Thermodynamic Properties of Inorganic Salts in Nonaqeous Solvents. IV. Apparent Molar Volumes and Compressibilities of Divalent Transition-Metal Bromides and Chlorides in Acetonitrile

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The densities of divalent transition-metal bromides and chlorides in acetonitrile at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K and sound velocities at 298.15 K have been measured. From these data, apparent molar volumes V_Φ at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K and the apparent molar isentropic compressibility $K_{S,\Phi}$ at $T = 298.15$ K of transition-metal bromides and chloride in acetonitrile have been determined.

Introduction

This study is a part of an investigation of the volumetric properties of nonaqueous solutions.[1−3] Divalent first-row transition-metal cations are known to form well-defined coordination forms in acetonitrile (AN) and to exist as $M(AN)_6^{2+}$ solvates in the absence of coordinating anions.[4] It has been established that the volumetric properties of such solvates exhibit variation, which can be interpreted in terms of ligand field theory.[5,6] Unlike perchlorates, the divalent transition-metal bromides and chlorides dissolved in acetonitrile exhibit a variety of electrolytic behaviors due to a more complicated system of complex formation equilibria. Acetonitrile solutions of $CoBr_2$ have been investigated spectrophotometrically,[7−9] and these studies have yielded good evidence for the existence of two pseudotetrahedral species, $[CoBr_2(CH_3CN)_2]$ and $[CoBr_3(CH_3CN)]^-$. In the case of $MnBr_2$ acetonitrile solutions, ions form the $[Mn(CH_3CN)_6]^{2+}\cdot 2[MnBr_3(CH_3CN)]^-$ (disproportionation) cation and anion complex. The most characteristic feature of the acetonitrile solutions of $ZnBr_2$ is the existence of electrically neutral tetrahedral complexes of $ZnBr_2(CH_3CN)_2$.

The dissolution of anhydrous cobalt(II) chloride in acetonitrile is accompanied by two reactions[10]

$$CoCl_2 + 2CH_3CN = [CoCl_2(CH_3CN)_2]$$

and

$$3CoCl_2 + 8CH_3CN = [Co(CH_3CN)_6]^{2+} + 2[CoCl_3(CH_3CN)]^-$$

Consequently, in the solution, the following equilibrium establishes (with an equilibrium constant of ca. $5\cdot 10^{-3}$)

$$3[CoCl_2(CH_3CN)_2] + 2CH_3CN = [Co(CH_3CN)_6]^{2+} + 2[CoCl_3(CH_3CN)]^-$$

Coordination properties of cobalt(II) and zinc(II) are known to be rather similar, and the equilibrium

$$3[ZnCl_2(CH_3CN)_2] + 2CH_3CN = [Zn(CH_3CN)_6]^{2+} + 2[ZnCl_3(CH_3CN)]^-$$

was found to be responsible for the electrical conductivity of $ZnCl_2$ in acetonitrile. However, the extreme stability of tetrahedral complexes of zinc(II) appears to be amenable for the existence of the neutral $[ZnCl_2(CH_3CN)_2]$ complexes in solution in the presence of a small amount of the $[Zn(CH_3CN)_6]^{2+}$ and $[ZnCl_3(CH_3CN)]^-$ complex electrolyte.

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

$$V_\Phi = (V - n_0V_0^{\,0})/n_S \tag{1}$$

where V denotes the volume of the solution; n_0 and n_S are the number of moles of the solvent and salt, respectively; and $V_0^{\,0}$ is the molar volume of pure solvent. The adiabatic compressibility, defined by the thermodynamic relation

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

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

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

providing the link between thermodynamics and acoustics.

In this paper, experimental data at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, and 323.15) K for density of $MnBr_2$, $CoBr_2$, $ZnBr_2$, $CoCl_2$, and $ZnCl_2$ and data at 298.15 K for sound velocity of studied bromides and cobalt(II) chloride 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 anhydrous $CoBr_2$, $MnBr_2$, $ZnBr_2$, $CoCl_2$, and $ZnCl_2$ were prepared from the corresponding hydrates by drying under a vacuum initially at 353 K and then at 423 K. These were recrystallized at least twice from anhydrous acetonitrile. The stock solutions were obtained by dissolution of the solids in

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Table 1. Densities of the Pure Acetonitrile, d_0, and the Solutions, d, of the Metal Halides in Acetonitrile at Different Temperatures

	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
				$MnBr_2$			
0.04150	793.652	788.260	782.850	777.408	771.942	766.441	755.330
0.05130	795.156	789.764	784.353	778.907	773.433	767.926	756.805
0.06115	796.676	791.280	785.862	780.415	774.941	769.432	758.311
0.07131	798.243	792.850	787.428	781.978	776.494	770.984	759.855
0.08138	799.819	794.414	788.989	783.537	778.054	772.539	761.403
0.09054	801.238	795.840	790.408	784.953	779.461	773.940	762.804
0.1006	802.824	797.413	791.982	786.518	781.030	775.513	764.368
0.1214	806.091	800.671	795.230	789.765	784.269	778744	767.585
0.1406	809.125	803.696	798.249	792.776	787.272	781.741	770.567
0.1603	812.287	806.853	801.398	795.916	790.407	784.868	773.687
0.1712	814.024	808.580	803.121	797.634	792.128	786.584	775.396
0.1804	815.501	810.054	804.590	799.110	793.589	788.041	776.847
0.1995	818.585	813.117	807.642	802.149	796.622	791.065	779.856
AN	787.299	781.923	776.525	771.097	765.640	760.148	749.055
				$CoBr_2$			
0.06384	797.529	792.118	786.677	781.218	775.720	770.192	759.026
0.08092	800.300	794.880	789.432	783.966	778.458	772.920	761.738
0.09698	802.926	797.495	792.044	786.563	781.049	775.500	764.302
0.1125	805.465	800.033	794.565	789.080	783.570	778.020	766.801
0.1286	808.142	802.700	797.232	791.742	786.222	780.656	769.421
0.1428	810.505	805.061	799.583	794.089	788.550	782.985	771.734
0.1587	813.161	807.703	802.224	796.713	791.168	785.595	774.335
0.1900	818.466	812.988	807.489	801.964	796.411	790.822	779.533
0.2204	823.615	818.130	812.623	807.083	801.513	795.917	784.593
0.2527	829.214	823.715	818.194	812.642	807.057	801.450	790.088
0.2636	831.140	825.637	820.113	814.557	808.967	803.340	791.988
0.2777	833.591	828.085	822.557	816.995	811.404	805.778	794.405
0.3089	839.134	833.612	828.072	822.494	816.889	811.253	799.854
AN	787.315	781.939	776.538	771.112	765.653	760.164	749.073
				$ZnBr_2$			
0.03209	792.171	786.781	781.365	775.922	770.453	764.950	753.836
0.04040	793.435	788.040	782.622	777.179	771.701	766.197	755.075
0.04717	794.467	789.072	783.650	778.202	772.724	767.215	756.090
0.05609	795.839	790.436	785.044	779.559	774.080	768.567	757.437
0.06324	796.938	791.534	786.108	780.651	775.170	769.655	758.516
0.07124	798.167	792.766	787.332	781.876	776.393	770.874	759.730
0.07952	799.446	794.033	788.597	783.143	777.651	772.126	760.980
0.09524	801.876	796.466	791.020	785.546	780.047	774.520	763.359
0.1099	804.162	798.743	793.295	787.860	782.357	776.822	765.649
0.1252	806.567	801.138	795.677	790.202	784.687	779.149	767.969
0.1317	807.593	802.157	796.698	791. 221	785.702	780.162	768.971
0.1402	808.922	803.487	798.026	792.539	787.024	781.476	770.273
AN	787.313	781.935	776.535	771.106	765.650	760.159	749.070
				$CoCl_2$			
0.08764	795.418	790.014	784.590	779.137	773.654	768.139	756.997
0.1171	798.185	792.779	787.348	781.889	776.401	770.881	759.736
0.1460	800.890	795.475	790.038	784.571	779.078	773.545	762.939
0.1743	803.599	798.184	792.742	787.274	781.773	776.240	765.073
0.2031	806.356	800.934	795.487	790.011	784.510	778.973	767.796
0.2318	809.121	803.697	798.244	792.763	787.256	781.714	770.528
0.2600	811.836	806.407	800.953	795.467	789.954	784.407	773.206
0.2873	814.493	809.058	803.595	798.109	792.590	787.039	775.843
AN	787.297	781.919	776.518	771.090	765.631	760.142	749.056
				$ZnCl_2$			
0.05257	791.935	786.551	781.150	775.724	770.266	764.781	753.694
0.06571	793.095	787.712	782.313	776.886	771.431	765.940	754.859
0.07576	794.000	788.618	783.217	777.790	772.330	766.841	755.760
0.08438	794.764	789.380	783.985	778.553	773.096	767.607	756.526
0.1077	796.850	791.469	786.068	780.640	775.184	769.697	758.618
0.1280	798.676	793.289	787.887	782.455	777.003	771.516	760.435
0.1487	800.536	795.155	789.746	784.317	778.858	773.372	762.295
0.1684	802.335	796.955	791.541	786.115	780.661	775.165	764.103
0.1902	804.302	798.922	793.519	788.091	782.635	777.148	766.072
0.2114	806.244	800.862	795.456	790.032	784.575	779.089	768.014
AN	787.303	781.922	776.522	771.095	765.637	760.151	749.071

anhydrous solvent. The stock solutions of the metal halides were prepared and analyzed for the respective metals by standard EDTA titration. At least ten determinations were performed in each case, and the relative standard deviations were smaller than $\pm$ 0.1 %. Solutions for the density measurements were prepared by weighed dilutions of the corresponding stock solutions, and the vacuum corrections were taken into account. All the preparations and manipulations involving anhydrous materials

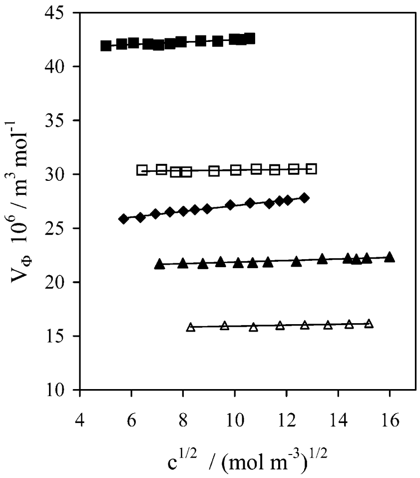

Figure 1. Apparent molar volumes, V_Φ, against the square root of molarity, c, in acetonitrile solutions at 298.15 K of: ◆, $MnBr_2$; ▲, $CoBr_2$; ■, $ZnBr_2$; △, $CoCl_2$; and □, $ZnCl_2$.

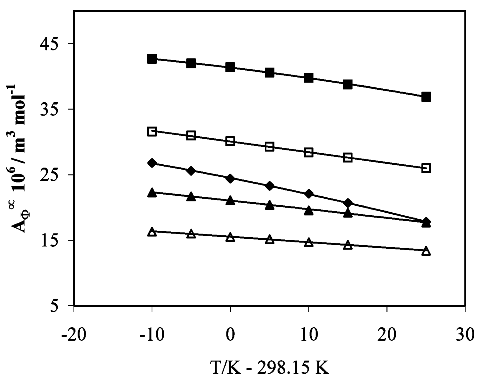

Figure 2. Values of the coefficient of eq 5, A_Φ^∞, against temperature from T = (288.15 to 323.15) K in acetonitrile solutions for: ◆, $MnBr_2$; ▲, $CoBr_2$; ■, $ZnBr_2$; △, $CoCl_2$; and □, $ZnCl_2$.

were performed in dryboxes. Acetonitrile (Aldrich, H_2O < $5 \cdot 10^{-3}$ %) was dried with 4A molecular sieves.

The densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with a precision of $1.0 \cdot 10^{-3}$ kg·m^{-3} and uncertainties of $5.0 \cdot 10^{-3}$ kg·m^{-3} for a single measurement. The instrument was equipped with the 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 with uncertainties ± 0.001 K. The uncertainties of the density measurements and purity of the solvents were verified by measurements of their densities at 298.15 K. The density value of (776.532 ± 0.007) kg·m^{-3} for acetonitrile was found, whereas the literature values[11,12] vary from 775.9 kg·m^{-3} to 776.85 kg·m^{-3}.

The sound velocities were measured using the sound analyzer OPTIME 1.0 from Optel (Poland) with a precision of 0.05 m·s^{-1} by measuring the time it takes for a pulse of ultrasound to travel from one transducer to another (*pitch-catch*) or to return to the same transducer (*pulse-echo*). The cell was thermostated at (298.15 ± 0.005) K and calibrated with double distilled water, and the value of 1496.69 m·s^{-1} for the sound velocity in pure water has been used.[13] A value of 1278.28 m·s^{-1} obtained for sound velocity in pure acetonitrile compares reasonably well with literature values,[14] 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 bromides and chlorides are given in Table 1. The corresponding values of the apparent molar volumes, V_Φ/m^3·mol^{-1}, were calculated using the equation

$$V_\Phi = M/d_0 - (d - d_0)/(m_S d d_0) \tag{4}$$

where m_S/mol·kg^{-1} denotes the number of moles of the solute per kilogram of the solution (molonity (m_S), $m_S \cdot d$ is equal to the molarity, c/mol·m^{-3}); d/kg·m^{-3} and d_0/kg·m^{-3} are the densities of the solution and the solvent, respectively; and M/kg·mol^{-1} is the molar mass of the solute.

Figure 1 shows the apparent molar volume plotted against the square root of concentration for $MnBr_2$, $CoBr_2$, $ZnBr_2$, $CoCl_2$, and $ZnCl_2$ in acetonitrile solution at 298.15 K. As seen, the plots are linear and the equation

$$V_\Phi = A_\Phi^\infty + A_\Phi^S \cdot c^{1/2} \tag{5}$$

is valid. The same finding, i.e., linearity of the V_Φ vs $c^{1/2}$ plots, is observed for all bromides and chlorides irrespective of temperature. Moreover, the values of the apparent molar volume for $ZnBr_2$ are much higher than for other studied bromides, due to the ability of the Zn(II) ion to form the tetrahedral and neutral complexes, caused by the smallest effect of electrostriction in the solution of $ZnBr_2$.

The respective coefficients of eq 5, A_Φ^∞ and A_Φ^S, 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 bromides and chlorides are listed in Table 2.

Inspection of the data listed in Table 2 reveals that an increase in temperature causes a distinct decrease in the values of coefficients of eq 5, A_Φ^∞, of the metal bromides and chlorides.

Table 2. Parameters of Equation 5 for Metal Bromides and Chlorides in Acetonitrile at Different Temperatures

salt		$A_\Phi^\infty \cdot 10^6$ m^3·mol^{-1}	$A_\Phi \cdot 10^6$ (m^9·mol^{-3})$^{1/2}$	$\sigma \cdot 10^6$ m^3·mol^{-1}
	288.15 K	26.8 ± 0.43	0.21 ± 0.035	0.12
	293.15 K	25.6 ± 0.29	0.24 ± 0.022	0.072
	298.15 K	24.4 ± 0.35	0.27 ± 0.031	0.088
$MnBr_2$	303.15 K	23.3 ± 0.33	0.27 ± 0.029	0.080
	308.15 K	22.1 ± 0.44	0.29 ± 0.037	0.12
	313.15 K	20.7 ± 0.52	0.31 ± 0.045	0.13
	323.15 K	17.8 ± 0.60	0.36 ± 0.051	0.26
	288.15 K	22.3 ± 0.20	0.10 ± 0.016	0.051
	293.15 K	21.7 ± 0.27	0.09 ± 0.018	0.065
	298.15 K	21.1 ± 0.32	0.07 ± 0.021	0.076
$CoBr_2$	303.15 K	20.4 ± 0.32	0.06 ± 0.025	0.082
	308.15 K	19.8 ± 0.42	0.05 ± 0.027	0.10
	313.15 K	19.2 ± 0.38	0.02 ± 0.028	0.11
	323.15 K	17.7 ± 0.40	0.00 ± 0.031	0.11
	288.15 K	42.7 ± 0.36	0.11 ± 0.035	0.081
	293.15 K	42.0 ± 0.29	0.12 ± 0.030	0.068
	298.15 K	41.4 ± 0.35	0.11 ± 0.034	0.084
$ZnBr_2$	303.15 K	40.6 ± 0.42	0.12 ± 0.041	0.095
	308.15 K	39.8 ± 0.56	0.12 ± 0.056	0.14
	313.15 K	38.8 ± 0.46	0.13 ± 0.052	0.12
	323.15 K	36.9 ± 0.56	0.14 ± 0.056	0.14
	288.15 K	16.3 ± 0.35	0.06 ± 0.028	0.069
	293.15 K	16.0 ± 0.31	0.05 ± 0.026	0.062
	298.15 K	15.5 ± 0.30	0.04 ± 0.026	0.062
$CoCl_2$	303.15 K	15.15 ± 0.25	0.025 ± 0.021	0.054
	308.15 K	14.7 ± 0.31	0.01 ± 0.024	0.060
	313.15 K	14.3 ± 0.25	0.00 ± 0.019	0.048
	323.15 K	13.4 ± 0.27	−0.03 ± 0.026	0.058
	288.15 K	31.6 ± 0.36	0.02 ± 0.027	0.080
	293.15 K	31.0 ± 0.35	0.01 ± 0.032	0.086
	298.15 K	30.1 ± 0.35	0.03 ± 0.031	0.090
$ZnCl_2$	303.15 K	29.3 ± 0.30	0.03 ± 0.030	0.079
	308.15 K	28.4 ± 0.30	0.03 ± 0.030	0.073
	313.15 K	27.6 ± 0.29	0.03 ± 0.029	0.074
	323.15 K	26.0 ± 0.41	0.00 ± 0.043	0.11

Table 3. Parameters of Equation 6 for Metal Bromides and Chlorides in Acetonitrile

salt	$10^6 \cdot A_T(A_\Phi^\infty)$ / $m^3 \cdot mol^{-1}$	$10^7 \cdot B_T$ / $m^3 \cdot mol^{-1} \cdot K^{-1}$	$10^9 \cdot C_T$ / $m^3 \cdot mol^{-1} \cdot K^{-2}$	$10^6 \cdot \sigma$ / $m^3 \cdot mol^{-1}$
$MnBr_2$	24.4 ± 0.35	-2.37 ± 0.070	-0.9 ± 0.36	0.12
$CoBr_2$	21.1 ± 0.32	-1.28 ± 0.062	-0.3 ± 0.33	0.11
$ZnBr_2$	41.4 ± 0.35	-1.46 ± 0.041	-1.4 ± 0.22	0.064
$CoClr_2$	15.15 ± 0.25	-0.08 ± 0.013	-	0.068
$ZnCl_2$	30.1 ± 0.35	-0.165 ± 0.011	-	0.081

Table 4. Ultrasonic Velocity, u (1278.28 $m \cdot s^{-1}$ for Pure Acetonitrile), Adiabatic Compressibility, κ_s ($7.881 \cdot 10^{-10}$ $m^2 \cdot N^{-1}$ for Pure Acetonitrile), and Apparent Molar Compressibility, $K_{S,\Phi}$, for Metal Bromides and Chloride in Acetonitrile Solutions at 298.15 K

salt	m_S / $mol \cdot kg^{-1}$	u / $m \cdot s^{-1}$	$10^{10} \cdot \kappa_S$ / $m^2 \cdot N^{-1}$	$10^{13} \cdot K_{S,\Phi}$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
	0.06115	1277.23	7.800	−1.474
	0.08138	1276.92	7.773	−1.472
$MnBr_2$	0.1006	1276.65	7.747	−1.471
	0.1406	1276.11	7.693	−1.463
	0.1712	1275.69	7.651	−1.455
	0.1995	1275.31	7.613	−1.446
	0.09698	1277.02	7.809	−1.491
	0.1286	1276.04	7.754	−1.484
	0.1587	1275.30	7.712	−1.477
$CoBr_2$	0.1900	1274.64	7.672	−1.467
	0.2204	1273.90	7.631	−1.457
	0.2636	1273.20	7.591	−1.443
	0.3089	1272.10	7.535	−1.426
	0.02964	1277.07	7.851	−9.813
	0.04717	1276.38	7.833	−9.783
$ZnBr_2$	0.06324	1275.72	7.816	−9.740
	0.07952	1275.06	7.800	−9.662
	0.1099	1273.60	7.771	−9.359
	0.1317	1272.55	7.751	−9.128
	0.1554	1271.25	7.730	−8.876
	0.08764	1279.85	7.781	−1.331
	0.1171	1280.49	7.746	−1.340
	0.1460	1281.10	7.712	−1.345
$CoCl_2$	0.1743	1281.80	7.678	−1.348
	0.2031	1282.50	7.643	−1.349
	0.2318	1283.23	7.608	−1.352
	0.2600	1283.95	7.574	−1.351
	0.2873	1284.75	7.539	−1.353

This effect is presented in Figure 2 as the function $A_\Phi^\infty = f(T)$. The plots are linear for chlorides and not linear for bromides, where the best fit is obtained using the equation

$$A_\Phi^\infty = A_T + B_T(T/K - 298.15) + C_T(T/K - 298.15)^2 \quad (6)$$

The coefficients of eq 6 are listed in Table 3 along with the respective values of the residual variance, and in the case of the coefficients of chlorides, only A_T and B_T are presented, due to the linear correlation. It is evident that the first of the coefficients in eq 6 is identical to A_Φ^∞ 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 an electrostriction effect higher.

The experimental data for the sound velocity obtained at 298.15 K are presented in Table 4. The apparent molar isentropic compressibility, $K_{S,\Phi}/m^5 \cdot (mol \cdot N)^{-1}$, for the metal bromides and cobalt(II) chloride in acetonitrile solution were calculated according to

$$K_{S,\Phi} = (\kappa_S d_0 - \kappa_{S,0} d)/(m_S d d_0) + M \cdot \kappa_S / d \quad (7)$$

where $M/kg \cdot mol^{-1}$ is the molecular mass of the salt; $m_S/mol \cdot kg^{-1}$ denotes the number of moles of the solute per kilogram of the solution (molonity); and $d/kg \cdot m^{-3}$ and $d_0/kg \cdot m^{-3}$ are the densities of the solution and the solvent, respectively. The terms $\kappa_S/m^2 \cdot N^{-1}$ and $\kappa_{S,0}/m^2 \cdot N^{-1}$ in eq 7 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. Inspection of the presented data shows that an increase in the concentration of the salt causes an increase in the apparent molar isentropic compressibility of the bromide solution and a decrease in the apparent molar isentropic compressibility of the chloride solution, as can be observed in Figure 3, and the equation

$$K_{S,\Phi} = A_K^\infty + A_K{}^1 c^{1/2} + A_K{}^2 c \quad (8)$$

satisfactorily describes the concentration dependence. The coefficients (A_K^∞, A_K^1, and A_K^2) of eq 8, their standard deviations, and the respective values of the residual variance, σ, are given in Table 5. The negative values of $K_{S,\Phi}$ are an indication of the more close-packed structure of the studied solutions than those of the pure solvent.

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

$$y = A_1 + A_2 c^{1/2} + A_3 c \quad (9)$$

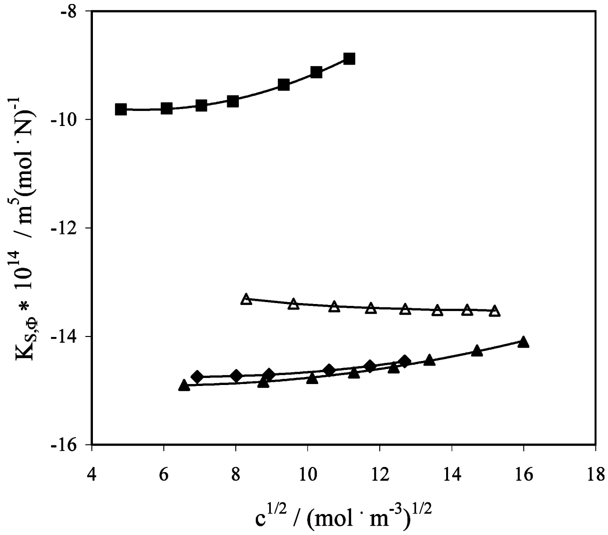

Figure 3. Apparent molar compressibility, $K_{S,\Phi}$, against the square root of molarity, c, in acetonitrile solutions at 298.15 K of: ◆, $MnBr_2$; ▲, $CoBr_2$; ■, $ZnBr_2$; and △, $CoCl_2$.

Table 5. Parameters of Equation 8 and the Mean Deviations for Metal Bromides and Cobalt(II) Chloride in Acetonitrile Solutions at 298.15 K

salt	$10^{13} \cdot A_K^\infty$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$	$10^{15} \cdot A_K^1$ / $(m^{13} \cdot N^{-2} \cdot mol^{-3})^{1/2}$	$10^{17} \cdot A_K^2$ / $m^8 \cdot N^{-1} \cdot mol^{-2}$	$10^{16} \cdot \sigma$ / $m^5 \cdot N^{-1} \cdot mol^{-1}$
$MnBr_2$	-1.44 ± 0.030	-0.11 ± 0.53	8 ± 2.7	0.65
$CoBr_2$	-1.47 ± 0.022	-0.8 ± 0.43	8 ± 4.3	1.6
$ZnBr_2$	-0.90 ± 0.035	-3.1 ± 0.91	29 ± 6.0	2.1
$CoCl_2$	-1.24 ± 0.027	-1.5 ± 0.42	5 ± 1.9	0.85

Table 6. Parameters of Equation 9 for the Speed of Sound (and the Mean Deviations) for the Metal Bromides and Cobalt(II) Chloride in Acetonitrile Solutions at 298.15 K

salt	$10^2 \cdot A_2$ / $(m^5 \cdot s^{-2} \cdot mol^{-1})^{1/2}$	$10^3 \cdot A_3$ / $m^4 \cdot s^{-1} \cdot mol^{-1}$	σ / $m \cdot s^{-1}$
$MnBr_2$	-5.65 ± 0.57	-14.0 ± 0.53	0.0088
$CoBr_2$	-1.0 ± 0.94	-27.8 ± 0.70	0.025
$ZnBr_2$	7 ± 5.6	-62 ± 5.9	0.095
$CoCl_2$	-10.5 ± 2.6	35 ± 2.3	0.056

Table 7. Parameters of Equation 9 for the Density (and the Mean Deviations) for the Metal Bromides and Chlorides in Acetonitrile Solutions at 298.15 K

salt		d_0 (kg·m^{-3})	$A_2 \cdot 10^2$ ((kg^2·m^{-3}·mol^{-1})$^{1/2}$)	$A_3 \cdot 10^3$ (kg·mol^{-1})	σ (kg·m^{-3})
	288.15 K	787.299	1.4 ± 0.43	190.6 ± 0.37	0.012
	293.15 K	781.923	1.6 ± 0.57	191.2 ± 0.55	0.016
	298.15 K	776.525	1.8 ± 0.60	191.9 ± 0.56	0.018
$MnBr_2$	303.15 K	771.097	1.8 ± 0.57	192.8 ± 0.56	0.018
	308.15 K	765.640	1.9 ± 0.66	193.6 ± 0.66	0.019
	313.15 K	760.148	2.0 ± 0.71	194.5 ± 0.70	0.022
	323.15 K	749.055	2.2 ± 0.81	196.4 ± 0.75	0.023
	288.15 K	787.315	1.2 ± 0.57	199.2 ± 0.40	0.020
	293.15 K	781.939	1.0 ± 0.52	200.0 ± 0.39	0.019
	298.15 K	776.525	0.8 ± 0.45	201.0 ± 0.39	0.018
$CoBr_2$	303.15 K	771.112	0.7 ± 0.53	201.8 ± 0.40	0.019
	308.15 K	765.653	0.6 ± 0.51	202.7 ± 0.42	0.019
	313.15 K	760.164	0.35 ± 0.43	203.6 ± 0.36	0.016
	323.15 K	749.073	0.1 ± 0.50	205.5 ± 0.41	0.018
	288.15 K	787.313	0.6 ± 0.28	190.0 ± 0.35	0.0065
	293.15 K	781.935	0.65 ± 0.28	190.8 ± 0.25	0.0064
	298.15 K	776.535	0.8 ± 0.68	191.3 ± 0.74	0.015
$ZnBr_2$	303.15 K	771.106	0.6 ± 0.78	192.5 ± 0.91	0.019
	308.15 K	765.650	0.6 ± 0.86	193.2 ± 0.96	0.020
	313.15 K	760.159	0.7 ± 0.74	194.0 ± 0.97	0.019
	323.15 K	749.070	0.7 ± 0.87	196 ± 1.2	0.020
	288.15 K	787.297	0.5 ± 0.44	115.9 ± 0.37	0.0097
	293.15 K	781.919	0.3 ± 0.60	116.6 ± 0.46	0.013
	298.15 K	776.528	0.2 ± 0.60	117.2 ± 0.46	0.014
$CoCl_2$	303.15 K	771.090	−0.4 ± 0.65	118.0 ± 0.50	0.014
	308.15 K	765.631	−0.1 ± 0.65	118.5 ± 0.51	0.014
	313.15 K	760.142	−0.3 ± 0.75	119.2 ± 0.58	0.016
	323.15 K	749.056	3 ± 9.6	118 ± 7.6	0.21
	288.15 K	787.297	0.2 ± 0.28	111.0 ± 0.26	0.0065
	293.15 K	781.919	0.2 ± 0.35	111.8 ± 0.33	0.0082
	298.15 K	776.528	0.3 ± 0.28	112.4 ± 0.25	0.0065
$ZnCl_2$	303.15 K	771.090	0.25 ± 0.25	113.2 ± 0.24	0.0063
	308.15 K	765.631	0.0 ± 0.25	114.1 ± 0.33	0.0074
	313.15 K	760.142	0.3 ± 0.27	114.8 ± 0.24	0.0058
	323.15 K	749.056	0.15 ± 0.37	116.6 ± 0.37	0.0091

Table 8. Parameters of Equation 9 for the Adiabatic Compressibility (and the Mean Deviations) for the Metal Bromides and Cobalt(II) Chloride in Acetonitrile Solutions at 298.15 K

salt	$10^{14} \cdot A_2$ ((m^7·N^{-2}·mol^{-1})$^{1/2}$)	$10^{14} \cdot A_3$ (m^5·N^{-1}·mol^{-1})	$10^{13} \cdot \sigma$ (m^2·N^{-1})
$MnBr_2$	−2.9 ± 0.28	−16.4 ± 0.29	0.4
$CoBr_2$	−14 ± 6.8	−15.0 ± 0.57	1.8
$ZnBr_2$	−12 ± 8.2	−11.2 ± 0.88	1.4
Col_2C	4.5 ± 0.78	−15.09 ± 0.060	0.17

where y denotes the speed of sound in the solution, u (then A_1 is the speed of sound in the pure solvent independently measured, $A_1 = u_0$); or the density of the solution, d (then A_1 is the density of the pure solvent independently measured, $A_1 = d_0$); or the adiabatic compressibility, κ_S (then A_1 is the adiabatic compressibility of the pure solvent independently calculated, $A_1 = \kappa_{S,0}$).

The coefficients of the polynomials, their standard deviations, and the respective values of the residual variance, σ, are given in Tables 6, 7, and 8. The different acoustic properties of the studied solutions are observed. The presence of the salt causes a decrease in the sound velocity for the metal bromides. The opposite effect is observed for cobalt(II) chloride. The difference is obviously related to the changes in solvent structure induced by the electrolytes. The studied salts exhibit different electrolytic behavior and exist as the complex electrolytes or electrically neutral species. Thus, their influence on compressibility and sound velocity is different.

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