Thermodynamic Properties of Inorganic Salts in Nonaqueous Solvents. II. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Perchlorates in Acetonitrile

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The densities of divalent transition-metal perchlorates in acetonitrile have been measured at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K. From these densities, apparent molar volumes, V_Φ, and partial molar volumes of the salts at infinite dilution, V_Φ^0, as well as the expansibilities, α_V^0, have been evaluated. Moreover, the apparent molar isenotropic compressibility, $K_{S,\Phi}$, of transition-metal perchlorates in acetonitrile have been determined from a sound velocity measurement at $T = 298.15$ K.

Introduction

Divalent first-row transition-metal cations are known to form well-defined coordination forms in acetonitrile (AN) and exist as $M(AN)_6^{2+}$ solvates in the absence of coordinating anions.[1] Furthermore, it has been established that the volumetric properties of such solvates exibit variation, which can be interpreted in terms of ligand field theory.[2,3]

The present work is part of a more general study of the volumetric properties of nonaqueous solutions. The adiabatic compressibility, κ_S, is studied because of its sensitivity to electrostriction.

The apparent molar volume, V_Φ, of a solute 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

$$V_\Phi = \frac{V - n_1 V_1^{\,0}}{n_2} \tag{1}$$

where V denotes the volume of the solution, n_1 and n_2 are number of moles of solvent and salt, respectively, and V_1^0 is the molar volume of pure solvent. The adiabatic compressibility, defined by the thermodynamic relation

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{2}$$

where V is volume, P is pressure, and S is entropy and is related to density, d, and sound velocity, u, by the Laplace equation

$$\kappa_S = \frac{1}{u^2 d} \tag{3}$$

providing the link between thermodynamics and acoustics.

The limiting values of the apparent molar volumes of electrolytes and limiting molar adiabatic compressibilities provide direct information on ion−solvent interactions and, in the case of small divalent cations, V_Φ^0 and $K_{S,\Phi}^0$, are mainly produced by electrostriction and take large negative values.

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In this paper, experimental data at 298.15 K for the sound velocity and at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 323.15) K for the density for transition-metal perchlorates in acetonitrile solutions are reported. The apparent molar volume, V_Φ, adiabatic compressibility, κ_S, and apparent molar adiabatic compressibility, $K_{S,\Phi}$, are obtained from the measured properties.

Experimental Section

The solvated metal perchlorates were obtained from the corresponding hydrates by dissolving them in acetonitrile. The removal of any excess solvent as well as the products of dehydration under reduced pressure at elevated temperature followed this step. Crystalline solids were obtained on cooling. These were recrystallized at least twice from anhydrous solvents. Stock solutions were obtained by dissolving the solids in anhydrous solvents. 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 standard deviations were smaller than ±0.1%. Solutions for the density measurements were prepared by weighed dilutions of the corresponding stock solutions, and vacuum corrections were taken into account. All preparations and manipulations involving anhydrous materials were performed in dryboxes. Acetonitrile (Aldrich, $H_2O < 5 \times 10^{-3}$%) was dried with 4 Å molecular sieves.

The densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with a precision of 1.0×10^{-3} kg·m^{-3} and an uncertainty of 5.0×10^{-3} kg·m^{-3} for a single measurement. The instrument was equipped with a Peltier-type thermostating unit, and the temperature was kept constant at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K to an accuracy of 0.001 K according to the producer's declaration. The uncertainties in the density measurements and purity of the solvents were verified by measurements of their densities at 298.15 K. A density of (776.532 ± 0.007) kg·m^{-3} for acetonitrile was found, whereas the literature values[4,5] vary from 775.9 kg·m^{-3} to 776.85 kg·m^{-3}.

The sound velocities were measured using sound analyzer OPTIME 1.0 from Optel (Poland) with an uncertainty of 0.05 m·s^{-1} by measuring the time it takes for an ultrasound pulse to travel from one transducer to another

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Table 1. Densities of Pure Acetonitrile d_0 and Solutions d of Metal Perchlorates in Acetonitrile from T = 298.15 K to 323.15 K

	d/kg·m^{-3}						
m_S/mol·kg^{-1}	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	323.15 K
			$Mn(ClO_4)_2$				
0.1308	812.076	806.744	801.389	796.009	790.599	785.164	774.198
0.1732	820.267	814.947	809.604	804.238	798.846	793.424	782.485
0.2160	828.628	823.320	817.989	812.633	807.252	801.843	790.933
0.2570	836.778	831.471	826.148	820.803	815.431	810.032	799.145
0.2980	845.062	839.769	834.455	829.123	823.764	818.379	807.522
0.3364	852.972	847.683	842.377	837.051	831.700	826.326	815.497
0.3745	860.854	855.574	850.277	844.960	839.624	834.260	823.454
0.4122	868.750	863.479	858.191	852.884	847.554	842.203	831.418
AN	787.308	781.932	776.531	771.102	765.645	760.156	749.070
			$Co(ClO_4)_2$				
0.06311	799.771	794.418	789.050	783.653	778.228	772.771	761.760
0.1115	809.436	804.100	798.743	793.363	787.958	782.523	771.558
0.1477	816.764	811.440	806.094	800.726	795.334	789.913	778.975
0.1815	823.650	818.333	812.996	807.639	802.256	796.848	785.942
0.2169	831.031	825.723	820.399	815.051	809.685	804.289	793.420
0.2496	837.824	832.525	827.210	821.873	816.516	811.134	800.293
0.2829	844.904	839.613	834.306	828.983	823.636	818.267	807.451
0.3172	852.306	847.023	841.727	836.410	831.074	825.719	814.932
0.3491	859.240	853.965	848.675	843.372	838.048	832.702	821.940
AN	787.307	781.933	776.535	771.114	765.664	760.181	749.107
			$Ni(ClO_4)_2$				
0.04923	797.088	791.730	786.350	780.945	775.512	770.049	759.023
0.08198	803.621	798.268	792.896	787.511	782.087	776.641	765.646
0.1087	809.018	803.673	798.312	792.927	787.516	782.077	771.110
0.1350	814.360	809.021	803.671	798.291	792.889	787.460	776.511
0.1611	819.735	814.406	809.058	803.686	798.299	792.880	781.957
0.1844	824.540	819.217	813.878	808.519	803.134	797.731	786.838
0.2114	830.147	824.830	819.495	814.141	808.766	803.366	792.486
0.2353	835.248	829.938	824.608	819.261	813.893	808.502	797.637
0.2607	840.618	835.309	829.987	824.647	819.287	813.905	803.067
AN	787.307	781.930	776.530	771.101	765.645	760.155	749.068
			$Cu(ClO_4)_2$				
0.05724	798.765	793.409	788.030	782.624	777.190	771.728	760.698
0.1013	807.682	802.334	796.961	791.568	786.147	780.696	769.697
0.1335	814.263	808.919	803.556	798.170	792.754	787.314	776.342
0.1645	820.660	815.323	809.967	804.588	799.184	793.753	782.802
0.1975	827.568	822.238	816.887	811.516	806.117	800.692	789.754
0.2264	833.698	828.373	823.028	817.660	812.272	806.857	795.939
0.2580	840.493	835.168	829.828	824.467	819.083	813.673	802.774
0.2850	846.334	841.014	835.678	830.323	824.946	819.544	808.660
0.3172	853.453	848.137	842.806	837.456	832.084	826.687	815.817
AN	787.308	781.932	776.532	771.102	765.645	760.155	749.067
			$Zn(ClO_4)_2$				
0.05169	797.728	792.369	786.992	781.587	776.154	770.690	759.656
0.09336	806.167	800.821	795.456	790.063	784.645	779.192	768.190
0.1233	812.307	806.971	801.611	796.227	790.815	785.374	774.390
0.1524	818.329	812.997	807.644	802.268	796.864	791.433	780.466
0.1817	824.450	819.125	813.780	808.412	803.019	797.595	786.657
0.2106	830.536	825.218	819.877	814.514	809.128	803.712	792.788
0.2379	836.415	831.101	825.768	820.412	815.033	809.624	798.715
0.2668	842.682	837.373	832.046	826.696	821.325	815.925	805.037
0.2944	848.641	843.338	838.017	832.675	827.308	821.916	811.045
AN	787.312	781.934	776.535	771.106	765.649	760.158	749.070

(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, and the value of 1496.69 m·s^{-1} for the sound velocity in pure water has been used.[6] The value of 1278.28 m·s^{-1} obtained for the sound velocity in pure acetonitrile compares reasonably well with literature values,[7,8] 1277.03 m·s^{-1} and 1280.80 m·s^{-1}.

Results and Discussion

The density data obtained for the solutions of the transition-metal perchlorates are given in Table 1. The corresponding values of the apparent molar volumes, V_Φ, were calculated using the equation

$$V_\Phi = \frac{M_2}{d_0} - \frac{d - d_0}{m_S d d_0} \tag{4}$$

where m_S denotes the number of moles of solute per unit mass of solution (molonity); d and d_0 are the densities of solution and solvent, respectively; and M_2 is the molar mass of the solute.

Figure 1 shows the apparent molar volume plotted against the square root of concentration for manganese(II) perchlorate in acetonitrile solution at all measured temperatures. As seen, the plots are perfectly linear, and the Masson equation

$$V_\Phi = V_\Phi^0 + S_V c^{1/2} \tag{5}$$

where V_Φ^0 and S_V are the apparent molar volume of solute at infinite dilution and the slope, can be used. The same finding (i.e., linearity of the V_Φ vs $c^{1/2}$ plots) is observed for all perchlorates irrespective of temperature.

We know that the use of the purely empirical Masson equation for the extrapolation of apparent molar volume to infinite dilution is at best a crude approximation. The proper extrapolation methods and procedures have been discussed recently by Marcus and Hefter.[9] However, the

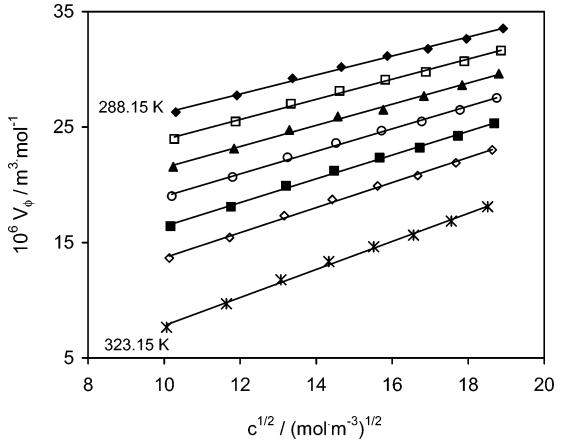

Figure 1. Apparent molar volumes V_Φ against the square root of molarity c of the $Mn(ClO_4)_2$ in acetonitrile solutions from T = 288.15 K to 323.15 K.

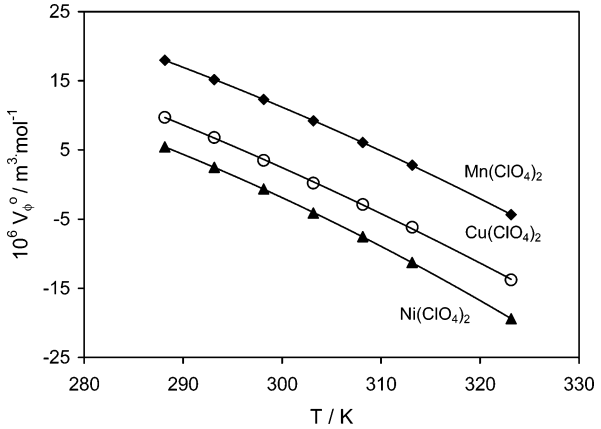

Figure 2. Limiting apparent molar volumes V_Φ^0 against temperature from T = 288.15 K to 323.15 K for the $Mn(ClO_4)_2$, $Cu(ClO_4)_2$, and $Ni(ClO_4)_2$ in acetonitrile solutions.

methods make use of the theoretical slope. The respective data required for calculating its value for acetonitrile are available at 298.15 K only.[10] The value of the pressure derivative of the relative permittivity of the solvent seems to be very sensitive to temperature. The observed differences amount to 20−30% for 298.15 and 303.15 K intervals,[10] whereas our data cover the temperature range from 288.15 to 323.15 K. Thus, we decided to fit our data to the simplest equation.

The respective coefficients of the Masson equation obtained at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K for the studied solutions of the metal perchlorates are listed in Table 2.

Previous studies[3] carried out in our laboratory dealt with solutions of metal perchlorates belonging to the Mn(II)−Zn(II) series in acetonitrile at T = (293.15 K, 298.15 K, and 303.15) K. We decided to reinvestigate the acetonitrile solutions because of serious improvement in our laboratory technique, manipulation of solution, and analytical procedures. Moreover, the temperature range is extended in the present work. It is not surprising that the differences are observed and the derived parameters of the Masson equation differ from the values reported previously. The greatest differences between actual and previously reported limiting values of apparent molar volumes for the metal perchlorates are observed for $Cu(ClO_4)_2$ and $Zn(ClO_4)_2$ and amount to 5.5×10^{-6} m^3·mol^{-1}. The results obtained for $Mn(ClO_4)_2$ are practically identical, whereas the differences observed for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ are smaller than 3.0×10^{-6} m^3·mol^{-1}. The formal analysis of the error propagation results in the uncertainty of the apparent molar volume amounting to 1.5×10^{-6} m^3·mol^{-1}.

Table 2. Masson Equation Parameters for Metal Perchlorates in Acetonitrile from T = 298.15 K to 323.15 K

salt	T / K	$10^6 V_\Phi^0$ / m^3·mol^{-1}	$10^6 S_V$ / (m^9·mol^{-3})$^{1/2}$	$10^6 \sigma$ / m^3·mol^{-1}
	288.15	18.0 ± 0.76	0.82 ± 0.052	0.16
	293.15	15.2 ± 0.79	0.87 ± 0.053	0.17
	298.15	12.3± 0.93	0.92 ± 0.064	0.20
$Mn(ClO_4)_2$	303.15	9.2 ± 0.80	0.98 ± 0.054	0.17
	308.15	6.1 ± 0.79	1.03 ± 0.053	0.17
	313.15	2.8 ± 0.84	1.09 ± 0.058	0.18
	323.15	−4.4 ± 1.00	1.22 ± 0.069	0.21
	288.15	7.6 ± 0.47	0.89 ± 0.033	0.12
	293.15	4.8 ± 0.47	0.93 ± 0.031	0.12
	298.15	1.6 ± 0.53	0.99 ± 0.035	0.14
$Co(ClO_4)_2$	303.15	−1.6 ± 0.51	1.04 ± 0.037	0.14
	308.15	−4.8 ± 0.53	1.09 ± 0.038	0.14
	313.15	−8.2 ± 0.51	1.14 ± 0.037	0.13
	323.15	−15.7 ± 0.50	1.25± 0.035	0.14
	288.15	5.4 ± 0.60	0.86 ± 0.052	0.16
	293.15	2.5 ± 0.71	0.92 ± 0.061	0.20
	298.15	−0.6 ± 0.77	0.97 ± 0.061	0.21
$Ni(ClO_4)_2$	303.15	−4.1 ± 0.71	1.04 ± 0.058	0.19
	308.15	−7.5 ± 0.77	1.10 ± 0.066	0.21
	313.15	−11.3 ± 0.79	1.17 ± 0.068	0.22
	323.15	−19.4 ± 0.91	1.32 ± 0.077	0.26
	288.15	9.7 ± 0.71	0.82 ± 0.054	0.20
	293.15	6.8 ± 0.74	0.88 ± 0.056	0.21
	298.15	3.5 ± 0.63	0.96 ± 0.047	0.18
$Cu(ClO_4)_2$	303.15	0.2 ± 0.67	1.02 ± 0.054	0.19
	308.15	−2.9 ± 0.89	1.06 ± 0.066	0.25
	313.15	−6.2 ± 0.79	1.11 ± 0.059	0.22
	323.15	−13.8 ± 0.79	1.25 ± 0.059	0.22
	288.15	9.2 ± 0.81	0.93 ± 0.064	0.23
	293.15	6.2 ± 0.80	0.99 ± 0.065	0.23
	298.15	3.0 ± 0.88	1.05 ± 0.069	0.25
$Zn(ClO_4)_2$	303.15	−0.4 ± 0.98	1.12 ± 0.077	0.28
	308.15	−4 ± 1.2	1.18 ± 0.085	0.30
	313.15	−8 ± 1.6	1.26 ± 0.090	0.33
	323.15	−15 ± 1.7	1.4 ± 0.12	0.38

An inspection of the data listed in Table 2 reveals that an increase in temperature causes a distinct decrease in the limiting apparent molar volumes of the metal perchlorates. This effect is presented in Figure 2 as the plots of the limiting values against temperature. The plots are not linear, and the best fit is obtained using equation

$$V_\Phi^0 = A_T + B_T(T/\mathrm{K} - 298.15) + C_T(T/\mathrm{K} - 298.15)^2 \quad (6)$$

Coefficients of eq 6 are listed in Table 3 along with the respective values of the residual variance. It is evident that the first of the coefficients in eq 6 is identical to $V_{\Phi,298}^0$ (i.e., to the value of the limiting molar volume of the salt at 298.15 K). The observed changes are related to the fact that the structure of the solvent is weakened by an elevation of temperature making the electrostriction effect higher.

Further discussion of the influence of temperature on the limiting values of the apparent molar volumes is possible in terms of a volume expansibility of limiting apparent molar volumes defined by eq 7

$$\alpha_V^0 = \frac{(\mathrm{d}V_\Phi^0/\mathrm{d}T)_P}{V_\Phi^0} \quad (7)$$

Table 3. Parameters of Equation 6 and Volume Expansibilities α_V^0 for Metal Perchlorates in Acetonitrile

salt	$10^6 A_T$ / $m^3 \cdot mol^{-1}$	$10^7 B_T$ / $m^3 \cdot mol^{-1}$	$10^9 C_T$ / $m^3 \cdot mol^{-1}$	$10^6 \sigma$ / $m^3 \cdot mol^{-1}$	$10^3 \alpha_V^o$ / K^{-1}
$Mn(ClO_4)_2$	12.3 ± 0.93	−5.95 ± 0.060	−2.8 ± 0.30	0.048	−48 ± 4.1
$Co(ClO_4)_2$	1.6 ± 0.53	−6.2 ± 0.25	−2.5 ± 0.11	0.15	−400 ± 15
$Ni(ClO_4)_2$	−0.6 ± 0.77	−6.5 ± 0.14	−4.2 ± 0.59	0.079	−1000 ± 1500
$Cu(ClO_4)_2$	3.5 ± 0.63	−6.3 ± 0.30	−2 ± 1.4	0.19	−180 ± 34
$Zn(ClO_4)_2$	3.0 ± 0.88	−6.6 ± 0.42	−2.5 ± 1.8	0.25	−220 ± 67

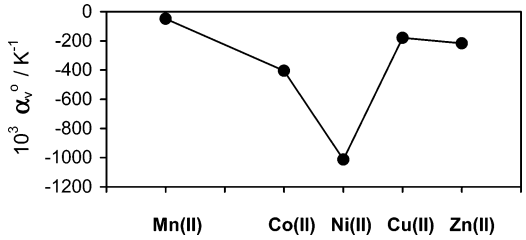

Figure 3. Variation of the volume expansibility α_V^0 for metal perchlorates in acetonitrile solutions at $T = 298.15$ K within the Mn(II)−Zn(II) series.

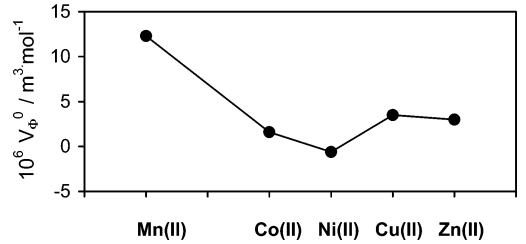

Figure 4. Limiting apparent molar volumes V_Φ^0 of the metal perchlorates in acetonitrile solutions at $T = 298.15$ K within the Mn(II)−Zn(II) series.

The respective values derived for 298.15 K using eqs 6 and 7 are listed in Table 3 and presented in Figure 3, demonstrating their variation within the manganese(II)−zinc(II) series (i.e., as a correlation with the number of 3d electrons), which may be considered to be a structural factor related to the electronic structure of the divalent transition-metal cations. An inspection of the graph shows that the values of the volume expansibility of the limiting apparent molar volumes vary in accordance with the sequence

$$Mn(II) > Co(II) > Ni(II) < Cu(II) > Zn(II)$$

which is known to be valid for some properties of the divalent transition-metal cations, hydrated as well as solvated.[2]

Figure 4 shows the respective variation of the limiting apparent molar volumes of the transition-metal perchlorates within the manganese(II)−zinc(II) series. An examination of Figure 4 and the data presented in Table 2 reveals that the same sequence is displayed irrespective of temperature. This observation indicates that the same structural factor related to the electronic structure of the $3d^n$ divalent cations is responsible for the differentiation of the properties of the metal perchlorates.

The experimental data for sound velocity obtained at 298.15 K are presented in Table 4. The apparent molar isentropic compressibility, $K_{S,\Phi}$, for metal perchlorates in acetonitrile solution was calculated according to

$$K_{S,\Phi} = \frac{\kappa_S d_0 - \kappa_{S,0} d}{m_S d d_0} + \frac{M_2 \kappa_{S,0}}{d_0} \quad (8)$$

where M_2 is the molecular mass of the salt, m_S denotes a number of moles of the solute per kilogram of solution (molonity); and d and d_0 are the densities of solution and solvent, respectively. The terms κ_S and $\kappa_{S,0}$ in eq 8 refer to the adiabatic compressibility of the solution and the solvent, respectively, calculated using eq 3. The obtained values of κ_S and $K_{S,\Phi}$ are shown in Table 4. An inspection of the presented data shows that an increase in concentration brings an increase in the adiabatic compressibility of the studied solutions and equation

$$K_{S,\Phi} = K_{S,\Phi}^0 + S_{K_S} c^{1/2} \quad (9)$$

Table 4. Ultrasonic Velocity u, Adiabatic Compressibility κ_S, and Apparent Molar Compressibility $K_{S,\Phi}$ for Metal Perchlorates in Acetonitrile Solutions at $T = 298.15$ K

salt	m_S / $mol \cdot kg^{-1}$	u / $m \cdot s^{-1}$	$10^{10} \kappa_S$ / $m^2 \cdot N^{-1}$	$10^{13} K_{S,\Phi}$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
$Mn(ClO_4)_2$	0.07666	1282.84	7.682	−3.142
	0.08738	1283.47	7.654	−3.131
	0.1308	1286.00	7.545	−3.033
	0.1732	1288.42	7.441	−2.959
	0.2160	1290.82	7.337	−2.884
	0.2570	1293.05	7.240	−2.818
	0.2980	1295.35	7.142	−2.759
	0.3364	1297.89	7.047	−2.724
	0.3745	1300.30	6.956	−2.680
	0.4122	1302.69	6.866	−2.635
$Co(ClO_4)_2$	0.06311	1282.38	7.706	−3.440
	0.1115	1285.12	7.581	−3.288
	0.1477	1287.04	7.489	−3.195
	0.1815	1288.98	7.403	−3.131
	0.2169	1290.74	7.316	−3.058
	0.2496	1292.58	7.236	−3.002
	0.2829	1294.53	7.152	−2.955
	0.3172	1296.40	7.069	−2.903
	0.3491	1298.21	6.991	−2.858
$Ni(ClO_4)_2$	0.04923	1281.81	7.740	−3.607
	0.08198	1284.05	7.649	−3.508
	0.1087	1285.82	7.576	−3.446
	0.1350	1287.53	7.506	−3.390
	0.1611	1289.38	7.435	−3.343
	0.1844	1290.89	7.373	−3.296
	0.2114	1292.70	7.302	−3.245
	0.2353	1294.14	7.241	−3.200
	0.2607	1295.85	7.175	−3.156
$Cu(ClO_4)_2$	0.05724	1281.63	7.726	−3.371
	0.1013	1284.29	7.607	−3.293
	0.1335	1286.22	7.522	−3.238
	0.1645	1288.15	7.437	−3.182
	0.1975	1289.99	7.356	−3.126
	0.2264	1291.75	7.282	−3.087
	0.2580	1293.72	7.200	−3.046
	0.2850	1295.37	7.131	−3.005
	0.3172	1297.32	7.050	−2.962
$Zn(ClO_4)_2$	0.05169	1280.24	7.753	−3.087
	0.09336	1281.89	7.650	−3.011
	0.1233	1283.07	7.578	−2.963
	0.1524	1284.25	7.507	−2.920
	0.1817	1285.44	7.437	−2.880
	0.2106	1286.77	7.366	−2.848
	0.2379	1287.87	7.301	−2.812
	0.2668	1288.98	7.234	−2.771
	0.2944	1290.34	7.167	−2.742

Table 5. Parameters of Equation 9 and Mean Deviations σ for Metal Perchlorates in Acetonitrile Solutions at T = 298.15 K

salt	$10^{13}K^{o}_{S,\Phi}$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{15}S_{K_S}$ / $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{14}\sigma$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
$Mn(ClO_4)_2$	−3.51 ± 0.025	4.7 ± 0.16	0.078
$Co(ClO_4)_2$	−3.83 ± 0.035	5.7 ± 0.25	0.096
$Ni(ClO_4)_2$	−3.94 ± 0.019	5.3 ± 0.17	0.046
$Cu(ClO_4)_2$	−3.68 ± 0.032	4.3 ± 0.24	0.082
$Zn(ClO_4)_2$	−3.35 ± 0.049	3.9 ± 0.39	0.14

Table 6. Parameters of Equation 10 for Speed of Sound u (and Mean Deviations σ) for Metal Perchlorates in Acetonitrile Solutions at T = 298.15 K

salt	10^2A_1 / $(m^5 \cdot s^{-2} \cdot mol^{-1})^{1/2}$	10^3A_2 / $m^4 \cdot s^{-1} \cdot mol^{-1}$	σ / $m \cdot s^{-1}$
$Mn(ClO_4)_2$	9 ± 4.1	864± 2.7	0.15
$Co(ClO_4)_2$	19 ± 2.3	56 ± 4.0	0.070
$Ni(ClO_4)_2$	13 ± 4.5	72.5 ± 3.4	0.11
$Cu(ClO_4)_2$	6 ± 2.6	68 ± 1.9	0.070
$Zn(ClO_4)_2$	0 ± 2.5	48.5 ± 1.8	0.066

which is analogous to the Masson equation, where $K^0_{S,\Phi}$ and S_{K_S} are the apparent molar adiabatic compressibility of the solute at infinite dilution and the slope, satisfactorily describes the concentration dependence. The coefficients of eq 9, their standard deviations, and the respective values of the residual variance, σ, are given in Table 5. The negative values of $K_{S,\Phi}$ and $K^0_{S,\Phi}$ are indication of the more close-packed structure of solution than that of pure solvent.

The concentration dependences of the speed of sound, density, and adiabatic compressibility of solution can be represented by polynomials using molar concentration c ($mol \cdot m^{-3}$)

$$y = A_0 + A_1 c^{1/2} + A_2 c \qquad (10)$$

where y denotes the speed of sound in solution (then A_0 is the speed of sound in pure solvent) or the density of solution (then A_0 is the density of the pure solvent) or the adiabatic compressibility (then A_0 is the adiabatic compressibility of the pure solvent). The coefficients of the polynomials, their standard deviations, and the respective values of the residual variance, σ, are given in Tables 6 to 8. The variation related to the electronic nature of the cations is observed for the volume expansibility and limiting apparent molar isentropic compressibility of the transition-metal perchlorates in acetonitrile as well as in DMF solutions.[11] However, the absolute values of the volume expansibility of the metal perchlorates in acetonitrile solutions are higher than the respective values for DMF solutions. This is probably due to the relatively high isobaric expansibility of this solvent, amounting to 1.38×10^{-3} K^{-1}, whereas the corresponding value for *N*,*N*-dimethylformamide[10] is 1.00×10^{-3} K^{-1}. Moreover, more negative values of $K^0_{S,\Phi}$ observed for acetonitrile solutions indicate the existence of strong effects due to cation solvation. To extract quantitative information concerning the tendency of the transition-metal cations to produce structural or solvation effects, the values of $K^0_{S,\Phi}$ obtained for the salts are split into the respective ionic contributions; the relation

$$K^0_{S,\Phi}(M^{2+}) = K^0_{S,\Phi}(M(ClO_4)_2) - 2K^0_{S,\Phi}(ClO_4^-) \qquad (11)$$

was used. The literature value of $-0.25 \times 10^{-13} m^5(N \cdot mol)^{-1}$ for the limiting apparent molar isentropic compressibility for the perchlorate ion[8] was employed in the calculation. Resulting values of the limiting apparent molar isentropic compressibility of metal ions are presented in Table 9 and Figure 5. An inspection of the presented data shows that the $K^0_{S,\Phi}(M^{2+})$ values are negative, indicating the strong effect related to the solvation effect. The presented variation of the limiting apparent molar isentropic compressibility within the manganese(II)−zinc(II) series corresponds to the sequence

$$Mn(II) > Co(II) > Ni(II) < Cu(II) < Zn(II)$$

The above series is close to the sequence observed for the limiting apparent molar volumes of the metal perchlorates as well as for their isobaric expansibilities.

Table 7. Parameters of Equation 10 for Density d (and Mean Deviations σ) for Metal Perchlorates in Acetonitrile Solutions from T = 298.15 K to 323.15K

salt	T / K	d_o / $kg \cdot m^{-3}$	A_1 / $(kg^2 \cdot m^{-3} \cdot mol^{-1})^{1/2}$	A_2 / $kg \cdot mol^{-1}$	σ / $kg \cdot m^{-3}$
	288.15	787.308	0.14 ± 0.028	0.220 ± 0.0019	0.073
	293.15	781.932	0.15 ± 0.030	0.222 ± 0.0021	0.075
	298.15	776.531	0.15 ± 0.032	0.223 ± 0.0018	0.077
$Mn(ClO_4)_2$	303.15	771.102	0.16 ± 0.030	0.224 ± 0.0023	0.080
	308.15	765.645	0.17 ± 0.033	0.226 ± 0.0021	0.083
	313.15	760.156	0.17 ± 0.034	0.227 ± 0.0022	0.085
	323.15	749.070	0.19 ± 0.035	0.230 ± 0.0026	0.091
	288.15	787.307	0.11 ± 0.034	0.234 ± 0.0025	0.091
	293.15	781.933	0.12 ± 0.034	0.235 ± 0.0023	0.095
	298.15	776.535	0.12 ± 0.036	0.237 ± 0.0026	0.097
$Co(ClO_4)_2$	303.15	771.114	0.13 ± 0.037	0.238 ± 0.0027	0.10
	308.15	765.664	0.13 ± 0.039	0.240 ± 0.0025	0.11
	313.15	760.181	0.14 ± 0.040	0.242 ± 0.0027	0.11
	323.15	749.107	0.15 ± 0.043	0.246 ± 0.0032	0.12
	288.15	787.307	0.08 ± 0.023	0.238 ± 0.0018	0.056
	293.15	781.930	0.08 ± 0.027	0.240 ± 0.0021	0.058
	298.15	776.530	0.09 ± 0.026	0.241 ± 0.0023	0.061
$Ni(ClO_4)_2$	303.15	771.101	0.09 ± 0.028	0.243 ± 0.0021	0.061
	308.15	765.645	0.10 ± 0.030	0.245 ± 0.0023	0.065
	313.15	760.155	0.10 ± 0.028	0.247 ± 0.0025	0.067
	323.15	749.068	0.11 ± 0.030	0.251 ± 0.0028	0.073
	288.15 K	787.308	0.09 ± 0.022	0.239 ± 0.0015	0.055
	293.15 K	781.932	0.10 ± 0.023	0.240 ± 0.0018	0.058
	298.15 K	776.532	0.10 ± 0.023	0.242 ± 0.0017	0.061
$Cu(ClO_4)_2$	303.15 K	771.102	0.11 ± 0.025	0.243 ± 0.0021	0.063
	308.15 K	765.645	0.11 ± 0.026	0.245 ± 0.0018	0.066
	313.15 K	760.155	0.12 ± 0.027	0.247 ± 0.0021	0.069
	323.15 K	749.067	0.13 ± 0.028	0.250 ± 0.0022	0.077
	288.15 K	787.312	0.10 ± 0.029	0.240 ± 0.0021	0.069
	293.15 K	781.934	0.10 ± 0.027	0.241 ± 0.0023	0.072
	298.15 K	776.535	0.105 ± 0.027	0.243 ± 0.0021	0.073
$Zn(ClO_4)_2$	303.15 K	771.106	0.11 ± 0.028	0.2445 ± 0.0021	0.075
	308.15 K	765.649	0.115 ± 0.029	0.246 ± 0.0024	0.078
	313.15 K	760.158	0.12 ± 0.030	0.248 ± 0.0024	0.080
	323.15 K	749.070	0.13 ± 0.033	0.2515 ± 0.0025	0.085

Table 8. Parameters of Equation 10 for Adiabatic Compressibility κ_S (and Mean Deviations σ) for Metal Perchlorates in Acetonitrile Solutions at T = 298.15 K

salt	$10^{13}A_1$ / $(m^7 \cdot N^{-2} \cdot mol^{-1})^{1/2}$	$10^{13}A_2$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{13}\sigma$ / $m^2 \cdot N^{-1}$
$Mn(ClO_4)_2$	−7 ± 2.0	−2.5 ± 0.13	7.1
$Co(ClO_4)_2$	−8 ± 2.1	−2.6 ± 0.16	5.6
$Ni(ClO_4)_2$	−5.5 ± 1.8	−2.9 ± 0.15	4.6
$Cu(ClO_4)_2$	−5.5 ± 2.0	−2.8 ± 0.15	5.5
$Zn(ClO_4)_2$	−4 ± 1.6	−2.6 ± 0.16	4.0

Table 9. Limiting Molar Ionic Adiabatic Compressibility $K^0_{S,\Phi}$(ion) in Acetonitrile Solution at T = 298.15 K

ion:	ClO_4^-	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$10^{13}K_{S,\Phi}{}^0/m^5 \cdot N^{-1} \cdot mol^{-1}$	−0.25	−3.01	−3.33	−3.44	−3.18	−2.85

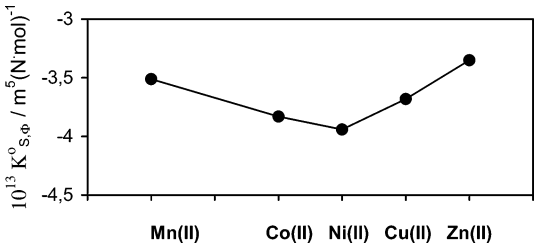

Figure 5. Limiting apparent molar compressibility $K^{o}_{S,\Phi}$ of the metal perchlorates in acetonitrile solutions at $T = 298.15$ K within the Mn(II)−Zn(II) series.

The presented observations suggest that the structural factor controlling the properties of the divalent transition-metal cations are related to the ligand field stabilization effect resulting in a particular position of the Ni^{2+} cation exhibiting the highest ability to form an octahedral structure, whereas the highest values of the limiting apparent molar isentropic compressibilities are observed for Mn^{2+} and Zn^{2+} solvates for which the ligand field stabilization effect is absent.

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