Measurements of the Speed of Sound and Density of Aqueous Solutions of the First-Row Transition Metal Halides. 3. Apparent Molar Compressibilities and Volumes of Aqueous CoI_2 and NiI_2 within the Temperature Range 291.15 K to 297.15 K

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The densities and speeds of sound in aqueous solutions of CoI_2 and NiI_2 were measured at concentrations from (0.1 to 1.4) mol·kg^{-1} and temperatures from (291.15 to 297.15) K. The adiabatic compressibility coefficients, κ_S, apparent molar volumes, V_Φ, and adiabatic compressibilities, $K_{S,\Phi}$, were determined. The corresponding limiting apparent molar quantities were found by extrapolation to infinite dilution. The measurement results were compared with those obtained previously for other copper and nickel halides.

1. Introduction

This study of aqueous solutions of CoI_2 and NiI_2 is a continuation of our previous studies on aqueous $CoCl_2$, $NiCl_2$, $CoBr_2$, and $NiBr_2$ solutions.[1,2] Because of the important role that cobalt and nickel play in many industrial processes and biological systems, the results may be of interest in that they suggest some differences in the effects of the cations and anions on the structure and thermodynamic properties of the solutions.

From the speed of sound and density measurements, the adiabatic compressibility coefficients and molar volumes as well as the corresponding apparent quantities for the solutions were determined and compared with those reported earlier.

It is worthwhile noting that the data concerning aqueous solutions of CoI_2 and NiI_2 are rather scarce in the literature, due probably to high instability of investigated systems.

In aqueous solutions the iodides are significantly hydrolyzed (e.g. $NiI_2 + H_2O \Leftrightarrow Ni(OH)I + HI$) and HI is spontaneously oxidized by air ($4HI + O_2 \Leftrightarrow 2I_2 + 2H_2O$). Especially unstable are aqueous solutions of CoI_2, since Co^{2+} is easily oxidized to Co^{3+}.

2. Experimental Section

2.1. Chemicals. CoI_2 of analytical grade (Aldrich) and $NiI_2·6H_2O$ (Johnson & Matthey) were recrystallized from redistilled water. The stock solutions were prepared by mass using the recrystallized salts and redistilled water. The electrolytic conductivity of the water was lower than 1.5×10^{-4} S·m^{-1}. The solutions used for the measurements were prepared from the stock solutions by weighing. The electrolyte concentrations in the stock solutions were determined by atomic emission spectroscopy (inductively coupled plasma, ICP) to give the concentrations of Co^{2+} and Ni^{2+} with an accuracy of 1.1% and a precision better than 0.3%. Additionally, the concentration of the I^- ions in the stock solutions was determined by the Höfer's volumetric method[3] with a precision better than 0.1%. Because of the instability of the iodide solutions mentioned above, the chemicals and solutions were kept under an inert atmosphere (dry nitrogen) at 253 K, in accordance with the producer's recommendation, and the speed of sound and density measurements were performed immediately after preparing the solutions. Nevertheless, some discrepancies observed in the measurement results are doubtlessly due to the lack of stability of the solutions under test.

2.2. Speed of Sound and Density Measurements. The speed of sound was measured using a sing-around measuring set designed and constructed in our laboratory and described elsewhere.[4] The precision of the speed of sound measurements was ± 0.05 m·s^{-1}, within the calibration limits, that is, for speeds ranging from (1472 to 1519) m·s^{-1}; outside those limits, it decreases and achieves a value of ± 0.5 m·s^{-1} for 1780 m·s^{-1} (for the confidence level of 95%). The repeatability was ± 0.02 m·s^{-1} over the whole measurement range. The temperature in the ultrasonic cell was measured with a quartz thermometer of resolution ± 0.001 K and with an accuracy of ± 0.01 K. The temperature deviations inside the measuring cell did not exceed a few thousandths of a degree.[5]

The densities of the solutions were measured using a bicapillary pycnometer[6] calibrated as described previously.[1] The temperature during the measurements was stabilized to ± 0.005 K using two thermostats in a cascade arrangement. The air density at the measured ambient temperature, the barometric pressure, and the relative humidity were taken into account in the calculation of the buoyancy correction.[6] The precision of the density measurements was better than 5×10^{-2} kg·m^{-3}. The ultrasound speeds and densities of the solutions under test were measured in narrow vicinities of the temperatures indicated in Tables 1 and 2 and interpolated to those by second-order polynomials.

3. Measurement Results and Calculations

3.1. Speeds of Sound and Densities. The speeds of sound, u, and densities, d, were measured at 1 K intervals from 291.15 K to 297.15 K and for molalities, m, ranging from 0.09 mol·kg^{-1} to 1.41 mol·kg^{-1} and from 0.01 mol·kg^{-1} to 1.05 mol·kg^{-1} for the CoI_2 and NiI_2 solutions, respec-

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Table 1. Speed of Sound in Aqueous Solutions of CoI_2 and NiI_2

m	u (m·s^{-1})						
(mol·kg^{1})	T = 291.15 K	T = 292.15 K	T = 293.15 K	T = 294.15 K	T = 295.15 K	T = 296.15 K	T = 297.15 K
				CoI_2			
0.0947	1472.51	1475.90	1478.89	1481.81	1484.63	1487.37	1490.02
0.2055	1469.62	1472.51	1475.33	1478.11	1480.83	1483.49	1486.10
0.2740	1467.81	1470.56	1473.26	1475.93	1478.56	1481.14	1483.69
0.4316	1464.46	1467.12	1469.70	1472.19	1474.62	1476.96	1479.22
0.6810	1461.89	1464.17	1466.41	1468.59	1470.72	1472.79	1474.81
0.8665	1461.15	1463.21	1465.23	1467.20	1469.12	1470.98	1472.32
1.1438	1463.38	1464.36	1466.66	1468.21	1469.72	1471.19	1472.59
1.4112	1468.59	1469.63	1470.82	1471.90	1472.95	1473.98	1474.69
				NiI_2			
0.0985	1471.87	1474.90	1477.87	1480.76	1483.57	1486.31	1488.98
0.1271	1470.77	1473.77	1476.70	1479.55	1482.33	1485.03	1487.65
0.2783	1465.51	1468.32	1471.06	1473.74	1476.34	1478.88	1481.34
0.4109	1462.05	1464.68	1467.25	1469.76	1472.21	1474.61	1476.94
0.6124	1458.56	1460.92	1463.23	1465.49	1467.68	1469.82	1471.90
0.8230	1456.91	1459.00	1461.05	1463.04	1464.98	1466.88	1468.73
0.8966	1456.68	1458.69	1460.66	1462.57	1464.43	1466.24	1468.00
1.0512	1456.99	1458.77	1460.51	1462.22	1463.90	1465.54	1467.14

Table 2. Densities of Aqueous Solutions of CoI_2 and NiI_2

m	d (kg·m^{-3})						
(mol·kg^{-1})	T = 291.15 K	T = 292.15 K	T = 293.15 K	T = 294.15 K	T = 295.15 K	T = 296.15 K	T = 297.15 K
				CoI_2			
0.0947	1024.81	1024.59	1024.36	1024.12	1023.86	1023.59	1023.30
0.2055	1054.43	1054.19	1053.93	1053.66	1053.38	1053.08	1052.78
0.2740	1073.60	1073.33	1073.04	1072.25	1072.44	1072.12	1071.80
0.4316	1115.65	1115.34	1115.02	1114.69	1114.34	1113.98	1113.60
0.6810	1181.32	1180.95	1180.56	1180.17	1179.77	1179.36	1178.94
0.8665	1229.29	1228.88	1228.46	1228.03	1227.58	1227.11	1226.64
1.1438	1299.81	1299.17	1298.69	1298.21	1297.72	1297.19	1296.67
1.4112	1366.22	1365.32	1364.80	1364.28	1363.75	1363.17	1362.61
				NiI_2			
0.0985	1025.70	1025.48	1025.24	1025.00	1024.74	1024.47	1024.19
0.1271	1033.58	1033.45	1033.10	1032.84	1032.58	1032.31	1032.02
0.2783	1074.85	1074.58	1074.31	1074.02	1073.72	1073.41	1073.09
0.4109	1110.70	1110.42	1110.12	1109.81	1109.48	1109.14	1108.78
0.6124	1164.81	1164.46	1164.10	1163.73	1163.35	1162.95	1162.55
0.8230	1219.53	1219.11	1218.69	1218.26	1217.84	1217.42	1217.00
0.8966	1238.58	1238.16	1237.73	1237.29	1236.84	1236.38	1225.91
1.0512	1278.36	1277.89	1277.42	1276.94	1276.46	1275.97	1275.48

Table 3. Parameters of Eq 1 for Aqueous Solutions of CoI_2 and NiI_2

T (K)	u_0 (m·s^{-1})	($a_u \pm s_a$) (m·kg·s^{-1}·mol^{-1})	($b_u \pm s_b$) (m·kg^2·s^{-1}·mol^{-2})	δ_u (m·s^{-1})	r
			CoI_2		
291.15	1476.04	−35.9 ± 0.3	21.7 ± 0.2	0.16	0.9999
292.15	1479.23	−37.1 ± 0.2	21.4 ± 0.2	0.14	0.9999
293.15	1482.34	−38.2 ± 0.2	21.4 ± 0.2	0.13	0.9999
294.15	1485.37	−39.4 ± 0.3	21.2 ± 0.2	0.15	0.9999
295.15	1488.32	−40.4 ± 0.3	21.0 ± 0.2	0.16	0.9999
296.15	1491.19	−41.8 ± 0.3	20.8 ± 0.2	0.18	0.9999
297.15	1493.98	−42.6 ± 0.4	20.6 ± 0.3	0.24	0.9999
			NiI_2		
291.15	1476.04	−43.9 ± 0.4	24.7 ± 0.5	0.18	0.9999
292.15	1479.23	−45.3 ± 0.4	24.8 ± 0.5	0.19	0.9999
293.15	1482.34	−46.6 ± 0.5	24.9 ± 0.5	0.20	0.9999
294.15	1485.37	−47.9 ± 0.5	24.9 ± 0.5	0.20	0.9999
295.15	1488.32	−49.2 ± 0.5	25.0 ± 0.5	0.20	0.9999
296.15	1491.19	−50.4 ± 0.5	25.0 ± 0.5	0.20	0.9999
297.15	1493.98	−51.6 ± 0.5	25.0 ± 0.5	0.20	0.9999

tively. The speed of sound and density values are collected in Tables 1 and 2.

The concentration dependences of the speed of sound can be reproduced by the following polynomial

$$u = u_0 + a_u m + b_u m^2 \tag{1}$$

where u_0 is the speed of sound in pure water,[7] while the densities are reproduced more satisfactorily by another polynomial often used for the concentration dependences of density[8]

$$d = d_0 + a_d m + b_d m^{1.5} \tag{2}$$

where d_0 is the density of pure water.[9]

The coefficients of eqs 1 and 2, their standard deviations, and the mean deviations from the regression line are given

Table 4. Parameters of Eq 2 for Aqueous Solutions of CoI_2 and NiI_2

T (K)	d_0 ($kg \cdot m^{-3}$)	($a_d \pm s_a$) ($kg^2 \cdot m^{-3} \cdot mol^{-1}$)	($b_d \pm s_b$) ($kg^{2.5} \cdot m^{-3} \cdot mol^{-1.5}$)	δ_d ($kg \cdot m^{-3}$)	r
			CoI_2		
291.15	998.60	275.5 ± 1.00	−10.6 ± 1.40	0.30	0.999 900
292.15	998.41	275.5 ± 0.70	−11.0 ± 1.00	0.20	0.999 994
293.15	998.20	275.3 ± 0.68	−11.0 ± 0.90	0.20	0.999 994
294.15	997.99	275.0 ± 0.70	−10.9 ± 0.90	0.20	0.999 994
295.15	997.77	274.6 ± 0.67	−10.8 ± 0.92	0.20	0.999 995
296.15	997.54	274.3 ± 0.68	−10.8 ± 0.93	0.20	0.999 994
297.15	997.30	274.0 ± 0.67	−10.7 ± 0.92	0.20	0.999 995
			NiI_2		
291.15	998.60	283.9 ± 1.2	−17.1 ± 1.3	0.28	0.999 992
292.15	998.41	283.6 ± 1.2	−17.1 ± 1.3	0.28	0.999 992
293.15	998.20	283.4 ± 1.2	−17.1 ± 1.3	0.28	0.999 992
294.15	997.99	283.1 ± 1.2	−17.1 ± 1.3	0.28	0.999 992
295.15	997.77	282.8 ± 1.2	−17.0 ± 1.4	0.29	0.999 992
296.15	997.54	282.4 ± 1.3	−16.9 ± 1.4	0.29	0.999 992
297.15	997.30	282.1 ± 1.3	−16.8 ± 1.4	0.29	0.999 991

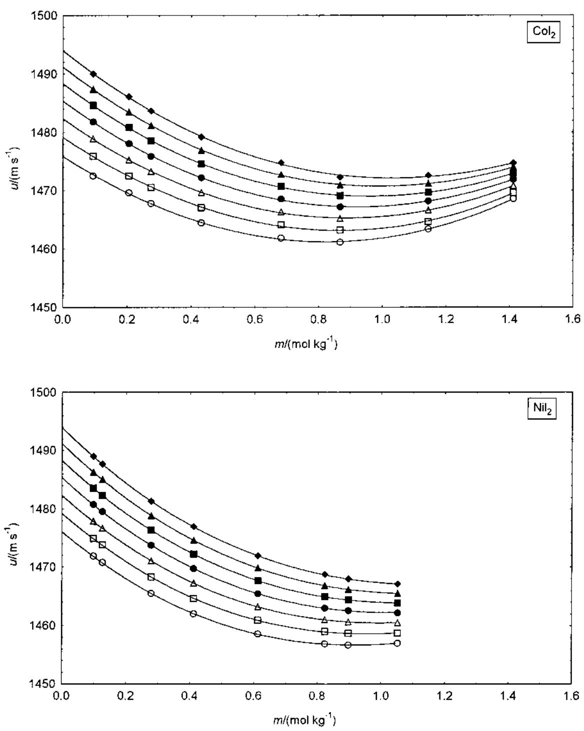

Figure 1. Speed of sound in CoI_2 and NiI_2 solutions versus molality: (○) 291.15 K; (□) 292.15 K; (△) 293.15 K; (●) 294.15 K; (■) 295.15 K; (▲) 296.15 K; (◆) 297.15 K; points, from experiment; solid lines, calculated from eq 1.

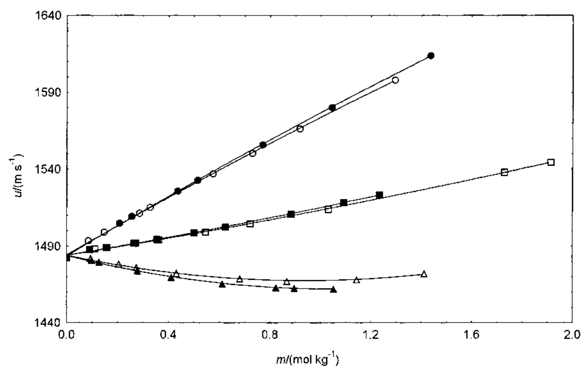

Figure 2. Speed of sound versus molality at 294.15 K: (○) $CoCl_2$; (●) $NiCl_2$;[1] (□) $CoBr_2$; (■) $NiBr_2$;[2] (△) CoI_2; (▲) NiI_2; points, from experiment; solid lines, calculated from eq 1.

Table 5. Parameters of Eq 6 for the Apparent Volumes of CoI_2 and NiI_2 in Aqueous Solutions

T (K)	$10^6(V_\Phi^\infty \pm s)$ ($m^3 \cdot mol^{-1}$)	$10^6(A_v \pm s)$ ($m^3 \cdot kg^{0.5} \cdot mol^{-1.5}$)	$10^6(B_v \pm s)$ ($m^3 \cdot kg \cdot mol^{-2}$)	r
		CoI_2		
291.15	37.03 ± 0.02	−0.54 ± 0.07	1.12 ± 0.05	0.999 8
292.15	36.90 ± 0.05	−0.37 ± 0.05	1.31 ± 0.03	0.999 9
293.15	37.15 ± 0.02	−0.42 ± 0.05	1.28 ± 0.04	0.999 9
294.15	37.42 ± 0.02	−0.48 ± 0.06	1.24 ± 0.04	0.999 9
295.15	37.71 ± 0.02	−0.55 ± 0.07	1.18 ± 0.04	0.999 8
296.15	37.98 ± 0.03	−0.60 ± 0.08	1.14 ± 0.05	0.999 7
297.15	38.27 ± 0.03	−0.67 ± 0.09	1.09 ± 0.06	0.999 5
		NiI_2		
291.15	34.794 ± 0.005	−0.13 ± 0.02	1.29 ± 0.01	0.999 99
292.15	35.007 ± 0.005	−0.15 ± 0.02	1.28 ± 0.01	0.999 99
293.15	35.191 ± 0.006	−0.16 ± 0.02	1.27 ± 0.01	0.999 99
294.15	35.426 ± 0.007	−0.19 ± 0.02	1.24 ± 0.02	0.999 99
295.15	35.673 ± 0.008	−0.23 ± 0.03	1.20 ± 0.02	0.999 98
296.15	35.925 ± 0.009	−0.28 ± 0.03	1.15 ± 0.02	0.999 97
297.15	36.189 ± 0.010	−0.33 ± 0.03	1.09 ± 0.03	0.999 96

in Tables 3 and 4. The concentration dependences of the speed of sound in the solutions versus temperature are shown in Figure 1.

In Figure 2 the speeds of sound in the CoI_2 and NiI_2 solutions at 294.15 K are compared with those in the $CoCl_2$, $NiCl_2$, $CoBr_2$, and $NiBr_2$ solutions.[1,2] The comparison constitutes strong evidence that both the speed of sound and its concentration dependence are determined essentially by the anion, while the transition metal cations have a minor effect on the propagation of the acoustic wave. The halide anions are of notably different size, while the sizes of the Co^{2+} and Ni^{2+} ions are very close to each other. Furthermore, both the d^8 Ni^{2+} and d^7 Co^{2+} cations form in aqueous solutions low-spin six-coordinate aqua-complexes of similar size and shape (a regular octahedron and a slightly distorted octahedron, respectively).[10]

The speeds of sound in the CoI_2 and NiI_2 solutions are lower than those in the solutions of the other cobalt and nickel halides. Furthermore, within the low concentration range, the speed of sound versus molality curves for the iodide solutions differ significantly from those for the chloride and bromide ones: the speed of sound decreases with increasing concentration ($\partial u/\partial m$ < 0), reaching a minimum at $m \approx 0.1$ $mol \cdot kg^{-1}$. In most aqueous solutions of simple electrolytes, the speed increases with increasing concentration; however, for some iodides of alkali metals (KI, LiI) and for some other iodides (NH_4I, SrI_2, CdI_2, ZnI_2), chlorides (UO_2Cl_2, $CdCl_2$), nitrates ($AgNO_3$, $UO_2(NO_3)_2$, $Pb(NO_3)_2$), and acetates ($Cd(CH_3COO)_2$, $Pb(CH_3COO)_2$) as well as for sulfuric acid, the speed of sound is decreasing up to concentrations of a few moles per kilogram.[11−13] Since the concentration dependences of the density, d, and the

Table 6. Parameters of Eq 6 for the Apparent Compressibilities of CoI_2 and NiI_2 in Aqueous Solutions

T (K)	$10^{14}(K^{\infty}_{S,\Phi} \pm s)$ ($m^5 \cdot N^{-1} \cdot mol^{-1}$)	$10^{14}(A_{K_s} \pm s)$ ($m^5 \cdot kg^{0.5} \cdot N^{-1} \cdot mol^{-1.5}$)	$10^{14}(B_{K_s} \pm s)$ ($m^5 \cdot kg \cdot N^{-1} \cdot mol^{-2}$)	r
		CoI_2		
291.15	−9.01 ± 0.04	1.18 ± 0.13	0.26 ± 0.08	0.9996
292.15	−8.90 ± 0.05	1.22 ± 0.13	0.26 ± 0.09	0.9996
293.15	−8.79 ± 0.05	1.21 ± 0.13	0.25 ± 0.09	0.9995
294.15	−8.68 ± 0.04	1.20 ± 0.13	0.25 ± 0.09	0.9995
295.15	−8.57 ± 0.04	1.19 ± 0.13	0.24 ± 0.09	0.9995
296.15	−8.46 ± 0.04	1.18 ± 0.13	0.23 ± 0.09	0.9995
297.15	−8.34 ± 0.04	1.18 ± 0.13	0.23 ± 0.09	0.9995
		NiI_2		
291.15	−8.64 ± 0.02	0.96 ± 0.08	0.28 ± 0.06	0.9998
292.15	−8.51 ± 0.02	0.95 ± 0.08	0.27 ± 0.06	0.9998
293.15	−8.38 ± 0.02	0.95 ± 0.08	0.27 ± 0.06	0.9998
294.15	−8.25 ± 0.02	0.93 ± 0.08	0.24 ± 0.06	0.9998
295.15	−8.13 ± 0.02	0.92 ± 0.08	0.22 ± 0.06	0.9998
296.15	−8.01 ± 0.02	0.91 ± 0.08	0.21 ± 0.06	0.9998
297.15	−7.90 ± 0.02	0.90 ± 0.08	0.20 ± 0.06	0.9998

Table 7. Limiting Apparent Molar Volumes $V^{\infty}_{\Phi}/(\times 10^{-6}(m^3 \cdot mol^{-1}))$ of CoI_2, NiI_2, and I^- at 298.15 K

CoI_2	NiI_2	I^-		
		calcd using $V^{\infty}_{\Phi}(Co^{2+})$ values reported in the lit.	calcd using $V^{\infty}_{\Phi}(Ni^{2+})$ values reported in the lit.	lit. data
38.4[a]	36.4[a]	31.2,[b] 37.1,[c] 37.6,[c] 31.5,[d] 32.1,[e] 32.1[f]	30.02,[b] 36.4,[c] 38.2,[c] 32.4,[d] 32.9,[e] 32.95[f]	36.22,[b] 42.0[c]

[a] This work (extrapolated to 298.15 K). [b] Calculated using $V^{\infty}_{\Phi}(Co^{2+}) = -24.0 \times 10^{-6}$ $m^3 \cdot mol^{-1}$; and $V^{\infty}_{\Phi}(Ni^{2+}) = -24.0 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ (ref 16). [c] Calculated using $V^{\infty}_{\Phi}(Co^{2+}) = -35.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ and -36.8×10^{-6} $m^3 \cdot mol^{-1}$; $V^{\infty}_{\Phi}(Ni^{2+}) = -36.3 \times 10^{-6}$ $m^3 \cdot mol^{-1}$; and -40.0×10^{-6} $m^3 \cdot mol^{-1}$ (ref 17). [d] Calculated using $V^{\infty}_{\Phi}(Co^{2+}) = -24.6 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ and $V^{\infty}_{\Phi}(Ni^{2+}) = -28.3 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ (ref 18). [e] Calculated using $V^{\infty}_{\Phi}(Co^{2+}) = -25.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ and $V^{\infty}_{\Phi}(Ni^{2+}) = -29.4 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ (refs 19−22). [f] Calculated using $V^{\infty}_{\Phi}(Co^{2+}) = -25.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ and $V^{\infty}_{\Phi}(Ni^{2+}) = -29.5 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ (ref 23).

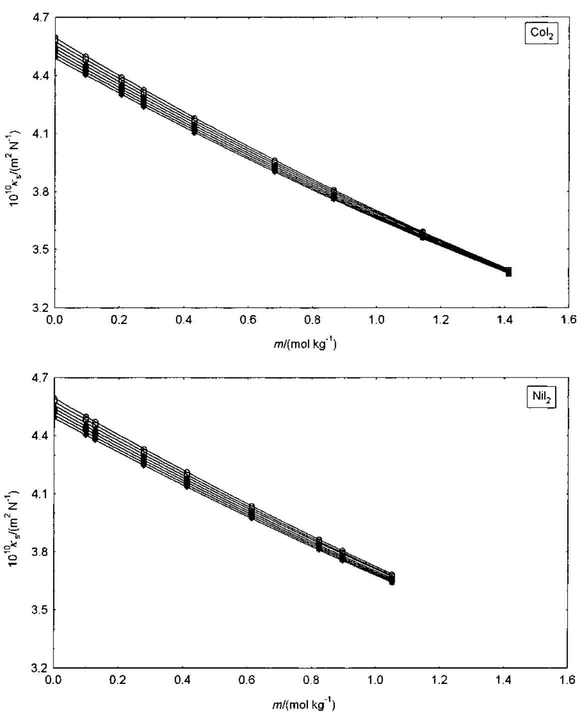

Figure 3. Adiabatic compressibility coefficient versus molality for aqueous CoI_2 and NiI_2 solutions: symbols as in Figure 1; points calculated from eq 3; lines calculated by the spline function.

adiabatic compressibility, κ_S, have for aqueous solutions always opposite signs ($(\partial d/\partial m)_T > 0$, $(\partial \kappa_S/\partial m)_T < 0$) and the derivatives are functions of concentration,[14] either a decrease or an increase of the speed of sound with concentration of the salt as well as extrema of the speed versus concentration curves may be expected. The concentration dependence of the speed reflects the complex interplay between the solute ions and the solvent molecules, which is difficult to rationalize. Roughly, the speed of sound depends on the ionic radius because of the electrostriction of water in the vicinity of the ion. Since the difference between the Co^{2+} and Ni^{2+} radii is negligible, the highest speed of sound should be expected in the chloride solutions, and the smallest one in the iodide solutions because of the sequence of the increasing anionic radii $R_{Cl^-} < R_{Br^-} < R_{I^-}$, according to observation; thus, as was to be expected, the speed of sound decreases with increasing electrostriction. We believe that the small difference between the speeds in the CoI_2 and NiI_2 solutions should rather not be discussed, since it can result from errors due to decomposition of the iodide solutions.

3.2. Adiabatic Compressibility. The adiabatic compressibility, $\kappa_S = -(1/V)(\partial V/\partial p)_S$, was calculated from the speed of sound and density values using the Laplace equation:

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

where u is the speed of sound and d is the density of the solution. As shown in Figure 3, the compressibilities of the iodide solutions decrease when the concentration and temperature increase. The adiabatic compressibilities extrapolated toward higher salt concentrations would probably become reversed at a concentration higher than $m \approx 5$ $mol \cdot kg^{-1}$, at which a flat minimum should appear. Because of the limited solubility of the investigated salts, those concentrations are not attainable.

3.3. Apparent and Molar Quantities. The apparent molar volumes, V_Φ, and apparent adiabatic compressibilities, $K_{S,\Phi}$, of the solutions under test were calculated from following equations:

$$V_\Phi = \frac{M}{d} - \frac{(d - d_0)}{m d d_0} \tag{4}$$

$$K_{S,\Phi} = \frac{\kappa_S d_0 - \kappa_{S,0} d}{m d d_0} + \frac{M \kappa_S}{d} \tag{5}$$

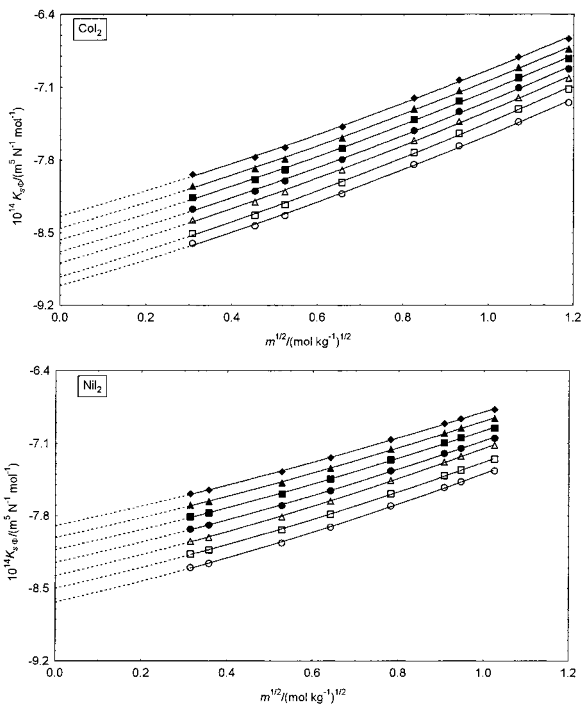

Figure 4. Apparent adiabatic molar compressibility versus $m^{0.5}$ for aqueous CoI_2 and NiI_2 solutions: symbols as in Figure 1; points calculated from eq 5; lines calculated from eq 6.

where M is the molecular weight of the salt and $\kappa_{S,0}$ is the adiabatic compressibility of pure water calculated from eq 3 using the speed of sound values of Del Grosso and Mader[7] and the densities taken from *Tabellenbuch Chemie*.[9]

The limiting apparent molar volumes, $V_{\Phi}^{\infty} = \lim(m\rightarrow 0)\, V_{\Phi}$, and compressibilities, $K_{S,\Phi}^{\infty} = \lim(m\rightarrow 0)\, K_{S,\Phi}$, were calculated using the following form of the Redlich−Mayer type equation:[15]

$$X_{\Phi} = X_{\Phi}^{\infty} + A_x m^{0.5} + B_x m \tag{6}$$

The parameters of the above equation are given in Tables 5 and 6 together with the standard deviations and correlation coefficients. The dependence of $K_{S,\Phi}^{\infty}$ on the molar concentration at a few temperatures is shown in Figure 4.

Table 7 shows the limiting apparent volumes of the I^- anion at 298.15 calculated on the basis of the additivity principle from our $V_{\Phi}^{\infty}(CoI_2)$ and $V_{\Phi}^{\infty}(NiI_2)$ volumes extrapolated to 298.15 K using different $V_{\Phi}^{\infty}(Co^{2+})$ and $V_{\Phi}^{\infty}(Ni^{2+})$ values reported in the literature. In the last column the literature data are given for comparison.

Literature Cited

(1) Ernst, S.; Manikowski, R.; Bebek, M. Measurements of the Speed of Sound and Density of Aqueous Solutions of the First-Row Transition Metal Halides. 1. Apparent and Molar Compressibilities and Volumes of Aqueous $CoCl_2$ and $CoBr_2$ within the Temperature Range 291.15 K to 297.15 K. *J. Chem. Eng. Data* **1996**, *41*, 397−401.

(2) Ernst, S.; Manikowski, R. Measurements of the Speed of Sound and Density of Aqueous Solutions of the First-Row Transition Metal Halides. 2. Apparent and Molar Compressibilities and Volumes of Aqueous $NiCl_2$ and $NiBr_2$ within the Temperature Range 291.15 K to 297.15 K. *J. Chem. Eng. Data* **1997**, *42*, 647−650.

(3) Höfer, P. Die Masanalytische Bestimmung Kleinster Mengen von Bromiden und Iodiden in Trink und Mineralwässern. *Ges. Ing.* **1953**, *74*, 224.

(4) Ernst, S.; Marczak W.; Manikowski, R.; Zorębski, E.; Zorębski, M. A Sing-Around Apparatus for Group Velocity Measurements in Liquids. Testing by Standard Liquids and Discussion of Error. *Acoust. Lett.* **1992**, *15*, 123−130.

(5) Ernst, S.; Marczak, W.; Manikowski, R. Temperature Fluctuations and Gradients in a Liquid Sample as a Source of Errors in Ultrasound Velocity Measurements. *Acoust. Lett.* **1993**, *16*, 177−183.

(6) Bauer, N.; Lewin, S. Z. In *Technique of Organic Chemistry*; Weissberger, A., Ed.; Interscience Publishers: New York, 1959; Vol. 1.

(7) Del Grosso, V. A.; Mader, C. V. Speed of Sound in Pure Water. *J. Acoust. Soc. Am.* **1972**, *52*, 1442−1446.

(8) Marcus, Y. Ionic radii in Aqueous Solutions. *Chem. Rev.* **1988**, *88*, 1475−1498.

(9) *Tabellenbuch Chemie*, Auflage 7; VEB Deutscher Verlag für Grundstoffindustrie: Leipizg, 1975.

(10) Drago, R. S. *Physical Methods in Inorganic Chemistry*; Van Nostrand Reinhold Company: New York, Cincinnati, Toronto, London, Melbourne, 1965.

(11) Stuehr, J.; Yeager, E. In *Physical Acoustics. Principles and Methods*; Mason, W. P., Ed.; Academic Press: New York and London, 1965; Vol. II, Part A.

(12) Hall, C.; Yeager, E. In *Electrochemistry*; Yeager, E., Salkind, A. J., Eds.; John Wiley & Sons: New York, 1973.

(13) Padmini, P. R. K. L.; Rao, B. R. Ultrasonic Velocity in Some Aqueous Solutions of Electrolytes. *Ind. J. Phys.* **1960**, *34*, 565−576.

(14) Allam, D. S.; Lee, W. H. Ultrasonic Studies of Electrolyte Solutions. Part I. Ultrasonic Velocities in Solutions of Inorganic Salts. *J. Chem. Soc.* **1964**, *34*, 6049−6053.

(15) Redlich, O.; Meyer, D. M. The Molal Volumes of Electrolytes. *Chem. Rev.* **1964**, *64*, 221−227.

(16) Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* **1971**, *71*, 147−176.

(17) Akitt, J. W. Limiting Single-Ion Molar Volumes. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 2259−2284.

(18) Spitzer, J. J.; Olofsson, I. V.; Singh, P. P.; Hepler, L. G. Apparent molar heat capacities and volumes of aqueous electrolytes at 298.15: $Ca(NO_3)_2$, $Co(NO_3)_2$, $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Mn(NO_3)_2$, $Ni(NO_3)_2$ and $Zn(NO_3)_2$. *J. Chem. Thermodyn.* **1979**, *11*, 233−238.

(19) Pogue, R. F.; Atkinson, G. Solution Thermodynamics of First Row Transition elements. 1. Apparent Molal Volumes of Aqueous $NiCl_2$, $Ni(ClO_4)_2$, $CuCl_2$ and $Cu(ClO_4)_2$ from 15 to 55 °C. *J. Chem. Eng. Data* **1988**, *33*, 370−376.

(20) Pogue, R. F.; Atkinson, G. Solution Thermodynamics of First Row Transition Elements. 2. Apparent Molal Volumes of Aqueous $MnCl_2$, $Mn(ClO_4)_2$, $CoCl_2$, $Co(ClO_4)_2$, $FeCl_2$ and $Fe(ClO_4)_2$ from 15 to 55 °C. *J. Chem. Eng. Data* **1989**, *34*, 227−232.

(21) Pogue, R. F.; Atkinson, G. Solution Thermodynamics of First Row Transition Elements. 3 Apparent Molal Volumes of Aqueous $ZnCl_2$ and $Zn(ClO_4)_2$ from 15 to 55 °C and an Examination of Solute−Solute and Solute−Solvent Interactions. *J. Solution Chem.* **1989**, *18*, 249−264.

(22) Pogue, R. F.; Atkinson, G. The Volume of Ions and Ion−Solvent Pair Correlation Functions. *J. Solution Chem.* **1993**, *22*, 689−702.

(23) Lo Surdo, A.; Millero, J. F. Apparent Molal Volumes and Adiabatic Compressibilities of Aqueous Transition Metal Chlorides at 25 °C. *J. Phys. Chem.* **1980**, *84*, 710−715.

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