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

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The densities of divalent transition-metal perchlorates 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 perchlorates in DMF have been determined from sound velocity data obtained at 298.15 K.

Introduction

This paper presents part of our study of thermodynamic properties of electrolyte solutions in nonaqueous solvents. It seems to be well established that the essential form of occurrence of the metal ions in donor solvents in the absence of coordinatively active anions is 4-, 6-, or 8-coordinated solvocations.[1−3] Moreover, it is well known[2] that the perchlorates of the divalent first-row transition-metal cations exist in solutions of *N*,*N*-dimethylformamide as the $M(DMF)_6^{2+}\cdot 2ClO_4^-$ type of complex electrolytes, where M = Mn, Co, Ni, Cu, and Zn. The analysis of the conductometric data shows that the properties of DMF-solvated divalent cations exhibit small, but distinct, variation within the Mn(II) to Zn(II) series, which is obviously related to the electronic structure and size of the central metal ion.[4]

Apparent molar volumes are key to an understanding of solvation phenomena. The present contribution deals with 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 perchlorates of the divalent metal cations belonging to the Mn(II) to Zn(II) series. Moreover, the influence of temperature on the limiting values of the apparent molar volume of the metal perchlorates is studied.

Experimental Section

The DMF-solvated metal perchlorates were obtained from the corresponding hydrates by dissolving the latter in anhydrous *N*,*N*-dimethylformamide and removing of any excess solvent, as well as water, under reduced pressure at 333 K. On cooling, the crystalline solids were obtained and recrystallized twice from anhydrous DMF (Fluka − puriss, H_2O <0.01%).

The stock solutions of the metal perchlorates were prepared and analyzed for the respective metals by standard EDTA titration. At least 10 determinations were performed in each case, and the relative errors were smaller than 0.1%. Solutions for density and speed-of-sound measurements were prepared by weighed dilutions.

The densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with a thermostatic system based on the Peltier unit with a repeatability of 1.0×10^{-3} kg·m^{-3} and an uncertainty of 5.0×10^{-3} kg·m^{-3} while the temperature was kept constant at (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, 333.15) K to 0.001 K, according to the producer's declaration. The accuracy of the density measurements and purity of the solvent were verified by measurements of their densities at 298.15 K. A density of (943.85 ± 0.06) kg·m^{-3} for *N*,*N*-dimethylformamide was found, whereas the literature[2,5] values vary from 944.03 kg·m^{-3} to 943.82 kg·m^{-3}.

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 thermostated at (298.15 ± 0.005) K and calibrated with double-distilled water, where a value of 1496.69 m·s^{-1} for the sound velocity in pure water has been used.[6] The speed of sound obtained for DMF was 1457.13 m·s^{-1}, whereas the corresponding literature[7,8] values are 1468.0 m·s^{-1} and 1448.55 m·s^{-1}.

Measurement Results and Calculations

Speed of Sound and Density. The densities and speed-of-sound values obtained for the solutions of the transition-metal perchlorates in DMF over the whole composition range are collected in Tables 1 and 2. The concentration dependences of the density and speed of sound can be represented by the following polynomial:

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

where y denotes density d or speed of sound u. 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 the density or speed of sound in pure DMF.

Adiabatic Compressibility. The speeds of sound and densities were used to determine the adiabatic compressibility K_S using the Laplace's equation

$$K_S = \frac{1}{u^2 d} \tag{2}$$

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Table 1. Densities *d* of the Solutions of the Metal Perchlorates 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	m_s/ mol·kg^{-1}	283.15	293.15	298.15	303.15	313.15	323.15	333.15
								d/kg·m^{-3}							
								$Mn(ClO_4)_2$							
0.04109	966.326	956.852	952.107	947.355	937.821	928.242	918.616	0.2395	1007.028	997.690	993.019	988.351	978.996	969.623	960.225
0.05823	969.773	960.312	955.574	950.830	941.313	931.759	922.147	0.2793	1015.470	1006.156	1001.499	996.842	987.519	978.179	968.812
0.08396	974.960	965.520	960.793	956.059	946.568	937.040	927.465	0.3166	1023.515	1014.222	1009.579	1004.936	995.645	986.342	977.019
0.1024	978.695	969.265	964.546	959.822	950.346	940.834	931.273	0.3529	1031.377	1022.108	1017.477	1012.848	1003.585	994.313	985.025
0.1233	982.926	973.513	968.799	964.082	954.629	945.142	935.612	0.3885	1039.212	1029.963	1025.345	1020.732	1011.504	1002.274	993.029
0.1616	990.785	981.396	976.698	971.997	962.575	953.124	943.633	DMF	958.077	948.565	943.797	939.017	929.437	919.807	910.120
0.2007	998.895	989.531	984.846	980.162	970.768	961.357	951.918								
								$Co(ClO_4)_2$							
0.02921	964.275	954.785	950.026	945.273	935.722	926.127	916.489	0.1735	994.845	985.454	980.747	976.035	966.596	957.130	947.626
0.03591	965.673	956.190	951.432	946.682	937.135	927.546	917.907	0.2007	1000.797	991.403	986.700	981.997	972.578	963.135	953.661
0.05081	968.790	959.315	954.565	949.820	940.290	930.711	921.090	0.2305	1007.325	997.940	993.248	988.552	979.153	969.730	960.286
0.05902	970.508	961.035	956.290	951.550	942.021	932.457	922.843	0.2574	1013.279	1003.907	999.223	994.536	985.152	975.753	966.326
0.08863	976.733	967.283	962.549	957.809	948.308	938.770	929.181	0.2840	1019.218	1009.857	1005.180	1000.505	991.143	981.766	972.371
0.1167	982.692	973.255	968.530	963.801	954.319	944.808	935.256	DMF	958.163	948.653	943.884	939.114	929.529	919.900	910.200
0.1455	988.838	979.414	974.697	969.980	960.520	951.034	941.509								
								$Ni(ClO_4)_2$							
0.02709	963.872	954.383	949.635	944.864	935.312	925.725	916.070	0.1332	986.418	976.985	972.262	967.533	958.059	948.552	939.005
0.04050	966.705	957.208	952.461	947.700	938.159	928.568	918.935	0.1592	992.026	982.603	977.888	973.170	963.711	954.224	944.695
0.05400	969.549	960.073	955.329	950.578	941.045	931.471	921.848	0.1864	997.967	988.557	983.849	979.136	969.697	960.230	950.732
0.06810	972.550	963.083	958.342	953.590	944.072	934.511	924.900	0.2118	1003.544	994.141	989.440	984.736	975.313	965.882	956.405
0.08156	975.396	965.940	961.200	956.460	946.947	937.400	927.809	0.2613	1014.546	1005.163	1000.470	995.784	986.394	976.988	967.560
0.1073	980.845	971.397	966.666	961.935	952.463	942.934	933.366	DMF	958.163	948.653	943.884	939.114	929.529	919.900	910.200
								$Cu(ClO_4)_2$							
0.03620	965.762	956.275	951.520	946.762	937.212	927.620	917.988	0.2084	1003.160	993.739	989.024	984.309	974.859	965.385	955.869
0.04897	968.496	959.009	954.258	949.505	939.972	930.338	920.756	0.2431	1010.942	1001.532	996.825	992.116	982.686	973.233	963.750
0.06040	970.938	961.462	956.715	951.971	942.440	932.866	923.242	0.2746	1018.010	1008.700	1003.950	999.200	989.830	980.454	970.858
0.07815	974.714	965.248	960.507	955.758	946.236	936.666	927.060	0.3065	1025.385	1015.993	1011.298	1006.602	997.202	987.786	978.345
0.1060	980.752	971.295	966.549	961.812	952.315	942.780	933.198	0.3377	1032.616	1023.235	1018.540	1013.848	1004.456	995.056	985.638
0.1390	987.892	978.445	973.718	968.984	959.500	949.979	940.416	DMF	958.075	948.565	943.797	939.017	929.437	919.807	910.120
0.1737	995.495	986.058	981.338	976.613	967.148	957.653	948.120								
								$Zn(ClO_4)_2$							
0.03554	965.795	956.309	951.555	946.800	937.255	927.660	918.015	0.2038	1002.648	993.242	988.537	983.828	974.394	964.934	955.438
0.04966	968.825	959.347	954.600	949.850	940.315	930.737	921.108	0.2374	1010.265	1000.868	996.170	991.474	982.063	972.635	963.178
0.05952	970.955	961.484	956.740	951.990	942.460	932.889	923.268	0.2701	1017.772	1008.392	1003.703	999.008	989.616	980.208	970.777
0.06946	973.095	963.626	958.885	954.139	944.619	935.058	925.449	0.3002	1024.718	1015.347	1010.665	1005.982	996.605	987.212	977.794
0.1039	980.554	971.105	966.376	961.642	952.143	942.607	933.036	0.3314	1032.040	1022.680	1018.006	1013.326	1003.970	994.605	985.215
0.1369	987.781	978.348	973.626	968.900	959.426	949.918	940.371	DMF	958.163	948.653	943.884	939.114	929.529	919.900	910.200
0.1700	995.118	985.700	980.987	976.267	966.813	957.333	947.816								

It has been found that for all of the solutions investigated the plots of adiabatic compressibility K_S against concentration are not linear and the best description is obtained using the equation

$$K_S = B_0 + B_1 c^{1/2} + B_2 c \tag{3}$$

where $B_0 = 4.99 \times 10^{-10}$ N·m^{-2} is the adiabatic compressibility of pure DMF K_{S_0} at 298.15 K, calculated using the values of density and speed of sound reported in the present study. Coefficients B_1 and B_2 of the polynomials and values of the residual variance σ are given in Table 5. An inspection of the presented data shows that values of B_1 vary within relatively narrow limits whereas the values of B_2 are identical.

Apparent and Partial Quantities. The apparent molar volume Φ_V and the apparent molar isentropic compressibility, Φ_{K_S}, of the electrolyte solutions were calculated from equations

$$\Phi_S = \frac{d_0 - d}{m_s d d_0} + \frac{M_2}{d_0} \tag{4}$$

$$\Phi_{K_S} = \frac{K_S d_0 - K_{S_0} d}{m_s d d_0} + \frac{M_2 K_S}{d_0} \tag{5}$$

where m_s denotes the number of moles of solute per kilogram of solution (molonity); d and d_0 are densities of solution and solvent, respectively; and M_2 is the molar mass of the solute. The equations derived on the basis of concentration c or molality m have somewhat different forms. Equations 4 and 5 making use of molonity were preferred because the value of m_s is a direct experimental quantity of the solution. It seems to be obvious that the calculation of the concentration is possible using the equation $c = m_s d$.

The limiting apparent molar volumes Φ_V^0 and the limiting apparent molar isentropic compressibilities $\Phi_{K_S}^0$ were obtained by extrapolating the linear plots of Φ_V or Φ_{K_S} against the square root of the concentration to zero concentration using the equation

$$\Phi_y = \Phi_V^0 + S_y c^{1/2} \tag{6}$$

where $y = V$ or K_S. The parameters of the plots and their standard deviations are collected in Tables 6 and 7. The necessity of extrapolating of the data using the empirical Masson equation (eq 6) results from the lack of physical data for DMF required for calculating of the limiting slope involved in equations proposed on the basis of the Debye–Hückel equation.[9] It is not suprising that the derived coefficients of the Masson equation for the apparent molar volume at 298.15 K differ to some extent from the values reported previously.[4] The data reported in the present work are of much higher quality because of the essential progress in the density measurement. However, the sequence of values of the limiting apparent molar volumes of the divalent metal perchlorates

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

is the same irrespective of temperature and reflects the

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

salt	m_s / mol·kg^{-1}	u / m·s^{-1}	$10^{10}K_s$ / m^2·N^{-1}	$10^{13}\Phi_{K_S}$ / m^5·N^{-1}·mol^{-1}	m_s / mol·kg^{-1}	u / m·s^{-1}	$10^{10}K_s$ / m^2·N^{-1}	$10^{13}\Phi_{K_S}$ / m^5·N^{-1}·mol^{-1}
	0.04109	1460.80	4.922	−1.53	0.2395	1478.35	4.608	−1.36
$Mn(ClO_4)_2$	0.08396	1464.59	4.852	−1.48	0.2793	1481.93	4.547	−1.33
	0.1233	1468.17	4.789	−1.45	0.3166	1485.59	4.488	−1.32
	0.1616	1471.40	4.729	−1.42	0.3529	1488.90	4.433	−1.29
	0.2007	1475.01	4.667	−1.39	0.3885	1492.50	4.378	−1.28
	0.02921	1459.61	4.941	−1.58	0.1735	1471.04	4.712	−1.42
	0.05081	1461.38	4.906	−1.54	0.2007	1472.85	4.672	−1.39
$Co(ClO_4)_2$	0.05902	1462.09	4.892	−1.54	0.2305	1475.38	4.625	−1.37
	0.08863	1464.23	4.846	−1.48	0.2574	1477.55	4.584	−1.35
	0.1167	1466.53	4.801	−1.46	0.2840	1479.74	4.543	−1.34
	0.1455	1468.53	4.757	−1.42				
	0.0270	1459.61	4.943	−1.65	0.1332	1467.81	4.774	−1.46
	0.04050	1460.65	4.921	−1.60	0.1592	1469.96	4.733	−1.44
$Ni(ClO_4)_2$	0.05400	1461.74	4.899	−1.57	0.1864	1471.76	4.692	−1.41
	0.06810	1462.87	4.876	−1.55	0.2118	1473.57	4.654	−1.39
	0.08156	1463.88	4.855	−1.53	0.2613	1477.55	4.578	−1.36
	0.1073	1466.02	4.813	−1.50				
	0.03620	1459.96	4.931	−1.53	0.2084	1473.21	4.659	−1.38
	0.06040	1461.74	4.892	−1.50	0.2431	1475.74	4.606	−1.35
$Cu(ClO_4)_2$	0.07815	1463.16	4.863	−1.48	0.2746	1478.28	4.558	−1.33
	0.1060	1465.30	4.819	−1.46	0.3065	1480.83	4.509	−1.32
	0.1390	1467.81	4.767	−1.43	0.3377	1483.76	4.463	−1.30
	0.1737	1470.32	4.714	−1.40				
	0.03554	1459.91	4.931	−1.55	0.2038	1472.12	4.668	−1.37
	0.05952	1461.74	4.892	−1.52	0.2374	1474.65	4.616	−1.35
$Zn(ClO_4)_2$	0.06946	1462.45	4.876	−1.50	0.2701	1477.19	4.566	−1.33
	0.1039	1464.95	4.822	−1.46	0.3002	1479.74	4.519	−1.32
	0.1369	1467.45	4.770	−1.43	0.3314	1482.10	5.472	−1.30
	0.1700	1469.6	4.720	−1.40				

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

salt	T/K	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}	temp/K	A_0 / kg·m^{-3}	A_1 / (kg·m^{-3}·mol^{-1})$^{1/2}$	A_2 / kg·m^6·mol^{-1}	σ_d / kg·m^{-3}
	283.15	958.077	0.09 ± 0.02	0.197 ± 0.002	0.09	313.15	929.437	0.11 ± 0.01	0.204 ± 0.002	0.2
$Mn(ClO_4)_2$	293.15	948.565	0.10 ± 0.03	0.199 ± 0.002	0.1	323.15	919.807	0.12 ± 0.01	0.206 ± 0.002	0.2
	298.15	943.797	0.10 ± 0.02	0.200 ± 0.002	0.1	333.15	910.120	0.13 ± 0.03	0.209 ± 0.002	0.2
	303.15	939.017	0.11 ± 0.02	0.201 ± 0.002	0.1					
	283.15	958.163	0.06 ± 0.02	0.207 ± 0.001	0.06	313.15	929.529	0.08 ± 0.02	0.214 ± 0.002	0.07
$Co(ClO_4)_2$	293.15	948.653	0.07 ± 0.02	0.210 ± 0.002	0.07	323.15	919.900	0.09 ± 0.03	0.217 ± 0.002	0.08
	298.15	943.884	0.07 ± 0.02	0.211 ± 0.002	0.07	333.15	910.200	0.10 ± 0.03	0.220 ± 0.002	0.08
	303.15	939.114	0.07 ± 0.02	0.212 ± 0.002	0.07					
	283.15	958.163	0.07 ± 0.02	0.209 ± 0.002	0.05	313.15	929.529	0.09 ± 0.02	0.216 ± 0.002	0.06
$Ni(ClO_4)_2$	293.15	948.653	0.07 ± 0.02	0.211 ± 0.002	0.05	323.15	919.900	0.09 ± 0.02	0.218 ± 0.002	0.06
	298.15	943.884	0.08 ± 0.02	0.212 ± 0.002	0.05	333.15	910.200	0.10 ± 0.02	0.221 ± 0.002	0.06
	303.15	939.114	0.08 ± 0.02	0.213 ± 0.002	0.05					
	283.15	958.077	0.08 ± 0.02	0.210 ± 0.002	0.09	313.15	929.437	0.10 ± 0.01	0.216 ± 0.002	0.1
$Cu(ClO_4)_2$	293.15	948.565	0.09 ± 0.03	0.212 ± 0.002	0.09	323.15	919.807	0.11 ± 0.02	0.219 ± 0.002	0.2
	298.15	943.797	0.09 ± 0.02	0.213 ± 0.002	0.09	333.15	910.120	0.12 ± 0.03	0.221 ± 0.002	0.2
	303.15	939.017	0.09 ± 0.03	0.214 ± 0.002	0.09					
	283.15	958.163	0.07 ± 0.02	0.212 ± 0.002	0.07	313.15	929.529	0.09 ± 0.02	0.219 ± 0.002	0.08
$Zn(ClO_4)_2$	293.15	948.653	0.08 ± 0.02	0.214 ± 0.001	0.07	323.15	919.900	0.10 ± 0.02	0.221 ± 0.002	0.09
	298.15	943.884	0.08 ± 0.02	0.215 ± 0.002	0.08	333.15	910.200	0.11 ± 0.03	0.221± 0.002	0.1
	303.15	939.114	0.09 ± 0.03	0.216 ± 0.002	0.08					

effects related to the electronic structure and the ionic radii of metal cations. The highest values of the limiting partial molar volumes are obtained for $Mn(ClO_4)_2$, whereas the lowest are obtained for $Ni(ClO_4)_2$. It seems to be evident that the difference is related to the ligand-field stabilization effect. The lowest value observed for $Ni(ClO_4)_2$ is related to the high stability of the octahedral $Ni(DMF)_6^{2+}$ solvate resulting from the highest ligand-field stabilization typical for the $3d^8$ ion, which is absent for the $3d^5$ ion (i.e., for the $Mn(DMF)_6^{2+}$ solvate). The relatively high value of the

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

salt	10^2A_1 / (m^5·s^{-2}·m^{-1})$^{1/2}$	10^3A_2 / m^4·s^{-1}·mol^{-1}	σ_u / m·s^{-1}
$Mn(ClO_4)_2$	7 ± 2	85 ± 2	0.2
$Co(ClO_4)_2$	10 ± 4	73 ± 3	0.1
$Ni(ClO_4)_2$	16 ± 4	68 ± 3	0.2
$Cu(ClO_4)_2$	7 ± 2	73 ± 2	0.1
$Zn(ClO_4)_2$	8 ± 3	70 ± 3	0.2

Table 5. Coefficients of Equation 3 for the Adiabatic Compressibility of the Solutions of the Metal Perchlorates in DMF at 298.15 K and Their Standard Deviations σ

salt	$10^{13}B_1$ / $(m^7 \cdot N^{-2} \cdot mol^{-1})^{1/2}$	$10^{13}B_2$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{12}\sigma$ / $m^2 \cdot N^{-1}$
$Mn(ClO_4)_2$	-3.3 ± 0.9	-1.38 ± 0.06	0.4
$Co(ClO_4)_2$	-2.1 ± 0.6	-1.43 ± 0.05	0.3
$Ni(ClO_4)_2$	-2.8 ± 0.6	-1.41 ± 0.05	0.2
$Cu(ClO_4)_2$	-2.7 ± 0.8	-1.40 ± 0.05	0.3
$Zn(ClO_4)_2$	-2.7 ± 0.6	-1.40 ± 0.04	0.3

Table 6. Coefficients of Equation 6 for the Apparent Molar Volume of the Solutions of the Metals Perchlorates in DMF at Different Temperatures

salt	T/K	$10^6\Phi_V^0$ / $m^3 \cdot mol^{-1}$	10^7S_V / $(m^9 \cdot mol^{-3})^{1/2}$	$10^6\sigma$ / $m^3 \cdot mol^{-1}$	T/K	$10^6\Phi_V^0$ / $m^3 \cdot mol^{-1}$	10^7S_V / $(m^9 \cdot mol^{-3})^{1/2}$	$10^6\sigma$ / $m^3 \cdot mol^{-1}$
	283.15	45.1 ± 0.4	5.1 ± 0.3	0.2	313.15	35.1 ± 0.5	6.8 ± 0.4	0.3
Mn-$(ClO_4)_2$	293.15	42.1 ± 0.4	5.6 ± 0.3	0.2	323.15	31.2 ± 0.5	7.5 ± 0.4	0.3
	298.15	40.4 ± 0.5	5.9 ± 0.3	0.2	333.15	27.0 ± 0.6	8.2 ± 0.4	0.3
	303.15	38.6 ± 0.5	6.3 ± 0.4	0.3				
	283.15	40.0± 0.4	5.3 ± 0.4	0.2	313.15	30.2 ± 0.4	7.1 ± 0.4	0.2
Co-$(ClO_4)_2$	293.15	37.2± 0.3	5.8 ± 0.3	0.2	323.15	26.4 ± 0.4	7.7± 0.4	0.3
	298.15	35.7 ± 0.3	6.0 ± 0.3	0.2	333.15	21.3 ± 0.8	9.0 ± 0.7	0.4
	303.15	33.9± 0.4	6.4 ± 0.3	0.2				
	283.15	37.7 ± 0.4	5.8 ± 0.4	0.2	313.15	28.0 ± 0.4	7.5 ± 0.4	0.2
Ni-$(ClO_4)_2$	293.15	34.9 ± 0.5	6.2± 0.4	0.2	323.15	24.0 ± 0.7	8.3 ± 0.7	0.3
	298.15	33.0 ± 0.6	6.7 ± 0.5	0.3	333.15	19.1 ± 0.8	9.5 ± 0.8	0.4
	303.15	31.8 ± 0.4	6.7 ± 0.4	0.2				
	283.15	41.1 ± 0.4	5.3 ± 0.3	0.2	313.15	31.5 ± 0.5	7.1 ± 0.4	0.2
Cu-$(ClO_4)_2$	293.15	38.4 ± 0.3	5.6 ± 0.3	0.2	323.15	28.3 ± 0.7	7.4 ± 0.6	0.4
	298.15	36.9 ± 0.3	6.0 ± 0.3	0.2	333.15	23.5 ± 0.7	8.7 ± 0.5	0.3
	303.15	35.0 ± 0.4	6.5 ± 0.4	0.2				
	283.15	40.9 ± 0.4	5.2 ± 0.3	0.2	313.15	31.1 ± 0.6	7.0 ± 0.4	0.3
Zn-$(ClO_4)_2$	293.15	38.1 ± 0.4	5.7± 0.3	0.2	323.15	27.4 ± 0.5	7.6 ± 0.4	0.3
	298.15	36.4 ± 0.4	6.0 ± 0.3	0.2	333.15	22.7 ± 0.6	8.6 ± 0.5	0.3
	303.15	34.8± 0.4	6.3± 0.4	0.2				

Table 7. Coefficients of Equation 6 for the Apparent Molar Compressibility of the Solutions of the Metals Perchlorates in DMF at 298.15 K

salt	$10^{13}\Phi_{K_S}^0$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{15}S_{K_S}$ / $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{14}\sigma$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
$Mn(ClO_4)_2$	-1.65 ± 0.01	1.9 ± 0.1	0.04
$Co(ClO_4)_2$	-1.69 ± 0.02	2.1 ± 0.2	0.07
$Ni(ClO_4)_2$	-1.76 ± 0.02	2.6 ± 0.2	0.09
$Cu(ClO_4)_2$	-1.64 ± 0.01	1.8 ± 0.2	0.05
$Zn(ClO_4)_2$	-1.66 ± 0.02	2.0 ± 0.1	0.05

partial molar volume obtained for $Cu(ClO_4)_2$ may result from a tetragonal distortion of the octahedral complex due to the Jahn−Teller effect. The limiting apparent molar isentropic compressibilities are practically, within experimental error, constant and independent of the nature of the metal cation.

Volume Expansibility. The limiting values of the apparent molar volumes of the metal perchlorates against temperature are not linear, and the best description is obtained using equation

$$\Phi_V^0 = A_T + B_T(T/K - 298.15) + C_T(T/K - 298.15)^2 \quad (7)$$

The coefficients of eq 7 are listed in Table 8 along with the respective values of the residual variance. It is evident that the first of the coefficients can be considered to be the value of the limiting molar volume at 298.15 K.

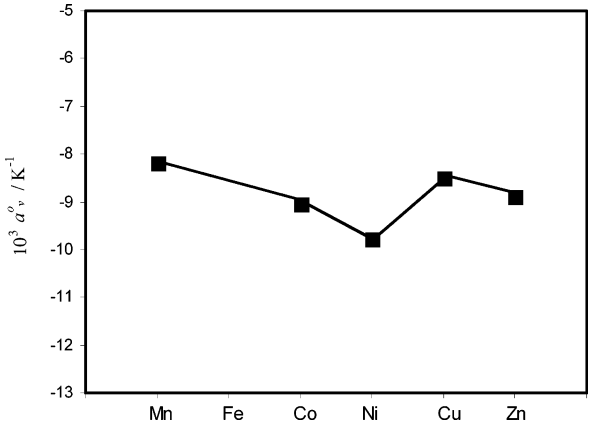

Figure 1. Volume expansibility for metal perchlorates in DMF at 298.15 K.

Table 8. Parameters of the Equation $\Phi_V^0 = A_T + B_T(T/K - 298.15) + C_T(T/K - 298.15)^2$ and the Volume Expansibility for Metal Perchlorates in DMF[a]

salt	10^6A_T / $m^3 \cdot mol^{-1}$	10^6B_T / $m^3 \cdot mol^{-1} \cdot K^{-1}$	10^6C_T / $m^3 \cdot mol^{-1} \cdot K^{-2}$	$10^6\sigma$ / $m^3 \cdot mol^{-1}$	$10^3\alpha_V^0$ / K^{-1}
$Mn(ClO_4)_2$	40.4 ± 0.5	-0.33 ± 0.01	-0.0014 ± 0.0003	0.1	-8.2 ± 0.3
$Co(ClO_4)_2$	35.7 ± 0.3	-0.32 ± 0.01	-0.0024 ± 0.0006	0.2	-9.0 ± 0.6
$Ni(ClO_4)_2$	33.0 ± 0.6	-0.32 ± 0.05	-0.0018 ± 0.0002	0.4	-10 ± 2
$Cu(ClO_4)_2$	36.9 ± 0.3	-0.31 ± 0.03	-0.002 ± 0.001	0.3	-8.4 ± 0.9
$Zn(ClO_4)_2$	36.4± 0.4	-0.32 ± 0.02	-0.0018 ± 0.0005	0.2	-8.9 ± 0.5

[a] Coefficient A_T is equal to $\Phi_{V,298}^0$.

The volume expansibilities, for the limiting values of the apparent molar volumes of the transition-metal perchlorates, defined by eq 8

$$\alpha_V^0 = \frac{(d\Phi_V^0/dT)_P}{\Phi_V^0} \quad (8)$$

and calculated using eq 7 are given in Table 8 and plotted against the number of 3d electrons in Figure 1. As is seen, once again the sequence

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

is observed. Moreover, it seems to be well established that the stability constants of the monohalide complexes of the divalent first-row transition-metal cations in water and some nonaqueous solvents, as well as some other properties of the solvated cations, follow this sequence.[10]

The distinct parallel between the presented properties of the studied salts, directly related to the nature of the metal cations, indictates that the essential factor responsible for the observed variation is the electronic structure of the metal cations and the ligand-field stabilization effect.

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