations. The most important factor controlling the volumetric and ultrasonic properties of transition metal halides in acetonitrile and metal chlorides in DMF is the relative stability of the tetrahedral and octahedral complexes.

In the present work, we report density at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) K and speed of sound at 298.15 K of divalent transition metal bromides in *N*,*N*-dimethylformamide solutions. We compare the results with the data for respective metal chlorides which have higher coordination ability and perchlorates which exist in DMF as $M(DMF)_6^{2+}\cdot 2ClO_4^-$ solvates.

So far, DMF solutions of manganese(II), cobalt(II), nickel(II), and copper(II) bromides have been investigated by calorimetry, conductometry, and spectrophotometry.[5−9] The authors demonstrated that weaker complexation abilities of bromide ions, compared to chloride ions, are almost entirely due to larger enthalpies of complexation for bromides.[8]

It has been shown that the dissolution of $CoBr_2$ and $CuBr_2$ in DMF results in the formation of $MBr_3(DMF)^-$ (M = Co, Cu) pseudotetrahedral tribromo complexes, while the dissolution of $NiBr_2$ is accompanied by formation of octahedral $Ni(DMF)_6^{2+}$ and $NiBr(DMF)_5^+$ species only.[5,6] It seems to be obvious that formation of the pseudotetrahedral anionic species is accompanied by coexistence of the respective cations, i.e., the six-coordinated complexes. Thus, taking the coordination and material equilibria as well as electrical balance into account, the dissolution of $CoBr_2$ in DMF results in the formation of the $Co(DMF)_6^{2+}\cdot 2CoBr_3(DMF)^-$ and $CoBr(DMF)_5^+\cdot CoBr_3(DMF)^-$ complex electrolytes, while the equilibria in the $NiBr_2$−DMF binary system can be ascribed to the coexistence of $Ni(DMF)_6^{2+}\cdot 2Br^-$ and $NiBr(DMF)_5^+\cdot Br^-$.

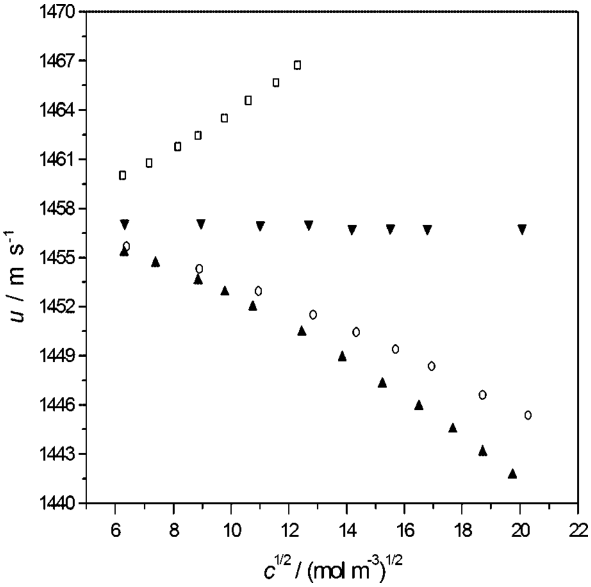

Figure 1. Velocities u against the square root of molarity c of cobalt(II), nickel(II), zinc(II), and copper(II) bromides in DMF at T = 298.15 K: ▼, $CoBr_2$; □, $NiBr_2$; ○, $CuBr_2$; ▲, $ZnBr_2$.

2. Experimental

Materials. Solid DMF-solvated metal bromides were obtained from the corresponding hydrates by dissolving them in *N*,*N*-dimethylformamide. This step was followed by removing any excess of solvent as well as products of dehydratation under reduced pressure at about 343 K. On cooling, the crystalline solids were obtained and recrystallized twice from *N*,*N*-dimethylformamide. The stock solutions of metal bromides were standardized by EDTA titration. At least ten determinations were carried out for each of the solutions, and the uncertainty in the solution composition was smaller than 0.1 %. Solutions for density and speed of sound measurements were prepared by weighed dilutions.

Anhydrous *N*,*N*-dimethylformamide (Fluka - puriss, $H_2O <$ 0.01 % and Aldrich - puriss, $H_2O <$ 0.005 %) was stored over

---

* Corresponding author. E-mail address: dorota@chem.pg.gda.pl.

[†] Part of the special issue “Robin H. Stokes Festschrift”.

10.1021/je8001877 CCC: $40.75

Table 1. Densities d of Solutions of Metal Bromides in DMF at Different Temperatures

	T/K						
m_s/mol·kg^{-1}	283.15	293.15	298.15	303.15	313.15	323.15	333.15
			d/kg·m^{-3}				
			$MnBr_2$				
0.00000	958.068	948.556	943.790	939.012	929.430	919.799	910.108
0.04558	966.845	957.193	952.340	947.480	937.775	928.052	918.270
0.06342	970.206	960.483	955.613	950.738	940.986	931.216	921.409
0.09167	975.483	965.675	960.769	955.868	946.060	936.248	926.411
0.1136	979.598	969.721	964.790	959.866	950.024	940.181	930.322
0.1357	983.754	973.816	968.861	963.913	954.038	944.174	934.300
0.1815	992.413	982.372	977.377	972.389	962.446	952.526	942.602
0.2232	1000.408	990.283	985.247	980.228	970.230	960.258	950.292
0.2659	1008.695	998.486	993.418	988.360	978.304	968.285	958.283
0.3076	1016.894	1006.608	1001.505	996.420	986.302	976.237	966.190
0.3463	1024.628	1014.278	1009.143	1004.030	993.865	983.753	973.662
0.3892	1033.286	1022.862	1017.695	1012.547	1002.325	992.163	982.030
0.4285	1041.321	1030.834	1025.640	1020.464	1010.192	999.985	989.820
			$CoBr_2$				
0.00000	958.068	948.556	943.790	939.012	929.430	919.799	910.108
0.03000	963.834	954.235	949.426	944.609	934.970	925.300	915.575
0.04202	966.096	956.474	951.658	946.841	937.188	927.498	917.754
0.05875	969.258	959.600	954.776	949.944	940.272	930.568	920.812
0.08348	973.918	964.227	959.387	954.541	944.846	935.122	925.347
0.1036	977.727	968.006	963.155	958.303	948.593	938.853	929.065
0.1252	981.863	972.115	967.250	962.385	952.653	942.894	933.091
0.1652	989.542	979.761	974.875	969.990	960.220	950.432	940.600
0.2048	997.300	987.449	982.541	977.638	967.836	958.019	948.164
0.2432	1004.931	995.026	990.098	985.172	975.333	965.480	955.595
0.2827	1012.871	1002.914	997.962	993.020	983.147	973.265	963.350
0.3387	1024.350	1014.335	1009.315	1004.342	994.401	984.490	974.525
0.3945	1036.048	1025.934	1020.913	1015.910	1005.926	995.945	985.946
			$NiBr_2$				
0.00000	958.187	948.678	943.910	939.138	929.557	919.923	910.235
0.02369	963.361	953.834	949.057	944.276	934.677	925.029	915.320
0.03148	965.054	955.522	950.744	945.955	936.347	926.693	916.975
0.04112	967.140	957.600	952.816	948.026	938.412	928.746	919.016
0.05368	969.858	960.305	955.522	950.728	941.104	931.427	921.670
0.06938	973.267	963.705	958.913	954.111	944.472	934.770	924.986
0.08151	975.914	966.340	961.541	956.736	947.088	937.370	927.549
0.09903	979.750	970.163	965.361	960.542	950.873	941.123	931.252
0.1157	983.419	973.822	969.011	964.186	954.494	944.711	934.781
0.1371	988.150	978.534	973.715	968.879	959.163	949.329	939.319
0.1547	992.055	982.429	977.602	972.758	963.014	953.136	943.064
			$CuBr_2$				
0.00000	958.068	948.565	943.790	939.012	929.430	919.799	910.108
0.04286	965.995	956.430	951.625	946.820	937.178	927.489	917.743
0.05879	968.968	959.381	954.568	949.748	940.087	930.375	920.610
0.08263	973.445	963.825	958.995	954.160	944.467	934.725	924.925
0.1047	977.622	967.970	963.128	958.277	948.552	938.778	928.955
0.1241	981.332	971.651	966.798	961.938	952.188	942.388	932.534
0.1691	989.989	980.251	975.370	970.481	960.674	950.814	940.900
0.2091	997.818	988.028	983.124	978.206	968.344	958.435	948.463
0.2487	1005.694	995.855	990.929	985.982	976.068	966.105	956.082
0.2879	1013.597	1003.707	998.753	993.780	983.816	973.798	963.715
0.3467	1025.654	1015.689	1010.694	1005.692	995.649	985.555	975.398
0.4023	1037.332	1027.293	1022.260	1017.224	1007.108	996.934	986.695
			$ZnBr_2$				
0.00000	958.187	948.678	943.910	939.138	929.557	919.923	910.235
0.04180	965.511	955.942	951.145	946.343	936.713	927.035	917.303
0.05710	968.224	958.633	953.826	949.013	939.365	929.669	919.920
0.08175	972.633	963.002	958.179	953.349	943.670	933.944	924.170
0.09949	975.830	966.173	961.336	956.494	946.790	937.044	927.252
0.1197	979.509	969.82	964.971	960.115	950.383	940.615	930.799
0.1593	986.779	977.035	972.147	967.26	957.485	947.666	937.803
0.1960	993.634	983.833	978.918	974.016	964.176	954.312	944.405
0.2356	1001.142	991.277	986.336	981.396	971.504	961.587	951.634
0.2742	1008.570	998.643	993.671	988.709	978.762	968.795	958.793
0.3124	1016.021	1006.037	1001.041	996.04	986.038	976.020	965.974
0.3476	1023.014	1012.963	1007.94	1002.914	992.859	982.799	972.705
0.3838	1030.300	1020.201	1015.151	1010.109	999.987	989.869	979.732

4 Å molecular sieves and was used without any further purification. The values of density (943.84 ± 0.069) kg·m^{-3} and ultrasonic velocity 1457.13 m·s^{-1} obtained for DMF were in good agreement with the best literature data 943.85 kg·m^{-3} and 943.87 kg·m^{-3}[10,11] and 1457.49 m·s^{-1} and 1457.30 m·s^{-1}.[12,13]

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 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 K according to

Table 2. Speed of Sound u, Isentropic Compressibility κ_s, and Apparent Molar Compressibility Φ_{KS} of Metal Bromides in DMF at 298.15 K

salt	m_S / $\mathrm{mol \cdot kg^{-1}}$	u / $\mathrm{m \cdot s^{-1}}$	$10^{10}\kappa_S$ / $\mathrm{m^2 \cdot N^{-1}}$	$10^{13}\Phi_{KS}$ / $\mathrm{m^5 \cdot N^{-1} \cdot mol^{-1}}$
$CoBr_2$	0.04202	1457.10	4.949	−0.91
	0.08348	1457.13	4.909	−0.89
	0.1252	1457.00	4.870	−0.86
	0.1652	1457.05	4.832	−0.85
	0.2048	1456.78	4.796	−0.83
	0.2432	1456.80	4.759	−0.82
	0.2827	1456.78	4.722	−0.81
	0.3945	1456.81	4.615	−0.79
$NiBr_2$	0.04112	1460.02	4.924	−1.74
	0.05368	1460.77	4.905	−1.70
	0.06938	1461.78	4.880	−1.68
	0.08151	1462.45	4.863	−1.65
	0.09903	1463.52	4.836	−1.63
	0.1157	1464.59	4.811	−1.62
	0.1371	1465.66	4.781	−1.59
	0.1547	1466.73	4.755	−1.58
$CuBr_2$	0.04286	1455.68	4.959	−6.02
	0.08263	1454.31	4.930	−5.93
	0.1241	1452.95	4.900	−5.88
	0.1691	1451.50	4.866	−5.85
	0.2091	1450.45	4.835	−5.87
	0.2487	1449.40	4.804	−5.87
	0.2879	1448.35	4.773	−5.85
	0.3467	1446.61	4.728	−5.77
	0.4023	1445.36	4.683	−5.76
$ZnBr_2$	0.04180	1455.32	4.964	−4.23
	0.05710	1454.66	4.955	−4.22
	0.08175	1453.60	4.939	−4.22
	0.09949	1452.90	4.928	−4.26
	0.1197	1452.00	4.915	−4.22
	0.1593	1450.45	4.890	−4.26
	0.1960	1448.90	4.866	−4.24
	0.2356	1447.30	4.840	−4.24
	0.2742	1445.91	4.814	−4.26
	0.3124	1444.52	4.787	−4.28
	0.3476	1443.13	4.764	−4.26
	0.3838	1441.75	4.739	−4.25

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

salt	T / K	d_o / $\mathrm{kg \cdot m^{-3}}$	A_{1d} / $\mathrm{(kg^2 \cdot m^{-3} \cdot mol^{-1})^{1/2}}$	A_{2d} / $\mathrm{kg \cdot mol^{-1}}$	σ_d / $\mathrm{kg \cdot m^{-3}}$
$MnBr_2$	283.15	958.068	0.140 ± 0.005	0.1801 ± 0.0003	0.03
	293.15	948.565	0.120 ± 0.003	0.1806 ± 0.0002	0.02
	298.15	943.790	0.110 ± 0.003	0.1810 ± 0.0002	0.02
	303.15	939.012	0.101 ± 0.003	0.1815 ± 0.0002	0.02
	313.15	929.430	0.087 ± 0.003	0.1825 ± 0.0002	0.01
	323.15	919.799	0.076 ± 0.002	0.1835 ± 0.0002	0.02
	333.15	910.108	0.068 ± 0.003	0.1847 ± 0.0002	0.02
$CoBr_2$	283.15	958.068	0.066 ± 0.003	0.1875 ± 0.0002	0.02
	293.15	948.556	0.055 ± 0.003	0.1884 ± 0.0002	0.02
	298.15	943.790	0.052 ± 0.003	0.1889 ± 0.0002	0.02
	303.15	939.012	0.048 ± 0.003	0.1895 ± 0.0002	0.02
	313.15	929.430	0.043 ± 0.004	0.1906 ± 0.0003	0.02
	323.15	919.799	0.039 ± 0.005	0.1919 ± 0.0003	0.03
	333.15	910.108	0.037 ± 0.006	0.1932 ± 0.0004	0.03
$NiBr_2$	283.15	958.187	0.055 ± 0.008	0.2165 ± 0.0008	0.02
	293.15	948.678	0.055 ± 0.008	0.2178 ± 0.0007	0.02
	298.15	943.910	0.056 ± 0.008	0.2184 ± 0.0008	0.02
	303.15	939.138	0.057 ± 0.008	0.2190 ± 0.0008	0.02
	313.15	929.557	$0.06_1 \pm 0.009_4$	0.2199 ± 0.0009	0.03
	323.15	919.923	$0.07_2 \pm 0.01_3$	0.2197 ± 0.0013	0.04
	333.15	910.235	$0.09_1 \pm 0.01_8$	0.2179 ± 0.0018	0.05
$CuBr_2$	283.15	958.068	0.021 ± 0.005	0.1890 ± 0.0004	0.03
	293.15	948.565	0.019 ± 0.005	0.1896 ± 0.0003	0.003
	298.15	943.790	0.019 ± 0.006	0.1900 ± 0.0004	0.003
	303.15	939.012	0.018 ± 0.005	0.1903 ± 0.0003	0.003
	313.15	929.430	0.016 ± 0.005	0.1910 ± 0.0003	0.02
	323.15	919.799	0.014 ± 0.005	0.1917 ± 0.0003	0.03
	333.15	910.108	0.016 ± 0.004	0.1922 ± 0.0003	0.02
$ZnBr_2$	283.15	958.187	−0.012 ± 0.003	0.1829 ± 0.0002	0.02
	293.15	948.678	−0.012 ± 0.003	0.1832 ± 0.0002	0.02
	298.15	943.910	−0.012 ± 0.004	0.1834 ± 0.0002	0.02
	303.15	939.138	−0.012 ± 0.003	0.1836 ± 0.0002	0.02
	313.15	929.557	−0.010 ± 0.003	0.1840 ± 0.0002	0.02
	323.15	919.923	−0.008 ± 0.003	0.1845 ± 0.0002	0.02
	333.15	910.235	−0.006 ± 0.003	0.1851 ± 0.0002	0.02

Table 4. Coefficients of Equation 2 for Speed of Sound in the Solutions of Metal Bromides in DMF at 298.15 K (A_{ou} =1457.13 $\mathrm{m \cdot s^{-1}}$)

salt	A_{1u} / $\mathrm{(m^5 \cdot s^{-2} \cdot mol^{-1})^{1/2}}$	A_{2u} / $\mathrm{m^4 \cdot s^{-1} \cdot mol^{-1}}$	σ_u / $\mathrm{m \cdot s^{-1}}$
$CoBr_2$	0.00 ± 0.03	−0.001 ± 0.002	0.09
$NiBr_2$	0.14 ± 0.04	0.052 ± 0.004	0.07
$CuBr_2$	−0.14 ± 0.06	−0.022 ± 0.004	0.3
$ZnBr_2$	−0.10 ± 0.04	−0.035 ± 0.002	0.2

Table 5. Coefficients of Equation 4 for Isentropic Compressibility of the Solutions of Metal Bromides in DMF at 298.15 K and their Standard Deviations σ

salt	$10^{13}B_1$ / $\mathrm{(m^7 \cdot N^{-2} \cdot mol^{-1})^{1/2}}$	$10^{13}B_2$ / $\mathrm{m^5 \cdot N^{-1} \cdot mol^{-1}}$	$10^{12}\sigma$ / $\mathrm{m^2 \cdot N^{-1}}$
$CoBr_2$	−1.4 ± 0.4	−0.87 ± 0.03	0.2
$NiBr_2$	−2.1 ± 0.4	−1.40 ± 0.04	0.08
$CuBr_2$	−0.17 ± 0.08	−0.740 ± 0.002	0.07
$ZnBr_2$	−0.11 ± 0.07	−0.640 ± 0.005	0.04

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 obtained density value of DMF was then used for calculating the apparent molar volumes of all solutions in one measurement series. It has been done for each series individually. The speed of sound was measured using the sound analyzer OPTIME 1.0 from OPTEL (Poland) with an uncertainty of 0.05 $\mathrm{m \cdot s^{-1}}$ 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 $\mathrm{m \cdot s^{-1}}$ of the sound velocity in pure water has been used.[14]

3. Results and Discussion

The two measured parameters, i.e., densities d and velocities u, obtained for solutions of transition metal bromides in DMF are listed in Tables 1 and 2. They are presented in the form of curve fitted quantities according to the respective equations

$$d = d_o + A_{1d} \cdot c^{1/2} + A_{2d} \cdot c \tag{1}$$

$$u = 1457.13 + A_{1u} \cdot c^{1/2} + A_{2u} \cdot c \tag{2}$$

The polynomial coefficients and respective values of the residual variance σ are given in Tables 3 and 4 (d_o corresponds to the density of pure DMF at respective temperature). Figure 1 shows the velocities for cobalt(II), nickel(II), zinc(II), and copper(II) bromides in DMF against square root of molar concentration. Due to high damping, sound velocity measurements for manganese(II) bromide solution were not carried out. Inspection of the presented data shows that the highest values of velocities are observed for $NiBr_2$ solutions, while the lowest values were recorded for the $ZnBr_2$ system. The increase in concentration brings about the decrease of velocities of zinc(II) and copper(II) bromides (the same effect was observed for respective salts in acetonitrile[4]) and the increase of velocities of nickel(II) bromide. Addition of cobalt(II) bromide to DMF has practically no influence on sound velocity observed for pure solvent.

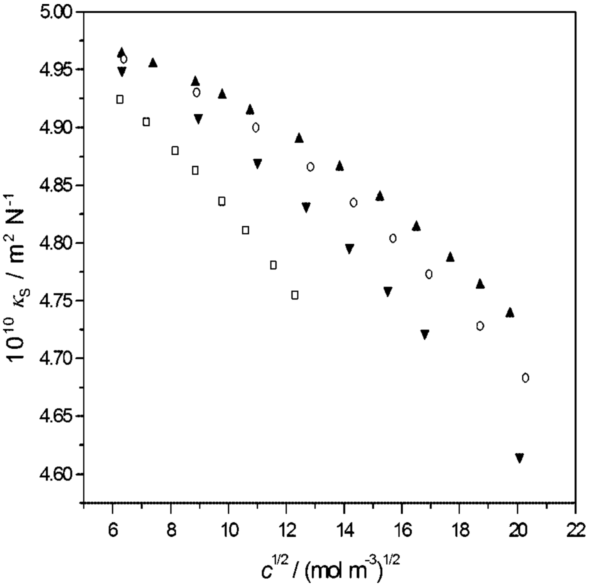

Figure 2. Isentropic compressibility coefficient κ_S against the square root of molarity c of cobalt(II), nickel(II), zinc(II), and copper(II) bromides in DMF at T = 298.15 K: ▼, $CoBr_2$; □, $NiBr_2$; ○, $CuBr_2$; ▲, $ZnBr_2$.

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

salt	$10^{13}a_o$ $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{16}a_1$ $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{14}\sigma$ $m^5 \cdot N^{-1} \cdot mol^{-1}$
$CoBr_2$	−0.96 ± 0.02	9.2 ± 0.9	0.05
$NiBr_2$	−1.90 ± 0.03	26 ± 3	0.05
$CuBr_2$	−0.610 ± 0.009	1.5 ± 0.6	0.03
$ZnBr_2$	−0.0035 ± 0.0004	−0.3 ± 0.2	0.02

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

salt	T K	10^6A_o $m^3 \cdot mol^{-1}$	10^8A_1 $(m^9 \cdot mol^{-3})^{1/2}$	$10^6\sigma$ $m^3 \cdot mol^{-1}$
$CuBr_2$	283.15	32.54 ± 0.06	11.7 ± 0.4	0.03
	293.15	32.53 ± 0.06	10.6 ± 0.5	0.03
	298.15	32.41 ± 0.05	10.3 ± 0.4	0.03
	303.15	32.35 ± 0.05	9.9 ± 0.4	0.02
	313.15	32.17 ± 0.04	9.3 ± 0.3	0.02
	323.15	32.00 ± 0.04	8.9 ± 0.3	0.02
	333.15	31.54 ± 0.05	9.5 ± 0.4	0.02
$ZnBr_2$	283.15	44.98 ± 0.05	−6.8 ± 0.3	0.02
	293.15	45.11 ± 0.05	−6.9 ± 0.4	0.03
	298.15	45.12 ± 0.04	−6.7 ± 0.3	0.02
	303.15	45.17 ± 0.06	−6.9 ± 0.4	0.03
	313.15	44.89 ± 0.04	−5.8 ± 0.3	0.02
	323.15	44.47 ± 0.04	−4.6 ± 0.3	0.02
	333.15	44.00 ± 0.03	−3.9 ± 0.3	0.02

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

salt	T K	10^6A_o $m^3 \cdot mol^{-1}$	10^6A_1 $(m^9 \cdot mol^{-3})^{1/2}$	10^8A_2 $m^6 \cdot mol^{-2}$	$10^6\sigma$ $m^3 \cdot mol^{-1}$
$MnBr_2$	283.15	4 ± 2	2.3 ± 0.3	−5 ± 1	0.3
	293.15	5 ± 3	2.3 ± 0.4	−6 ± 2	0.4
	298.15	7 ± 3	2.2 ± 0.4	−5 ± 2	0.3
	303.15	9 ± 2	2.0 ± 0.3	−5 ± 1	0.3
	313.15	11 ± 3	1.8 ± 0.3	−4 ± 2	0.3
	323.15	13 ± 3	1.7 ± 0.4	−4 ± 2	0.4
	333.15	14 ± 2	1.5 ± 0.4	−4 ± 2	0.3
$CoBr_2$	283.15	13 ± 2	1.7 ± 0.3	−5 ± 1	0.3
	293.15	15 ± 2	1.4 ± 0.3	−3.8 ± 0.9	0.3
	298.15	17 ± 1	1.2 ± 0.2	−3.2 ± 0.7	0.2
	303.15	17.8 ± 0.8	1.1 ± 0.2	−2.7 ± 0.5	0.2
	313.15	19.0 ± 0.5	0.85 ± 0.09	−2.0 ± 0.4	0.1
	323.15	19.1 ± 0.5	0.74 ± 0.08	−1.7 ± 0.3	0.1
	333.15	19.0 ± 0.6	0.63 ± 0.09	−1.4 ± 0.4	0.1
$NiBr_2$	283.15	−15.4 ± 0.9	1.7 ± 0.3	−5 ± 2	0.09
	293.15	−17 ± 1	1.8 ± 0.3	−5 ± 2	0.1
	298.15	−18 ± 1	1.7 ± 0.3	−5 ± 2	0.1
	303.15	−19.0 ± 0.7	1.8 ± 0.3	−5 ± 2	0.07
	313.15	−20.7 ± 0.7	1.7 ± 0.2	−5 ± 2	0.07
	323.15	−23.3 ± 0.8	1.8 ± 0.3	−4 ± 2	0.08
	333.15	−25.9 ± 0.3	1.9 ± 0.2	−3.3 ± 0.5	0.03

The sound velocity, u, and isentropic compressibility, κ_S, values are listed in Table 2. The κ_S values were calculated using the Laplace equation

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

In the concentration range studied, the isentropic compressibility values decrease nonlinearly according to the equation

$$\kappa_S = B_o + B_1 \cdot c^{1/2} + B_2 \cdot c \tag{4}$$

where $B_o = 4.99 \cdot 10^{-10}\ N \cdot m^{-2}$ is the isentropic compressibility of pure DMF at 298.15 K estimated using the values of density and speed of sound reported in the present study. The respective coefficients B_1 and B_2 of the polynomials together with the values of the residual variance σ for all electrolytes studied are given in Table 5, while Figure 2 shows the isentropic compressibility coefficients of cobalt(II), nickel(II), zinc(II), and copper(II) bromides in DMF against the square root of concentration. Inspection of the data shows that the highest impact on solution compressibility has nickel(II) bromide, while the lowest influence on solution compressibility is observed for zinc(II) bromide. This variation of velocity and isentropic compressibility values of the studied electrolyte solutions can be interpreted in terms of the ability of the respective metal ion to form tetrahedral complexes. The higher the tendency arising from the electronic structure of the metal ion, the lower the velocity and the higher the isentropic compressibility or the smaller the electrostriction effect. Four-coordinate structures are suggested for $ZnBr_2(DMF)_2$ and $ZnBr_3(DMF)$, and thus the six-coordinate, octahedral structure of $Zn(DMF)_6^{2+}$ changes upon complexation.[15] The complex $NiBr(DMF)_5^+$ remains octahedral.[6]

Apparent molar volumes Φ_V and apparent molar compressibilities Φ_{KS} were calculated from relative density and velocity ratios using the following equations

$$\Phi_V = (d_o - d)/(m_S d d_o) + M_2/d_o \tag{5}$$

$$\Phi_{KS} = (\kappa_S d_o - \kappa_{So} d)/(m_s d d_o) + M_2 \kappa_S/d_o \tag{6}$$

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; M_2 is the molar mass of the solute; and κ_S and κ_{So} are the isentropic compressibility of solution and solvent, respectively.

The Φ_{KS} values for all salts studied are presented in Table 2. The apparent molar isentropic compressibilities of cobalt(II), nickel(II), zinc(II), and copper(II) bromides, together with the corresponding values for perchlorates and chlorides[1,3] in DMF are plotted against the square root of concentration in Figure 3. All plots of Φ_{KS} against $c^{1/2}$ for bromides show a good linearity. For this reason, empirical Masson-type equations

$$\Phi_{KS} = a_o + a_1 \cdot c^{1/2} \tag{7}$$

were used, where a_o and a_1 are obtained as the intercept and slope, respectively, of a (presumed) linear fit of the data. The coefficients a_o and a_1 and values of the residual variance σ are given in Table 6. The most negative Φ_{KS} values were obtained

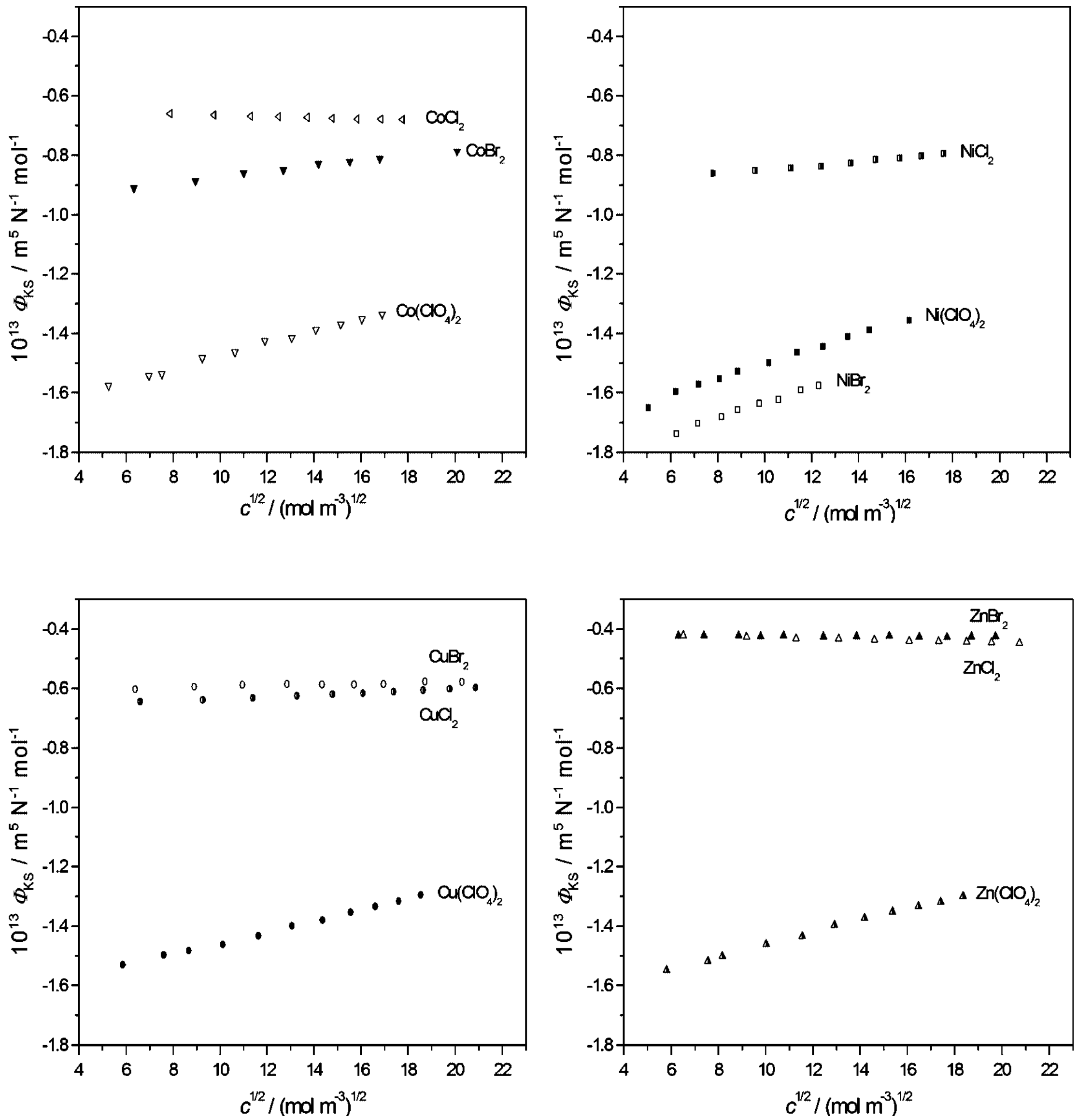

Figure 3. Apparent molar compressibility Φ_{KS} against the square root of molarity c of cobalt(II), nickel(II), zinc(II), and copper(II) bromides, chlorides, and perchlorates in DMF at $T = 298.15$ K: symbols as in Figure 1, this work; ▽, $Co(ClO_4)_2$; ■, $Ni(ClO_4)_2$; ●, $Cu(ClO_4)_2$; △, $Zn(ClO_4)_2$, ref 1; open triangle pointing left, $CoCl_2$; ◨, $NiCl_2$; ◑, $CuCl_2$; ▲, $ZnCl_2$, ref 3.

for metal perchlorates, which exist in DMF as the $M(DMF)_6^{2+}\cdot 2ClO_4^-$-type solvates, and thus the electrostriction influence is the highest. One exception is $NiBr_2$ for which the apparent molar isentropic compressibilities are lower than Φ_{KS} values obtained for $Ni(ClO_4)_2$. Nickel(II) bromide exists in DMF as a mixture of octahedral complex electrolytes $Ni(DMF)_6^{2+}\cdot 2Br^-$ and $NiBr(DMF)_5^+\cdot Br^-$, and the compressibility of the bromide anion is much lower than the perchlorate anion.[6,16] As seen, the Φ_{KS} values of cobalt(II) chloride are higher than those for cobalt(II) bromide. It is due to the different coordination states of cobalt(II) halides in *N*,*N*-dimethylformamide. $CoCl_2$ in DMF solutions appears, within a broad concentration range, as the following complex electrolyte: $Co(DMF)_6^{2+}\cdot 2CoCl_3(DMF)^-$ that consists of the octahedral solvocation and pseudotetrahedral trichloroanions. The corresponding tribromo complexes of cobalt(II) are less stable, and a markedly high fraction of cobalt(II) in the solution of $CoBr_2$ appears as the octahedral monobromide complex.[5] The values of the apparent molar compressibilities of zinc(II) chlorides and bromides are nearly the same. Tetrahedral complexes of zinc show an exceptional stability which leads to the existence of neutral $ZnCl_2(DMF)_2$ complexes in the solution in the presence of a small amount of $Zn(DMF)_6^{2+}\cdot 2ZnCl_3(DMF)^-$ complex electrolyte.[17]

Figure 4 shows the apparent molar volumes of metal bromides, Φ_V, plotted against the square root of concentration $c^{1/2}$. It can be observed that the variation of Φ_V values of copper(II) and zinc(II) bromides over the concentration range studied is relatively small. Moreover, the plots of Φ_V against $c^{1/2}$ are found to be linear over the concentration as well as temperature range studied. Therefore, the Masson-type equation

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

can be employed. The coefficients of the equation, their standard deviations, and σ are given in Table 7. Further inspection of Figure 4 shows that the variation of apparent molar volumes of manganese(II), cobalt(II), and nickel(II) bromide with concentration are considerably more significant, and the $\Phi_V = f(c^{1/2})$ function is not linear. Thus, to describe the concentration dependences of the apparent molar volumes

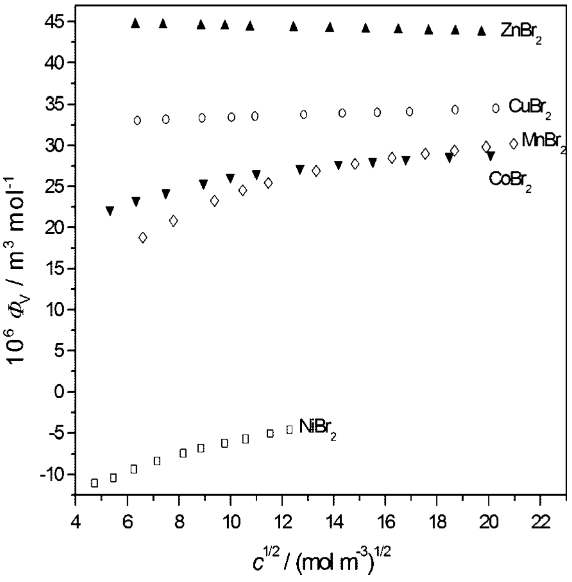

Figure 4. Apparent molar Volumes Φ_V against the square root of molarity *c* of the divalent transition metal bromides in DMF at $T = 298.15$ K: ◇, $MnBr_2$; ▼, $CoBr_2$; □, $NiBr_2$; ○, $CuBr_2$; ▲, $ZnBr_2$.

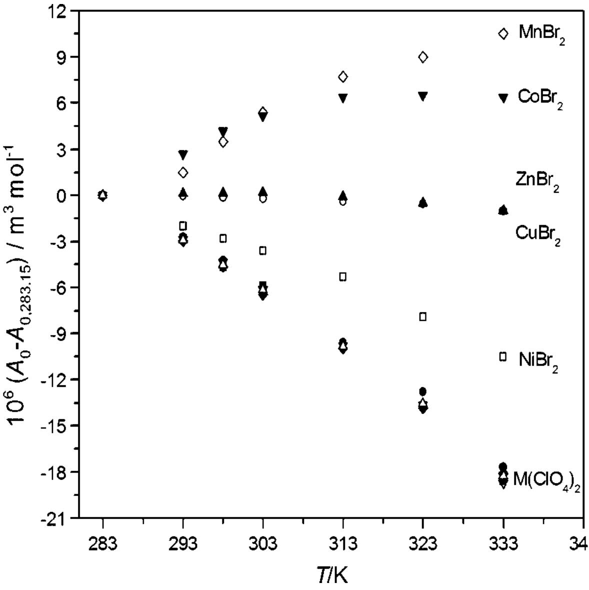

Figure 5. Apparent molar volumes at infinite dilution against the temperature of the divalent transition metal bromides in DMF: symbols as in Figure 4, this work; ◆, $Mn(ClO_4)_2$; ▽, $Co(ClO_4)_2$; ■, $Ni(ClO_4)_2$; ●, $Cu(ClO_4)_2$; △, $Zn(ClO_4)_2$, ref 1.

of respective salt solutions, Redlich−Rosenfeld−Meyer (RRM)-type equations

$$\Phi_V = A_o + A_1 \cdot c^{1/2} + A_2 \cdot c \qquad (9)$$

were used. The respective coefficients of the polynomial (9) and the σ values are presented in Table 8.

DMF is a solvent of relatively low dielectric constant, and thus molar isentropic compressibilities and apparent molar volumes can be affected by ion pairing. Therefore, the coefficients A_o in eqs 7, 8, and 9 are the limiting values of Φ_V and Φ_{KS} but cannot be considered as the values of the partial molar isentropic compressibilities or partial apparent molar volumes of the electrolytes studied.[18]

The highest values of the apparent molar volumes were obtained for zinc(II) bromide, while the lowest were observed for nickel(II) bromide solutions. These volume differences result from the different structure of complexes existing in solutions studied.

Figure 5 illustrates the influence of temperature on the values of the apparent molar volumes of divalent transition metal bromides at infinite dilution. An increase in temperature causes an increase of the apparent molar volumes at infinite dilution for manganese(II) bromide solutions. For nickel(II), zinc(II), and copper(II) bromides, a decrease in apparent molar volumes with raising temperature was observed. For cobalt(II) bromide solutions, a slight maximum of the apparent molar volumes at infinite dilution at 313.15 K was observed. Finally, the apparent molar volumes at infinite dilution of zinc(II) and copper(II) bromide are nearly insensitive to the temperature change. The limiting apparent molar volumes of respective metal perchlorates decrease with increasing temperature (see ref 1). Furthermore, they are sensitive to the temperature change to an equal extent. The apparent molar volume is defined as the difference between the volume of the solution and the volume of the pure solvent per mole of solute and is given by

$$\Phi_V = \frac{V - n_1 V_1^o}{n_2} \qquad (10)$$

where *V* denotes the volume of the solution; n_1 and n_2 are the number of moles of the solvent and salt, respectively; and V_1^o is the molar volume of pure solvent. The increase of temperature causes the increase of both the volume of the solution and the volume of the pure solvent. The total change of Φ_V depends on the magnitude of one of those two terms. Due to the electrostriction of the solvent molecules, an increase of molar volumes of octahedral metal perchlorates is lower than the increase of molar volume of pure solvent, and in consequence, the molar volumes of salts decrease with temperature. The variety of change of Φ_V for metal bromides with temperature may indicate the change of the coordination geometry around a metal ion with temperature.

Literature Cited

(1) 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.

(2) Krakowiak, J.; Warmińska, D.; Grzybkowski, W. Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. II. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Perchlorates in Acetonitrile. *J. Chem. Eng. Data* **2005**, *50* (3), 832–837.

(3) Warmińska, D.; Krakowiak, J.; Grzybkowski, W. Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. III. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Chlorides in N,N-Dimethylformamide. *J. Chem. Eng. Data* **2007**, *52* (6), 2099–2104.

(4) Krakowiak, J.; Warmińska, D.; Grzybkowski, W. Thermodynamic Properties of Inorganic Salts in Nonaqeous Solvents. IV. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Bromides and Chlorides in Acetonitrile. *J. Chem. Eng. Data* **2007**, *52* (6), 2105–2109.

(5) Pilarczyk, M.; Klinszporn, L. Ionization equilibria in solutions of cobaltbromide in N,N-dimethylformamide. *Electrochim. Acta* **1986**, *31*, 185–192.

(6) Pilarczyk, M.; Klinszporn, L. Equilibria of Nickel(II) Bromide in N,N-Dimethylformamide Solutions. *Bull. Acad. Polon. Sci., Ser. Sci., Chim.* **1986**, *34*, 53–63.

(7) Pilarczyk, M.; Grzybkowski, W.; Klinszporn, L. Spectrophotometric and conductometric study of copper(II) bromide N,N-dimethylformamide solutions. *Polyhedron* **1987**, *6*, 1399–1405.

(8) Ozutsumi, K.; Ishiguro, S.-i. Calorimetric and spectrophotometric studies of complexation of manganese(II), cobalt(II) and nickel(II) with bromide ions in N,N-dimethylformamide. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (2), 271–275.

(9) Ishiguro, S.-i.; Ozutsumi, K.; Nagy, L.; Ohtaki, H. Calorimetric and spectrophotometric studies of bromo complexes of copper(II) in N,N-dimethylformamide. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1691–1698.

(10) Venkatesu, P.; Lee, M. J.; Lin, H. M. Volumetric properties of (N,N-dimethylformamide+aliphatic diethers) at temperatures ranging from (298.15 to 358.15) K. *J. Chem. Thermodyn.* **2005**, *37*, 996–1002.

(11) Wurm, B.; Münsterer, M.; Richardi, J.; Buchner, R.; Barthel, J. Ion association and solvation of perchlorate salts in-dimethylformamide and N,N-dimethylacetamide: A dielectric relaxation study. *J. Mol. Liq.* **2005**, *119* (1−3), 97–106.

(12) Papamatthaiakisa, D.; Aronia, F.; Havredaki, V. Isentropic compressibilities of (amide + water) mixtures: A comparative study. *J. Chem. Thermodyn.* **2008**, *40* (1), 107–118.

(13) Miyai, K.; Nakamura, M.; Tamura, K.; Murakami, S. Isotope effects on thermodynamic properties in four binary systems: Water (or heavy water) + dimethylsulfoxide (or N,N-Dimethylformamide) at 25 °C. *J. Solution Chem.* **1997**, *26* (10), 973–988.

(14) Del Grosso, W. A.; Mader, C. W. Speed of sound in pure water. *J. Acoust. Soc. Am.* **1972**, *52*, 1442–1446.

(15) Ishiguro, S.-i.; Miyauchi, M.; Ozutsumi, K. Thermodynamics of formation of binary and ternary complexws of zinc(II) with halide and thiocyanate ions and 2,2′-bipyridine in dimethylformamide. *J. Chem. Soc., Dalton Trans.* **1990**, 2035–2041.

(16) Das, D.; Das, B.; Hazra, D. K. Ultrasonic velocities and isentropic compressibilities of some symmetrical tetraalkylammonium salts in N,N-dimethylacetamide at 298.15 K. *J. Mol. Liq.* **2004**, *111* (1−3), 15–18.

(17) Grzybkowski, W. Electrolytic behaviour of transition metal bromides in acetonitrile solution. *J. Chem. Soc., Dalton Trans.* **1987**, 2863–2866.

(18) Marcus, Y.; Hefter, G. Standard Partial Molar Volumes of Electrolytes and Ions in Nonaqueous Solvents. *Chem. Rev.* **2004**, *104* (7), 3405–3452.

Received for review March 17, 2008. Accepted July 06, 2008. Support from the State Committee for Scientific Research (KBN) within the grant 7 T09A 016 021 is acknowledged.

JE8001877