Adiabatic Compressibilities of Divalent Transition-Metal Perchlorates and Chlorides in *N,N*-Dimethylacetamide and Dimethylsulfoxide

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Sound velocities of solutions of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates and chlorides in *N,N*-dimethylacetamide (DMA) and dimethylsulfoxide (DMSO) were measured at 298.15 K. Adiabatic compressibility coefficients of the solutions were determined, and apparent adiabatic molar compressibilities of the salts at infinite dilution were evaluated and discussed.

Introduction

This work is a continuation of an investigation of nonaqueous transition-metal salt solution properties in light of the future possible application of these systems in chloride hydrometallurgy, that is, the technological process involving the transformation of insoluble metal sulfides and oxides into soluble salts.

The present study is a part of our systematic investigation of thermodynamic properties of divalent transition-metal perchlorates and halides in dipolar aprotic solvents. In our previous papers, partial molar volumes of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates and chlorides in *N,N*-dimethylacetamide (DMA) and in dimethylsulfoxide (DMSO) were reported.[1,2] Differences between volumetric properties of DMA and DMSO solutions of respective perchlorates and chlorides were presented and explained in terms of chlorocomplex formation of the divalent transition-metal cations. The results demonstrated that the relative stability of the octahedral and tetrahedral complexes is the essential factor controlling the solvation of metal ions and complex formation.

Results of sound velocity measurements provide useful information about ion−ion and ion−solvent interactions and are of significant help in understanding the behavior of electrolytes in solutions.

In this Article, the concentration dependencies of sound velocity and adiabatic compressibility coefficients for solutions of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates and chlorides in DMA and DMSO at 298.15 K are reported. From these data, the apparent adiabatic molar compressibilities are calculated. The sensitive nature of this function to structural and Coulombic effects in solutions makes it useful in supplementing volume data toward a more complete picture of the structure of electrolyte solutions.

Experimental Section

The DMA-solvated metal perchlorates and chlorides were obtained from the corresponding hydrates by dissolving them in *N,N*-dimethylacetamide. The removal of any excess solvent as well as the products of dehydration under reduced pressure at elevated temperature followed this step. Upon cooling, crystalline solids were obtained, which then were recrystallized at least twice from anhydrous solvent. The same procedure was used to obtain DMSO-solvated perchlorates and chlorides of the transition metals studied.

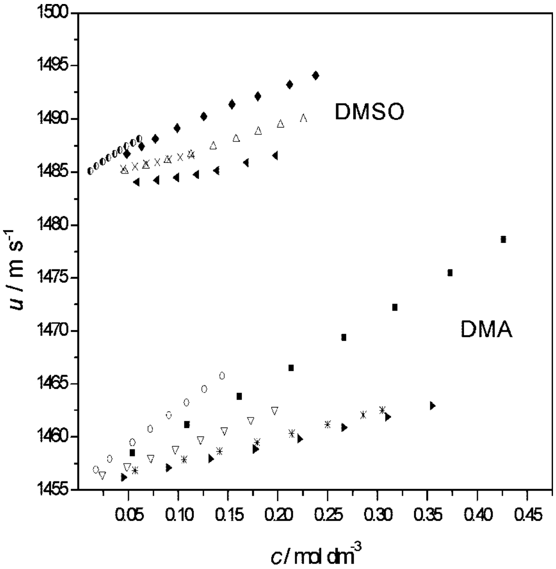

Figure 1. Plots of sound velocities, *u*, against concentration, *c*, for metal perchlorates $M(ClO_4)_2$ (M = Mn, Co, Ni, Cu, Zn) in DMA and DMSO at 298.15 K. DMA: ◭, $Mn(ClO_4)_2$; ●, $Co(ClO_4)_2$; ◇, $Ni(ClO_4)_2$; ▲, $Cu(ClO_4)_2$; left open triangle, $Zn(ClO_4)_2$. DMSO: ◨, $Mn(ClO_4)_2$; right open triangle, $Co(ClO_4)_2$; solid pentagon, $Ni(ClO_4)_2$; +, $Cu(ClO_4)_2$; □, $Zn(ClO_4)_2$.

The stock solutions of metal salts were obtained by dissolution of the solid solvates in anhydrous solvent. The stock solutions were analyzed for the respective metals by standard EDTA titration. At least 12 determinations were performed in each case, and the relative standard deviations were less than ± 0.1 %. Solutions for measurements were prepared by weighed dilution of the corresponding stock solutions. All preparations and manipulations involving anhydrous materials were performed in dry boxes.

DMA and DMSO (Fluka, puriss, absolute, mass fraction of H_2O < $1 \cdot 10^{-4}$) were dried with 0.4 nm molecular sieves.

The sound velocities were measured with an uncertainty of 0.1 $m \cdot s^{-1}$ using sound analyzer OPTIME 0.1 (Optel, Poland). The cell was thermostatted at (298.15 ± 0.01) K and calibrated with double-distilled water, and the value of 1496.69 $m \cdot s^{-1}$ for sound velocity in pure water was used.[3] The velocity of sound in DMA was found to be 1455.37 $m \cdot s^{-1}$, whereas the literature

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Table 1. Sound Velocities, Densities, Adiabatic Compressibilities, and Apparent Molar Adiabatic Compressibilities of Metal Perchlorates in DMA at T = 298.15 K

m_s	u	d	$10^{10}\cdot\kappa_S$	$10^8\cdot K_{S,\Phi}$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{m}\cdot\text{s}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$	Pa^{-1}	$\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$
		$Mn(ClO_4)_2$		
DMA	1455.37	0.936213	5.0429	
0.03006	1459.48	0.942406	4.9816	−19.75
0.05909	1463.09	0.948611	4.9246	−19.34
0.08863	1466.76	0.954924	4.8676	−18.95
0.11770	1470.43	0.961136	4.8120	−18.60
0.14656	1474.12	0.967302	4.7574	−18.28
0.17475	1477.62	0.973327	4.7056	−17.91
0.20176	1481.24	0.979100	4.6550	−17.66
0.22874	1485.03	0.984866	4.6042	−17.43
		$Co(ClO_4)_2$		
DMA	1455.37	0.936233	5.0428	
0.02900	1459.32	0.942693	4.9811	−21.38
0.04235	1461.04	0.945675	4.9538	−21.04
0.05501	1462.69	0.948505	4.9278	−20.81
0.08591	1466.71	0.955413	4.8654	−20.30
0.11439	1470.38	0.961778	4.8091	−19.85
0.14150	1474.02	0.967838	4.7554	−19.52
0.16923	1477.81	0.974036	4.7010	−19.20
0.19726	1481.56	0.980300	4.6473	−18.84
0.22142	1484.94	0.985701	4.6008	−18.57
		$Ni(ClO_4)_2$		
DMA	1455.37	0.936168	5.0431	
0.03452	1460.49	0.943693	4.9679	−21.66
0.06515	1464.29	0.950677	4.9058	−20.91
0.09600	1468.23	0.957709	4.8437	−20.44
0.12790	1472.35	0.964983	4.7803	−19.99
0.16042	1476.53	0.972395	4.7171	−19.54
0.18978	1480.43	0.979089	4.6602	−19.18
0.21979	1484.59	0.98593	4.6019	−18.85
0.25038	1488.99	0.992904	4.5426	−18.55
		$Cu(ClO_4)_2$		
DMA	1455.37	0.936110	5.0434	
0.06523	1463.13	0.950245	4.9158	−18.73
0.09641	1466.36	0.957338	4.8580	−18.35
0.14337	1471.32	0.968019	4.7720	−17.80
0.18940	1476.46	0.978490	4.6881	−17.35
0.23360	1481.48	0.988543	4.6091	−16.90
0.27736	1486.86	0.998499	4.5301	−16.53
0.32044	1492.25	1.008297	4.4538	−16.15
0.36403	1498.06	1.018213	4.3763	−15.79
		$Zn(ClO_4)_2$		
DMA	1455.37	0.936150	5.0432	
0.04286	1460.78	0.945119	4.9584	−18.62
0.08313	1464.87	0.954115	4.8843	−18.00
0.12315	1469.05	0.963055	4.8114	−17.53
0.16253	1473.18	0.971852	4.7412	−17.06
0.20130	1477.55	0.980513	4.6716	−16.70
0.23960	1481.93	0.989070	4.6038	−16.33
0.27714	1486.32	0.997457	4.5382	−15.98
0.31480	1490.75	1.005869	4.4735	−15.62

Table 2. Sound Velocities, Densities, Adiabatic Compressibilities, and Apparent Molar Adiabatic Compressibilities of Metal Perchlorates in DMSO at T = 298.15 K

m_s	u	d	$10^{10}\cdot\kappa_S$	$10^8\cdot K_{S,\Phi}$
$\text{mol}\cdot\text{kg}^{-1}$	$\text{m}\cdot\text{s}^{-1}$	$\text{g}\cdot\text{cm}^{-3}$	Pa^{-1}	$\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$
		$Mn(ClO_4)_2$		
DMSO	1484.12	1.095193	4.145	
0.02110	1485.33	1.099482	4.122	−7.26
0.02843	1485.76	1.100977	4.115	−7.26
0.03700	1486.24	1.102731	4.105	−7.21
0.04758	1486.85	1.104898	4.094	−7.18
0.05763	1487.48	1.106966	4.083	−7.19
0.07358	1488.35	1.110261	4.066	−7.10
0.09456	1489.65	1.114615	4.043	−7.09
0.1139	1490.8	1.118653	4.022	−7.04
0.1337	1492	1.122816	4.001	−6.99
0.1566	1493.4	1.127655	3.976	−6.94
0.1754	1494.6	1.131673	3.956	−6.91
		$Co(ClO_4)_2$		
DMSO	1484.12	1.095193	4.145	
0.02150	1485.50	1.099775	4.120	−8.12
0.03236	1486.20	1.102100	4.108	−8.09
0.04309	1486.90	1.104405	4.095	−8.06
0.05528	1487.72	1.107026	4.081	−8.04
0.06505	1488.35	1.109136	4.070	−8.00
0.08726	1489.80	1.113971	4.044	−7.93
0.1069	1491.04	1.118267	4.022	−7.84
0.1285	1492.45	1.123025	3.998	−7.78
0.1480	1493.65	1.127381	3.976	−7.70
0.1695	1495.15	1.132180	3.95	−7.66
0.1911	1496.61	1.137050	3.926	−7.61
		$Ni(ClO_4)_2$		
DMSO	1484.12	1.095194	4.145	
0.01259	1484.98	1.097895	4.131	−8.49
0.02515	1485.83	1.100595	4.116	−8.41
0.03816	1486.66	1.103403	4.100	−8.33
0.05100	1487.55	1.106185	4.085	−8.28
0.06341	1488.36	1.108878	4.071	−8.20
0.07675	1489.25	1.111785	4.056	−8.15
0.08797	1490.03	1.114242	4.042	−8.13
0.1004	1490.95	1.116985	4.027	−8.12
0.1125	1491.70	1.119667	4.014	−8.05
0.1251	1492.60	1.122433	4.000	−8.02
		$Cu(ClO_4)_2$		
DMSO	1484.12	1.095200	4.146	
0.01425	1485.02	1.098306	4.129	−8.27
0.02779	1485.89	1.101264	4.113	−8.23
0.04190	1486.83	1.104347	4.096	−8.20
0.05636	1487.74	1.107535	4.079	−8.13
0.07067	1488.67	1.110703	4.063	−8.09
0.08366	1489.5	1.113582	4.048	−8.04
0.09783	1490.43	1.116735	4.031	−7.99
0.1114	1491.43	1.119784	4.015	−7.99
0.1251	1492.23	1.122854	3.999	−7.91
0.1384	1493.28	1.125854	3.983	−7.92
		$Zn(ClO_4)_2$		
DMSO	1484.12	1.095198	4.145	
0.02918	1485.73	1.10158	4.112	−7.76
0.03465	1486.03	1.102776	4.106	−7.73
0.05104	1486.91	1.10639	4.088	−7.65
0.06794	1487.83	1.110133	4.069	−7.59
0.08574	1488.85	1.114099	4.049	−7.56
0.1022	1489.68	1.117798	4.031	−7.47
0.1190	1490.69	1.121580	4.012	−7.45
0.1435	1492.18	1.127136	3.984	−7.41
0.1685	1493.65	1.132850	3.957	−7.36

values are included in the range from (1456.48 to 1468) m·s^{-1}.[4−8] The speed of sound obtained for DMSO was 1484.12 m·s^{-1}, whereas the corresponding literature values range from (1484.98 to 1494.0) m·s^{-1}.[5,6,9,10]

Densities of the solutions were measured using an Anton Paar DMA 5000 densimeter with thermostat system based on a Peltier unit with a repeatability of 1·10^{-6} g·cm^{-3} and an uncertainty of 5·10^{-6} g·cm^{-3}. The temperature was kept constant at 298.15 K with a precision of 0.001 K according to the manufacturer's declaration. Before each measurement series, the accuracy of the density measurements and the purity of the solvents was verified by measuring their density at 298.15 K. The density values of (0.936228 ± 0.000086) g·cm^{-3} for DMA and (1.095196 ± 0.000004) g·cm^{-3} for DMSO were found in the present study, whereas literature values vary from (0.936076 to 0.93659) g·cm^{-3} for DMA and (1.095271 to 1.0972) g·cm^{-3} for DMSO.[11−14]

Results and Discussion

The adiabatic (isentropic) compressibility of solution, κ_S, is defined by the thermodynamic relation

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

where *V* and *P* are the volume and pressure, respectively.

This quantity is related to density (*d*) and sound velocity (*u*) by the Laplace equation

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

which provides the link between thermodynamics and acoustics.

The apparent molar adiabatic compressibility can be calculated according to the equation

$$K_{S,\Phi} = (\kappa_S d_0 - \kappa_{S,0} d)/(m_S d d_0) + M_2 \kappa_{S,0}/d_0 \tag{3}$$

where κ_S and $\kappa_{S,0}$ are isentropic compressibilities of solution and solvent, respectively; m_S denotes the number of moles of the solute per unit mass of solution (molonity), *d* and d_0 are densities of solution and solvent; and M_2 is the molar mass of the solute. The values of molonity may be converted to molarities using the simple equation

$$c = m_S \cdot d \tag{4}$$

Table 3. Sound Velocities, Densities, Adiabatic Compressibilities, and Apparent Molar Adiabatic Compressibilities of Metal Chlorides in DMA at *T* = 298.15 K

m_s / $\text{mol}\cdot\text{kg}^{-1}$	u / $\text{m}\cdot\text{s}^{-1}$	d / $\text{g}\cdot\text{cm}^{-3}$	$10^{10}\cdot\kappa_S$ / Pa^{-1}	$10^8\cdot K_{S,\Phi}$ / $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$
		$MnCl_2$		
DMA	1455.37	0.936233	5.0428	
0.05753	1458.54	0.942406	4.9930	−7.63
0.11464	1461.18	0.948611	4.9456	−7.54
0.16907	1463.82	0.954924	4.9003	−7.47
0.22202	1466.51	0.961136	4.8559	−7.41
0.27558	1469.39	0.967302	4.8106	−7.36
0.32661	1472.24	0.973327	4.7673	−7.31
0.38126	1475.47	0.979100	4.7204	−7.26
0.43295	1478.64	0.984866	4.6759	−7.22
		$CoCl_2$		
DMA	1455.37	0.936417	5.0418	
0.02558	1456.48	0.938700	5.0218	−6.43
0.05173	1457.27	0.941280	5.0027	−6.42
0.07676	1458.05	0.943750	4.9842	−6.40
0.10240	1458.88	0.946279	4.9653	−6.39
0.12889	1459.80	0.948892	4.9454	−6.39
0.15386	1460.67	0.951355	4.9267	−6.37
0.18103	1461.64	0.954035	4.9063	−6.35
0.20561	1462.57	0.956460	4.8876	−6.33
		$NiCl_2$		
DMA	1455.37	0.936230	5.0428	
0.01900	1456.96	0.938196	5.0212	−11.04
0.03382	1457.95	0.939871	5.0055	−10.92
0.05743	1459.51	0.942540	4.9806	−10.78
0.07634	1460.77	0.944678	4.9608	−10.70
0.09563	1462.05	0.946859	4.9407	−10.61
0.11402	1463.26	0.948937	4.9218	−10.53
0.13266	1464.51	0.951046	4.9025	−10.47
0.15126	1465.76	0.953148	4.8833	−10.40
		$CuCl_2$		
DMA	1455.37	0.936304	5.0424	
0.04793	1456.23	0.941347	5.0094	−6.08
0.09502	1457.12	0.946260	4.9774	−5.95
0.13902	1457.99	0.950849	4.9474	−5.87
0.18516	1458.89	0.955662	4.9164	−5.77
0.23064	1459.86	0.960406	4.8856	−5.69
0.27550	1460.88	0.965086	4.8552	−5.63
0.31937	1461.89	0.969661	4.8256	−5.56
0.36403	1462.93	0.974319	4.7957	−5.49
		$ZnCl_2$		
DMA	1455.37	0.936220	5.0428	
0.05996	1456.87	0.942244	5.0003	−5.93
0.11173	1457.90	0.947615	4.9649	−5.81
0.14875	1458.67	0.951455	4.9397	−5.75
0.18749	1459.52	0.955473	4.9132	−5.69
0.22296	1460.32	0.959152	4.8890	−5.63
0.25951	1461.18	0.962944	4.8640	−5.58
0.29554	1462.06	0.966681	4.8393	−5.52
0.31480	1462.52	0.968679	4.8263	−5.49

Table 4. Sound Velocities, Densities, Adiabatic Compressibilities, and Apparent Molar Adiabatic Compressibilities of Metal Chlorides in DMSO at *T* = 298.15 K

m_s / $\text{mol}\cdot\text{kg}^{-1}$	u / $\text{m}\cdot\text{s}^{-1}$	d / $\text{g}\cdot\text{cm}^{-3}$	$10^{10}\cdot\kappa_S$ / Pa^{-1}	$10^8\cdot K_{S,\Phi}$ / $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$
		$MnCl_2$		
DMSO	1484.12	1.095195	4.145	
0.04414	1486.73	1.100109	4.112	−5.86
0.05720	1487.45	1.101478	4.103	−5.69
0.06981	1488.16	1.102792	4.095	−5.58
0.08942	1489.17	1.104863	4.081	−5.43
0.1135	1490.28	1.107392	4.066	−5.23
0.1386	1491.39	1.110033	4.050	−5.08
0.1616	1492.14	1.112454	4.037	−4.88
0.1900	1493.24	1.115492	4.020	−4.76
0.2130	1494.11	1.117932	4.007	−4.66
		$CoCl_2$		
DMSO	1484.12	1.095195	4.145	
0.04252	1485.09	1.099762	4.123	−3.62
0.06132	1485.59	1.101773	4.112	−3.64
0.08074	1486.15	1.103853	4.102	−3.64
0.1018	1486.68	1.106100	4.090	−3.67
0.1220	1487.43	1.108290	4.078	−3.72
0.1423	1488.16	1.110486	4.066	−3.74
0.1621	1488.84	1.112633	4.055	−3.76
0.1818	1489.47	1.114767	4.043	−3.77
0.2020	1490.01	1.116975	4.032	−3.78
		$NiCl_2$		
DMSO	1484.12	1.095195	4.145	
0.01103	1485.10	1.096811	4.134	−9.71
0.01653	1485.54	1.097610	4.128	−9.52
0.02222	1485.96	1.098433	4.123	−9.31
0.02764	1486.35	1.099214	4.118	−9.16
0.03328	1486.73	1.100026	4.113	−9.02
0.03812	1487.06	1.100720	4.108	−8.92
0.04374	1487.43	1.101526	4.103	−8.82
0.04953	1487.79	1.102355	4.098	−8.70
0.05501	1488.16	1.103132	4.093	−8.64
		$CuCl_2$		
DMSO	1484.12	1.095198	4.146	
0.04097	1485.31	1.100005	4.121	−4.46
0.05136	1485.53	1.101208	4.115	−4.34
0.06160	1485.80	1.102392	4.109	−4.29
0.07134	1485.96	1.103528	4.104	−4.20
0.08195	1486.20	1.104769	4.098	−4.16
0.09202	1486.40	1.105944	4.093	−4.11
0.1022	1486.63	1.107132	4.087	−4.09
		$ZnCl_2$		
DMSO	1484.12	1.095198	4.146	
0.05319	1484.06	1.100613	4.125	−1.77
0.07120	1484.25	1.102488	4.117	−1.94
0.08920	1484.49	1.104340	4.109	−2.05
0.1070	1484.79	1.106216	4.100	−2.16
0.1251	1485.16	1.108115	4.091	−2.27
0.1517	1485.90	1.110903	4.077	−2.43
0.1776	1486.56	1.113650	4.063	−2.52

The sound velocity data obtained for solutions of the transition-metal perchlorates and chlorides in DMA and DMSO are given in Tables 1 and 2 and Tables 3 and 4, together with respective density values as well as the adiabatic compressibility coefficients and apparent molar adiabatic compressibilities. It has been found that for all of the solutions investigated, the plots of adiabatic compressibility, κ_S, against concentration are not linear, and the best description is obtained using the equation

$$\kappa_S = \kappa_S^0 + A_1\sqrt{c} + A_2 c \tag{5}$$

Coefficients A_1 and A_2 as well as the respective values of residual deviations are given in Tables 5 and 6.

The concentration dependencies of sound velocity and adiabatic compressibility coefficients for solutions of manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) perchlorates and chlorides in DMA and in DMSO at 298.15 K are presented in Figures 1, 2, and 3. As one can observe, the presence of each electrolyte studied causes an increase in sound velocity and a decrease in solution compressibility. However, the magnitude of these changes is strongly related to the solvent and the coordination number of the metal ion. The higher the concentration of a salt, the higher the number of solvent molecules that are involved in the solvation process. This effect is reflected in sound velocity as well as in solution compressibility because the solution is becoming more structured. Solvent molecules in the solvation sphere of an ion are less compressible than those in the bulk solvent. Some authors even assumed that solvent molecules in the solvation cosphere are incompressible.[15] However, it seems to be obvious that this assumption is an oversimplification.[16,17]

Table 5. Coefficients of Equation $\kappa_S = \kappa_S^0 + A_1\sqrt{c} + A_2c$ for Adiabatic Compressibilities of the Solutions of Metal Perchlorates and Chlorides in DMA at Temperature 298.15 K, Where $\kappa_S^0 = 5.043 \cdot 10^{-10}$ Pa^{-1}

	$10^{12} \cdot A_1$	$10^{10} \cdot A_2$	$10^{10} \cdot \sigma$
salt	$\mathrm{dm^{3/2} \cdot mol^{-1/2} \cdot Pa^{-1}}$	$\mathrm{dm^3 \cdot mol^{-1} \cdot Pa^{-1}}$	$\mathrm{Pa^{-1}}$
$Mn(ClO_4)_2$	−8 ± 3.1	−1.78 ± 0.011	0.0019
$Co(ClO_4)_2$	−8 ± 2.3	−1.87 ± 0.063	0.0021
$Ni(ClO_4)_2$	−11 ± 3.0	−1.81 ± 0.059	0.0021
$Cu(ClO_4)_2$	−13 ± 3.2	−1.59 ± 0.065	0.0033
$Zn(ClO_4)_2$	−12 ± 3.4	−1.60 ± 0.068	0.0030
$MnCl_2$	−1.95 ± 0.096	−0.837 ± 0.0020	0.0002
$CoCl_2$	−1.6 ± 0.36	−0.753 ± 0.0087	0.0003
$NiCl_2$	−2.4 ± 0.37	−1.05 ± 0.016	0.0003
$CuCl_2$	−1.9 ± 0.59	−0.67 ± 0.015	0.0006
$ZnCl_2$	−2.0 ± 0.33	−0.67 ± 0.012	0.0003

Table 6. Coefficients of Equation $\kappa_S = \kappa_S^0 + A_1\sqrt{c} + A_2c$ for Adiabatic Compressibilities of the Solutions of Metal Perchlorates and Chlorides in DMSO at Temperature 298.15 K, Where $\kappa_S^0 = 4.145 \cdot 10^{-10}$ Pa^{-1}

	$10^{12} \cdot A_1$	$10^{10} \cdot A_2$	$10^{10} \cdot \sigma$
salt	$\mathrm{dm^{3/2} \cdot mol^{-1/2} \cdot Pa^{-1}}$	$\mathrm{dm^3 \cdot mol^{-1} \cdot Pa^{-1}}$	$\mathrm{Pa^{-1}}$
$Mn(ClO_4)_2$	−1.1 ± 0.35	−0.933 ± 0.0041	0.00035
$Co(ClO_4)_2$	−1.9 ± 0.58	−0.97 ± 0.016	0.00059
$Ni(ClO_4)_2$	−1.1 ± 0.36	−1.01 ± 0.016	0.00025
$Cu(ClO_4)_2$	−1.0 ± 0.42	−1.01 ± 0.017	0.00031
$Zn(ClO_4)_2$	−1.4 ± 0.31	−0.959 ± 0.0077	0.00021
$MnCl_2$	−5.2 ± 1.1	−0.48 ± 0.027	0.0010
$CoCl_2$	0.71 ± 0.24	−0.52 ± 0.015	0.0005
$NiCl_2$	−2.8 ± 0.34	−0.75 ± 0.020	0.0002
$CuCl_2$	−2.1 ± 0.27	−0.46 ± 0.011	0.0001
$ZnCl_2$	4.5 ± 0.78	−0.52 ± 0.020	0.0004

Table 7. Parameters of Gucker Equation and Mean Deviations, σ, for Metal Perchlorates and Chlorides in DMA Solutions at T = 298.15 K

	$10^8 \cdot K_{S,\Phi}^0$	$10^9 \cdot S_K$	$10^8 \cdot \sigma$
salt	$\mathrm{cm^3 \cdot mol^{-1} \cdot Pa^{-1}}$	$\mathrm{(cm^6 \cdot Pa^{-2} \cdot dm^3 \cdot mol^{-3})^{1/2}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot Pa^{-1}}$
$Mn(ClO_4)_2$	−21.1 ± 0.25	77 ± 6.1	0.064
$Co(ClO_4)_2$	−22.92 ± 0.071	92 ± 2.5	0.027
$Ni(ClO_4)_2$	−23.38 ± 0.099	97 ± 2.8	0.031
$Cu(ClO_4)_2$	−20.8 ± 0.17	82 ± 3.1	0.041
$Zn(ClO_4)_2$	−20.3 ± 0.17	83 ± 3.5	0.043
$MnCl_2$	−7.86 ± 0.017	9.7 ± 0.43	0.0046
$CoCl_2$	−6.55 ± 0.046	5 ± 1.8	0.014
$NiCl_2$	−11.39 ± 0.017	25.9 ± 0.51	0.0046
$CuCl_2$	−6.42 ± 0.032	15.4 ± 0.63	0.0088
$ZnCl_2$	−6.27 ± 0.022	13.9 ± 0.46	0.0052

Table 8. Parameters of Gucker Equation and Mean Deviations, σ, for Metal Perchlorates and Chlorides in DMSO Solutions at T = 298.15 K

	$10^8 \cdot K_{S,\Phi}^0$	$10^9 \cdot S_K$	$10^8 \cdot \sigma$
salt	$\mathrm{cm^3 \cdot mol^{-1} \cdot Pa^{-1}}$	$\mathrm{(cm^6 \cdot Pa^{-2} \cdot dm^3 \cdot mol^{-3})^{1/2}}$	$\mathrm{cm^3 \cdot mol^{-1} \cdot Pa^{-1}}$
$Mn(ClO_4)_2$	−7.47 ± 0.043	12 ± 1.6	0.064
$Co(ClO_4)_2$	−8.44 ± 0.068	17 ± 2.4	0.029
$Ni(ClO_4)_2$	−8.70 ± 0.043	18 ± 1.7	0.017
$Cu(ClO_4)_2$	−8.48 ± 0.062	14 ± 2.4	0.025
$Zn(ClO_4)_2$	−8.02 ± 0.047	16 ± 1.8	0.015
$MnCl_2$	−6.84 ± 0.071	45 ± 2.2	0.022
$CoCl_2$	−3.5 ± 0.11	−6 ± 3.4	0.031
$NiCl_2$	−10.58 ± 0.078	80 ± 3.9	0.022
$CuCl_2$	−5.1 ± 0.20	30 ± 5.9	0.024
$ZnCl_2$	−0.88 ± 0.080	−37 ± 2.4	0.015

Figure 1 shows the difference in the effect of metal perchlorates on the sound velocities in the two solvents studied. It is clear that the addition of $M(ClO_4)_2$ leads to a higher increase in u in DMA than in DMSO. One can assume that this phenomenon is connected with better ordering of DMSO itself and thus a smaller increase in ordering when the DMSO solvates are being formed.[18]

Moreover, in the case of the solutions of perchlorates in DMA, two distinct groups can be discerned for sound velocities and adiabatic compressibilities, whereas in DMSO, no such diversity can be observed.

Figure 1 shows that the speed of sound has the highest values in solutions of manganese(II), nickel(II), and cobalt(II) perchlorates in DMA. At the same time, these salts cause the most evident decrease in solution compressibility (Figure 3). Slightly smaller changes in sound velocity and solution compressibility are observed in the case of solutions of zinc(II) and copper(II) perchlorates. Furthermore, it has been demonstrated that the limiting molar conductances of zinc(II) and copper(II) ions are a little higher than those of manganese(II), nickel(II), and cobalt(II) ions in DMA.[19,20] It seems to be obvious that the differences observed are related to the structure of the solvated metal ions. It has been established that the coordination of

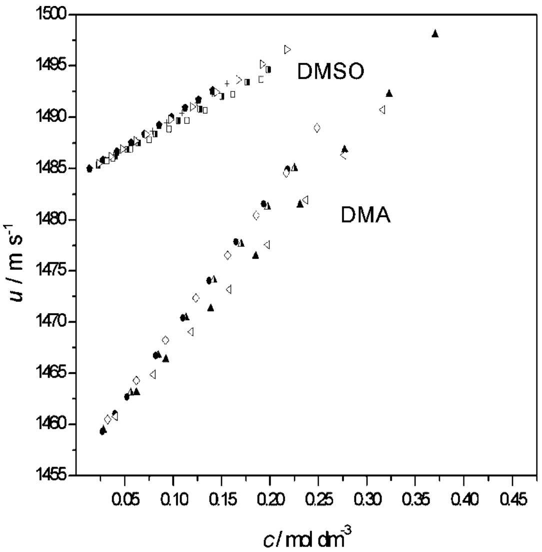

Figure 2. Plots of sound velocities, u, against concentration, c, for metal chlorides MCl_2 (M = Mn, Co, Ni, Cu, Zn) in DMA and DMSO at 298.15 K. DMA: ■, $MnCl_2$; ▽, $CoCl_2$; ○, $NiCl_2$; right solid triangle, $CuCl_2$; *, $ZnCl_2$. DMSO: ◆, $MnCl_2$; △, $CoCl_2$; ◐, $NiCl_2$; ×, $CuCl_2$; left solid triangle, $ZnCl_2$.

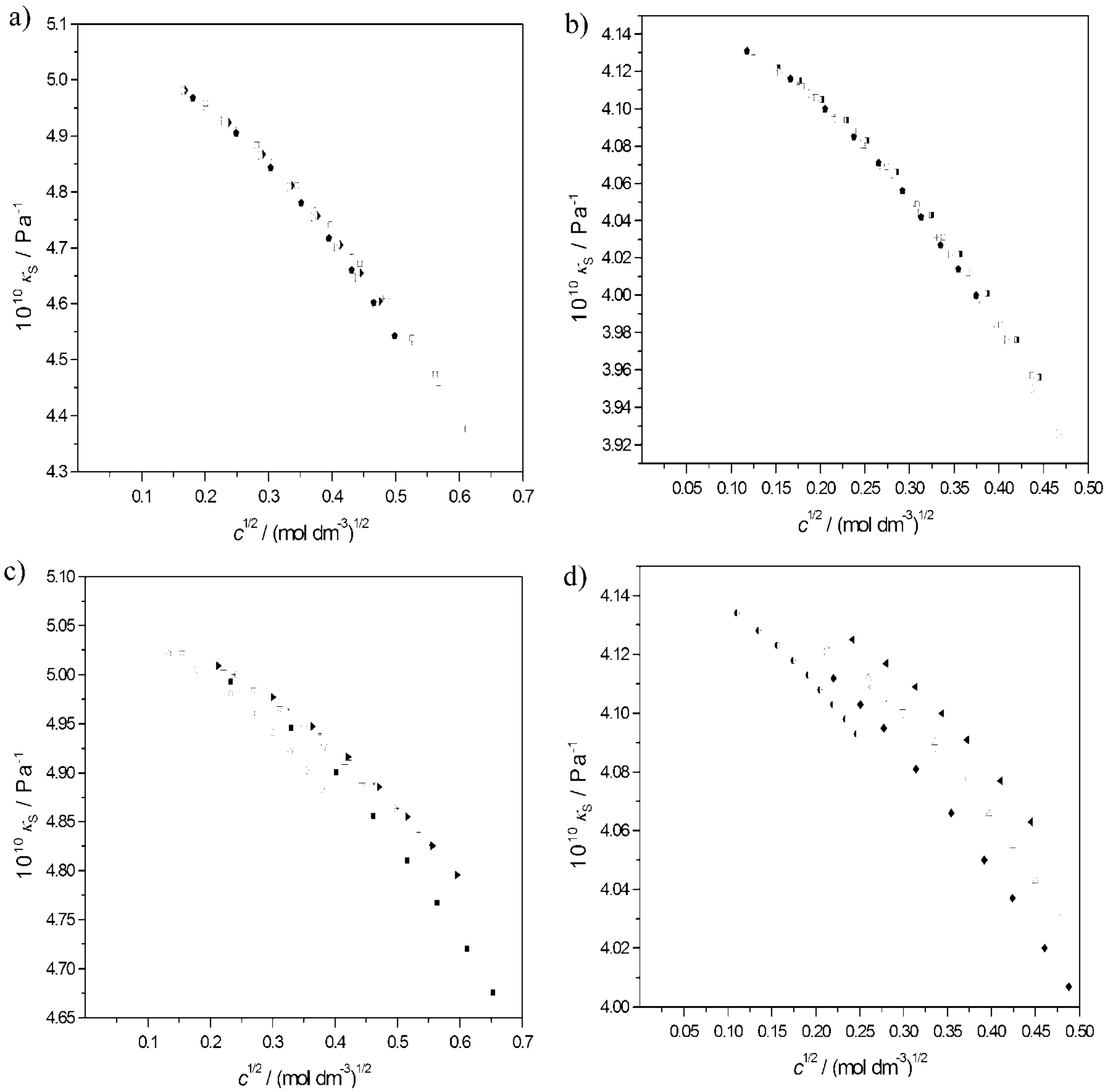

Figure 3. Plots of adiabatic compressibilities, κ_S, against the square root of concentration, $c^{1/2}$, for metal chlorides and perchlorates in DMA and DMSO at 298.15 K: (a) $M(ClO_4)_2$ − DMA, (b) $M(ClO_4)_2$ − DMSO, (c) MCl_2 − DMA, and (d) MCl_2 − DMSO. (Symbols are the same as those in Figures 1 and 2.)

solvent molecules to the divalent transition-metal cations is controlled by the equilibrium between the octahedral hexasolvates and tetrahedral tetrasolvates. The dominating form of the existence of manganese(II), nickel(II), and cobalt(II) cations in DMA is the octahedral hexasolvates, whereas zinc(II) ions mainly exist as tetrasolvates.[21] In the case of the copper(II) cation, the Jahn−Teller effect is responsible for the deformation of the octahedral structure. It has been known from EXAFS measurements that the axial Cu−O bond is weaker than the equatorial bond.[21]

Metal perchlorates of the Mn(II)−Zn(II) series in DMSO exist as six-coordinated solvates, and the small differences in velocities and compressibilities result from the differences in the electronic structure and the ionic radii of metal cations.[22−24]

Because of the variety of the structural form of metal chlorocomplexes in DMA and DMSO solutions, the values of solution compressibility and sound velocity vary within fairly wide limits.

The relatively high sound velocity in nickel(II) chloride solutions in both studied solvents is caused by significant contents of the solvation complex as well as the monochlorocomplex, which are mostly six- and five-coordinated.[25,26]

Manganese(II) chloride exists in DMA as an octahedral solvate in considerable amounts (ca. 25 %), but manganese(II) chlorocomplexes are mainly pseudotetrahedral.[27] Therefore, the influence of manganese(II) chloride on the speed of sound and solution compressibility is slightly smaller than that caused by the presence of nickel(II) chloride.

It has been deduced from spectrophotometric and conductometric measurements that the majority of cobalt(II) in $CoCl_2$ solution in DMA exists as the nonionic pseudotetrahedral $CoCl_2(DMA)_2$ complex.[27,28] In addition, there is also a few percent of a solvated cobalt(II) complex in the system considered.

In DMSO, coordinative disproportion producing the pseudotetrahedral $CoCl_3DMSO^-$ complex anion is shown to predominate in more concentrated solutions of $CoCl_2$.[29]

It has been established that an electrically neutral pseudotetrahedral $ZnCl_2X_2$ complex is an essential form of the existence of $ZnCl_2$ in DMA and DMSO.[30,31] There are only two solvent molecules in the coordination sphere of zinc(II), and their electrostriction is very small because of the nonionic form of zinc(II). All chlorocomplexes of zinc(II) are four-coordinated in DMA, and no solvation complex exists in $ZnCl_2$ solutions. In DMSO solutions, only monochlorocomplexes of zinc are

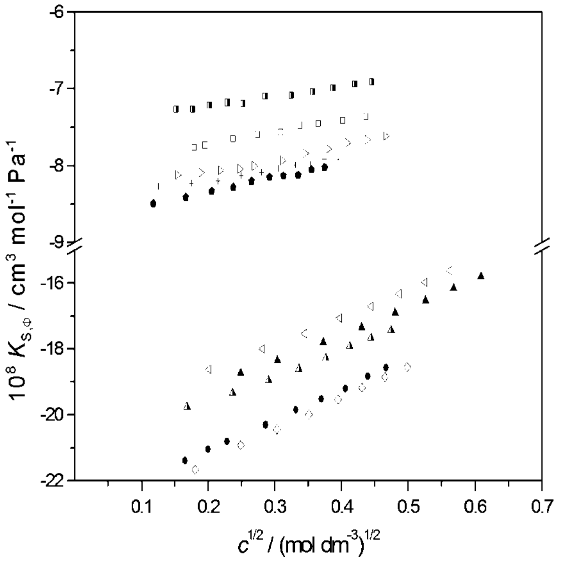

Figure 4. Plots of apparent molar compressibilities, $K_{S,\Phi}$, against the square root of concentration, $c^{1/2}$, for metal perchlorates $M(ClO_4)_2$ (M = Mn, Co, Ni, Cu, Zn) in DMA and DMSO at 25 °C. (Symbols are the same as those in Figure 1.)

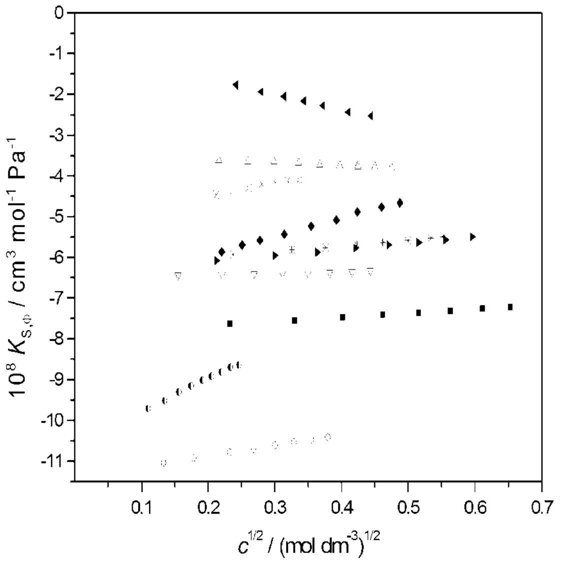

Figure 5. Plots of apparent molar compressibilities, $K_{S,\Phi}$, against the square root of concentration, $c^{1/2}$, for metal chlorides MCl_2 (M = Mn, Co, Ni, Cu, Zn) in DMA and DMSO at 298.15 K. (Symbols are the same as those in Figure 2.)

octahedral. Thereby, the presence of that salt weakly affects the sound velocity and the compressibility of the solution.

The structure of copper(II) chloride solution in DMA and DMSO is not yet known, but our results indicate that the coordination state of the salt is similar to the state of zinc(II) chloride in DMA.

The limiting values of the apparent molar adiabatic compressibility provide direct information on ion−solvent interactions. In the case of small divalent cations, $K^0_{S,\Phi}$ is mainly affected by electrostriction and takes large negative values. Unfortunately, there is no reliable method of splitting $K^0_{S,\Phi}$ values into ionic contributions.[32−34]

In Figures 4 and 5, the values of the apparent molar compressibilities of metal perchlorates and chlorides in DMA and DMSO are presented as a function of the square root of concentration.

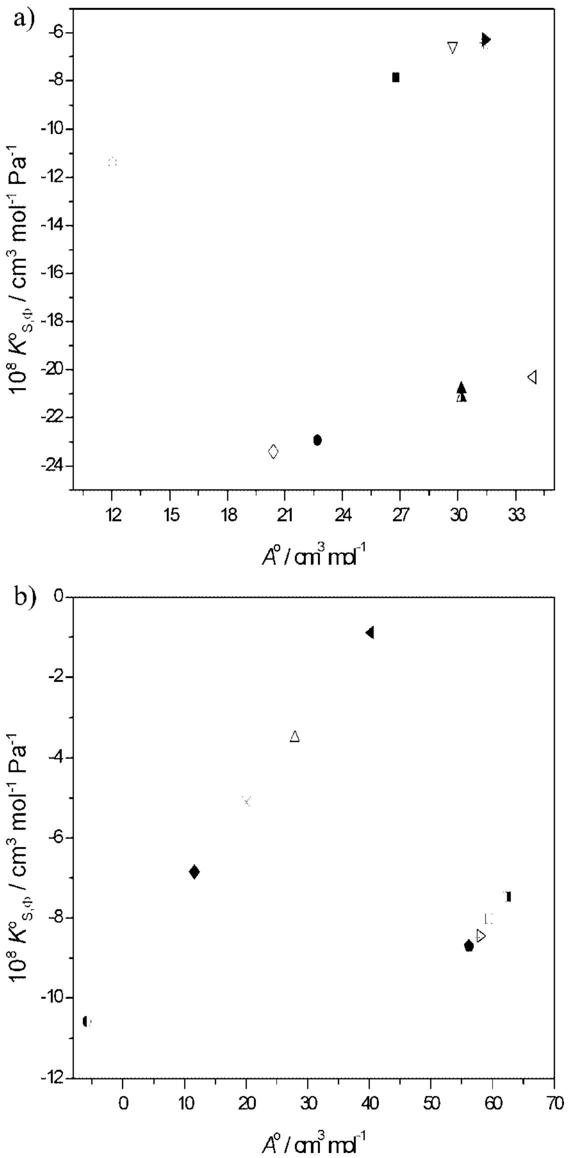

Figure 6. Plots of the limiting apparent molar compressibilities, $K^0_{S,\Phi}$, against the apparent molar volumes at infinite dilution, A^0, for transition-metal chlorides and perchlorates in (a) DMA and (b) DMSO. (Symbols are the same as those in Figures 1 and 2.)

As is seen, all plots are linear, which indicates that the equation

$$K_{S,\Phi} = K^0_{S,\Phi} + S_K \cdot c^{1/2} \tag{6}$$

where $K^0_{S,\Phi}$ represents the limiting apparent molar adiabatic compressibility and S_K is the experimental slope may be used for extrapolation. Equation 6, which has a form analogous to that of the Masson equation, was first introduced and applied by Gucker.[35] The coefficients of eq 6, their uncertainties, and the respective values of the residual deviations, σ, are collected in Tables 7 and 8. It is not surprising that for the salts with a common anion the limiting values of partial molar compressibility vary in the same order as the respective standard partial molar volumes. The dependencies between these quantities for metal perchlorates and chlorides in DMSO and DMA are presented in Figures 6a and 6b, respectively. Correlation coefficients varying from 0.994 to 0.996 were found for the respective relationships. A conclusion from this observation is that both of these sequences, which were formed by limiting apparent molar volumes and compressibilities, are determined by factors that control the electrostriction effect.

Concluding Remarks

The general conclusion ensuing from the inspection of the presented data is that the apparent molar compressibilities are much more sensitive to structural and Coulombic effects in solution than the volumes. Whereas the volumes of the metal perchlorates and chlorides are similar, the difference in the values of compressibility for both of these electrolyte types is quite large. The reason is the relatively small contribution of the intrinsic compressibility of the ion. In the case of the apparent molar volumes, the effect resulting from the difference in magnitude of electrostriction is covered to a significant extent by the large volume of the perchlorate anion. Consequently, one can state that the molar compressibility is a direct and precise measure of an electrostriction effect and thus the solute−solvent interactions in solution.

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