

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

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The speed of sound and density of aqueous solutions of CoCl_2 and CoBr_2 were measured at concentrations ranging from (0.1 to 2) $\text{mol}\cdot\text{kg}^{-1}$ and within the temperature limit (291.15 to 297.15) K. The dependences of the adiabatic compressibility coefficient, κ_S , the apparent molar compressibility, Φ_{κ_S} , and the apparent molar volume, Φ_v , on concentration and temperature were determined. The corresponding partial molar quantities were found by extrapolation to infinite dilution.

1. Introduction

Measurements of the speed of sound supplemented by density measurements have found wide acceptance as a satisfactory method of studying aqueous and nonaqueous solutions of electrolytes. The thermodynamic quantities determined in this way (adiabatic compressibility, molar and partial molar volume, and compressibility) and their dependence on concentration and temperature are related to structure-making and -breaking effects and to the solvation of ions (Stuehr and Yeager, 1968; Friedman and Krishnan, 1973; Hall and Yeager, 1973).

The apparent thermodynamic quantities seem to be more susceptible to variations of the water structure caused by the ions than the entropy, molar volume, and activity coefficient. Thus, because of the high precision of ultrasonic velocity measurements achieved during the past decades, the apparent and partial molar compressibilities are of special interest as parameters indicative of the structure of electrolyte solutions.

The focus of this paper is the ultrasound velocities in and densities of aqueous solutions of cobalt chlorides and bromides. Our interest in those solutions results from the role cobalt salts play in many industrial processes as well as in those occurring in biological systems in that the participation of cobalt is not yet entirely understood (Hay, 1981; Hay, 1982; Hay, 1987).

From the ultrasound velocity and density measurements, the adiabatic compressibility coefficients and molar volumes as well as the apparent molar compressibilities and volumes of the salts under study were determined. The latter were extrapolated to zero concentration in order to obtain the corresponding partial molar quantities at infinite dilution.

2. Experimental Section

2.1. Chemicals. $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ of analytical grade (Riedel de Haen) and CoBr_2 (Aldrich) were recrystallized from redistilled water. The stock solutions were prepared by mass from recrystallized salts and redistilled water having

specific conductance lower than $1.5 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$. The solution series used for the measurements were prepared from stock solutions. The electrolyte concentrations in the latter were determined by gravimetric determination of the Cl^- and Br^- concentrations (with an accuracy better than 0.2%) and by the atomic emission spectroscopy (inductively coupled plasma, ICP) determination of the concentration of Co^{2+} with an accuracy of 1.1% and precision better than 0.3%.

2.2. Speed of Sound and Density Measurements. The speed of sound was measured by a sing-around measuring set designed and constructed in our laboratory and described elsewhere (Ernst *et al.*, 1992, 1993). Water distilled three times over NaOH and KMnO_4 (specific conductance as given above) was used for the calibration of the measuring cell. The constants l and τ_0 in the equation

$$\tau = l/u + \tau_0 \quad (1)$$

(where τ = the pulse transit time in the electroacoustic loop, u = the speed of sound taken from Del Grosso and Mader (1972), l = the acoustic path length, and τ_0 = the total delay time) were determined at 22 temperatures ranging from 290 K to 308 K. The precision of the speed of sound measurements was $\pm 0.05 \text{ m}\cdot\text{s}^{-1}$ within the calibration limits, i.e., for velocities ranging from (1472 to 1519) $\text{m}\cdot\text{s}^{-1}$, and gradually decreased for higher velocities, achieving a value of $\pm 0.5 \text{ m}\cdot\text{s}^{-1}$ for 1780 $\text{m}\cdot\text{s}^{-1}$ (for the confidence level 95%). The repeatability was $\pm 0.02 \text{ m}\cdot\text{s}^{-1}$ over the whole measurement range. The temperature in the ultrasonic cell was measured with a quartz thermometer of resolution $\pm 0.001 \text{ K}$ and with an accuracy of $\pm 0.01 \text{ K}$. The temperature deviations inside the measuring cell did not exceed a few thousandths of a degree (Ernst *et al.*, 1993).

The densities of the solutions were measured with a bicapillary pycnometer. Redistilled water was used as a standard for calibration. Measuring the height of the meniscus in each capillary relative to the zero position by a cathetometer at seven temperatures, the parameters of the equation $V = V_0[1 + \alpha(T - T_{\text{ref}})]^3 + hP[1 + \alpha(T - T_{\text{ref}})]^2$ (where V = the volume of water, V_0 = the volume of the

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Table 1. Speed of Sound in Aqueous Solutions of CoCl₂ and CoBr₂

m/(mol·kg ⁻¹)	u/(m·s ⁻¹)						
	291.15 K	292.15 K	293.15 K	294.15 K	295.15 K	296.15 K	297.15 K
	CoCl ₂						
0.0859	1484.35	1487.48	1490.53	1493.51	1496.41	1499.23	1501.98
0.1485	1490.12	1493.20	1496.20	1499.13	1502.00	1504.78	1507.49
0.2866	1502.78	1505.75	1508.65	1511.47	1514.23	1516.92	1519.53
0.3277	1506.47	1509.42	1512.29	1515.09	1517.82	1520.46	1523.04
0.5749	1529.00	1531.73	1534.40	1537.00	1539.54	1542.00	1544.41
0.7303	1542.62	1545.24	1547.80	1550.29	1552.72	1555.09	1557.39
0.9179	1559.12	1561.57	1563.97	1566.31	1568.59	1570.82	1572.99
1.2946	1591.43	1593.61	1495.73	1597.80	1599.81	1601.77	1603.67
	CoBr ₂						
0.1115	1479.26	1482.34	1485.33	1488.25	1491.10	1493.87	1496.56
0.2648	1483.17	1486.11	1488.97	1491.77	1494.49	1497.15	1499.73
0.3619	1485.82	1488.82	1491.45	1494.17	1496.82	1499.39	1501.90
0.5457	1491.27	1493.94	1496.55	1499.11	1501.59	1504.02	1506.37
0.7220	1479.18	1499.68	1502.12	1504.51	1506.83	1509.09	1511.30
1.0311	1507.39	1509.62	1511.79	1513.91	1515.98	1518.00	1519.97
1.7287	1533.20	1534.80	1536.37	1537.90	1539.39	1540.84	1542.26
1.9119	1540.24	1541.70	1543.12	1544.50	1545.84	1547.14	1548.40

Table 2. Densities of Aqueous Solutions of CoCl₂ and CoBr₂

m/(mol·kg ⁻¹)	d/(kg·m ⁻³)						
	291.15 K	292.15 K	293.15 K	294.15 K	295.15 K	296.15 K	297.15 K
	CoCl ₂						
0.0859	1008.82	1008.61	1008.36	1008.12	1007.88	1007.62	1007.36
0.1485	1016.14	1015.92	1015.68	1015.43	1015.17	1014.91	1014.62
0.2866	1032.14	1031.89	1031.65	1031.39	1031.12	1030.82	1030.54
0.3277	1036.81	1036.54	1036.29	1036.03	1035.77	1035.48	1035.21
0.5749	1036.70	1064.43	1064.17	1063.96	1063.56	1063.26	1062.95
0.7303	1082.16	1081.85	1081.58	1081.24	1080.94	1080.60	1080.29
0.9179	1102.57	1102.25	1101.95	1101.62	1101.31	1100.99	1100.67
1.2946	1142.76	1142.38	1142.05	1141.67	1141.31	1140.94	1140.58
	CoBr ₂						
0.1115	1020.23	1020.01	1019.78	1019.55	1019.34	1019.04	1018.78
0.2648	1049.21	1048.98	1048.74	1048.48	1048.21	1047.92	1047.62
0.3619	1067.50	1067.21	1066.91	1066.61	1066.29	1065.97	1065.65
0.5457	1101.32	1101.03	1100.83	1100.43	1100.12	1099.81	1099.49
0.7220	1133.65	1133.35	1133.03	1132.70	1132.36	1132.01	1131.66
1.0311	1189.24	1188.91	1188.54	1188.15	1188.76	1187.37	1187.00
1.7287	1309.90	1309.46	1309.01	1308.56	1308.09	1307.62	1307.14
1.9119	1340.56	1340.18	1339.62	1339.14	1338.65	1338.17	1337.68

pycnometer at the zero position, i.e., the volume under the marked dashes on the capillaries, P = the cross-sectional area of the capillary, h = the height of the column of water in the capillary, α = the coefficient of thermal expansion of the pycnometer glass, and T_{ref} = the reference temperature) have been determined. 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 relative humidity were used in the calculation of the buoyancy correction (Bauer and Lewin, 1959). The precision of the mass determination by weighing was 1×10^{-8} kg, and that of the cathetometric determination of the meniscus was 5×10^{-5} m. Thus, the calculated sensitivity of the density determination is 5×10^{-3} . According to Bauer and Levin (1959), the highest attainable precision of the density measurements carried out with capillary pycnometers is 5×10^{-3} kg/m³, while the standard deviations of our measurements indicate a precision better than 5×10^{-2} kg/m³.

For some of the results given in Tables 1 and 2, the measurements were carried out in narrow vicinities of the temperatures indicated and interpolated to those temperatures by second-order polynomials.

3. Measurement Results and Calculations

3.1. Speed of Sound and Densities. The speed of sound, u , and densities, d , were measured at 1-degree

intervals from 291.15 K to 297.15 K and for molalities, m , ranging from 0.08 mol·kg⁻¹ to 1.3 mol·kg⁻¹ and from 0.11 mol·kg⁻¹ to 1.91 mol·kg⁻¹ for the CoCl₂ and CoBr₂ solutions, respectively. The speed of sound and density values are collected in Tables 1 and 2.

The concentration dependences of the speed of sound and density can be represented by polynomials suggested by Owen *et al.* (Owen and Simons, 1957; Owen and Kronick, 1961), using molality instead of molar concentration:

$$y = a_y + b_y m + c_y m^{1.5} \quad (2)$$

where $y = u$ or d , $a_u = u^*$ is the speed of sound in pure water (Del Grosso and Mader, 1972), and $a_d = d^*$ is the density of pure water (Tabellenbuch Chemie, 1975).

The coefficients of the polynomials, their standard deviations, s_a and s_b , and the mean deviations from the regression lines, δ_y , together with the correlation coefficients, r , are given in Tables 3 and 4. The speeds of sound measured together with the best fit curves are plotted against m for a few temperatures in Figure 1. It shows that the dependence of the speed of sound shows only a very slight deviation from linearity and CoCl₂ affects the speed of sound much stronger than CoBr₂ does.

Within the limits of the reproducibilities of the speed of sound and density, the replacement of the molality, m , by the molar concentration, c , according to the original polynomials of Owen and Simons (Owen and Simons, 1957;

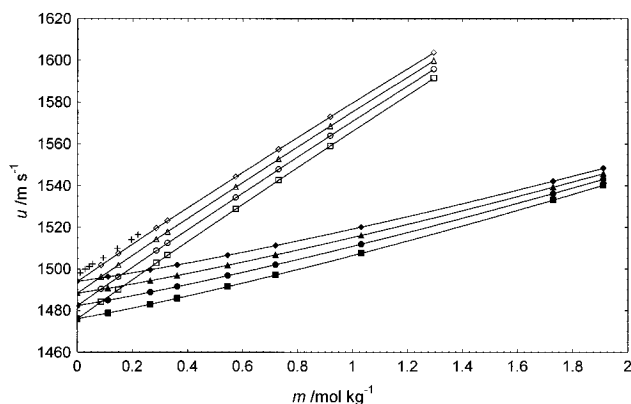


Figure 1. 1. Speed of sound vs molality: (CoCl₂) ◇, 297.15 K; △, 295.15 K; ○, 293.15 K; □, 291.15 K; ×, 298.15 K (according to Kawaizumi and Nomura (1987)); (CoBr₂) ◇, 297.15 K; △, 295.15 K; ○, 293.15 K; □, 291.15 K; points, experimental values; solid lines, calculated from eq 2.

Table 3. Parameters of Eq 2 for Aqueous Solutions of CoCl₂ and CoBr₂

<i>T</i> /K	$u^*/(\text{m}\cdot\text{s}^{-1})$	$(b_u \pm s_b)/(\text{m}\cdot\text{kg}\cdot\text{s}^{-1})$	$(c_u \pm s_c)/(\text{m}\cdot\text{kg}^{1.5}\cdot\text{s}^{-1}\cdot\text{mol}^{-1.5})$	$\delta_u/(\text{m}\cdot\text{s}^{-1})$	<i>r</i>
CoCl ₂					
291.15	1476.04	97.4 ± 0.27	-7.3 ± 0.27	0.08	0.999995
292.15	1479.23	96.7 ± 0.25	-7.3 ± 0.25	0.07	0.999996
293.15	1482.34	95.9 ± 0.24	-7.3 ± 0.24	0.08	0.999995
294.15	1485.37	95.2 ± 0.24	-7.4 ± 0.25	0.08	0.999995
295.15	1488.32	94.6 ± 0.25	-7.5 ± 0.25	0.09	0.999995
296.15	1491.19	93.9 ± 0.25	-7.5 ± 0.25	0.09	0.999995
297.15	1493.98	93.4 ± 0.27	-7.6 ± 0.27	0.1	0.999994
CoBr ₂					
291.15	1476.04	22.1 ± 0.3	8.3 ± 0.3	0.18	0.99993
292.15	1479.23	21.1 ± 0.3	8.4 ± 0.3	0.18	0.99992
293.15	1482.34	20.1 ± 0.3	8.4 ± 0.3	0.17	0.99993
294.15	1485.37	19.2 ± 0.3	8.4 ± 0.3	0.17	0.99990
295.15	1488.32	18.4 ± 0.3	8.5 ± 0.25	0.17	0.99993
296.15	1491.19	17.5 ± 0.4	8.5 ± 0.25	0.19	0.9992
297.15	1493.98	16.7 ± 0.4	8.5 ± 0.2	0.18	0.9997

Table 4. Parameters of Eq 2 for Aqueous Solutions of CoCl₂ and CoBr₂

<i>T</i> /K	$d^*/(\text{kg}\cdot\text{m}^{-3})$	$(b_d \pm s_b)/(\text{kg}^2\cdot\text{m}^{-3}\cdot\text{mol}^{-1})$	$(c_d \pm s_c)/(\text{kg}^{2.5}\cdot\text{m}^{-3}\cdot\text{mol}^{-1.5})$	$\delta_d/(\text{kg}\cdot\text{m}^{-3})$	<i>r</i>
CoCl ₂					
291.15	998.60	122.4 ± 0.3	-9.6 ± 0.3	0.09	0.999996
292.15	998.41	122.2 ± 0.3	-9.6 ± 0.3	0.09	0.999995
293.15	998.20	121.1 ± 0.35	-9.5 ± 0.35	0.10	0.999995
294.15	997.99	121.9 ± 0.35	-9.5 ± 0.35	0.11	0.999995
295.15	997.77	121.6 ± 0.4	-9.4 ± 0.4	0.11	0.999994
296.15	997.54	121.4 ± 0.4	-9.2 ± 0.4	0.12	0.999993
297.15	997.30	121.2 ± 0.45	-9.2 ± 0.45	0.13	0.999992
CoBr ₂					
291.15	998.60	199.8 ± 0.4	-15.0 ± 0.35	0.36	0.99997
292.15	998.41	199.6 ± 0.5	-15.0 ± 0.4	0.38	0.99997
293.15	998.20	199.5 ± 0.45	-15.0 ± 0.35	0.36	0.99997
294.15	997.99	199.1 ± 0.5	-14.9 ± 0.4	0.38	0.99997
295.15	997.77	199.7 ± 0.45	-15.3 ± 0.35	0.35	0.99997
296.15	997.54	198.7 ± 0.5	-14.7 ± 0.4	0.39	0.99996
297.15	997.30	198.5 ± 0.55	-14.7 ± 0.4	0.40	0.99996

Owen and Kronick, 1961) does not have a significant effect on the quality of the reproduction of the experimental values.

3.2. Adiabatic Compressibility. The speed of sound and densities calculated by eq 2 were used for the determination of the adiabatic compressibility, κ_S , from Laplace's equation

$$\kappa_S = 1/u^2 d \quad (3)$$

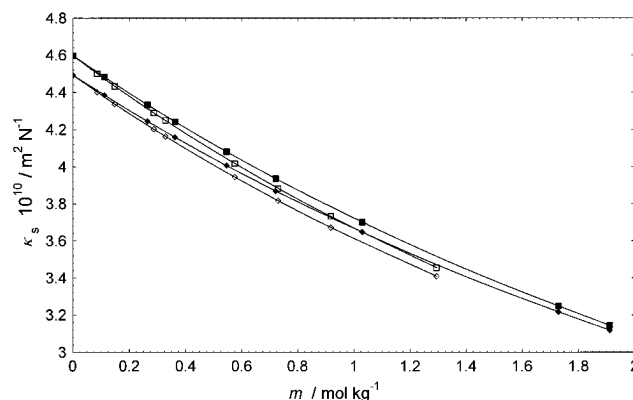


Figure 2. 2. Adiabatic compressibility coefficient vs molality: symbols as in Figure 1, points calculated from eq 3, lines calculated by the spline function.

From Figure 2 CoCl₂ decreases the compressibility of water to a higher degree than CoBr₂ does; the dependence on molality is nonlinear.

3.3. Apparent and Partial Molar Quantities. The apparent molar volumes, Φ_v , and apparent adiabatic compressibilities, Φ_{KS} , of the electrolytes were calculated using the densities and compressibility coefficients calculated from eqs 2 and 3:

$$\Phi_v = \frac{M}{d} - \frac{(d - d^*)}{m d d^*} \quad (4)$$

$$\Phi_{KS} = \frac{\kappa_S d^* - \kappa_S^* d}{m d d^*} + \frac{M \kappa_S}{d} \quad (5)$$

where M = the molecular mass of the electrolyte and κ_S^* = the adiabatic compressibility of pure water calculated from eq 2, using the speed of sound values in pure water of Del Grosso and Mader (1972) and the densities of pure water given in *Tabellenbuch Chemie* (1975). The concentration dependences of the apparent volume and apparent compressibility are described satisfactorily by a Redlich–Mayer-type equation (Redlich and Meyer, 1964)

$$\Phi_x = \Phi_{x,0} + \Phi_{x,1} m^{0.5} + \Phi_{x,2} m \quad (6)$$

(where $x = v$ or KS) used by many authors to reproduce the concentration dependence of these quantities (Millero, 1971; Pogue and Atkinson 1989). Since the directly measurable quantities d and u have been proven to fit in the polynomials in eq 2, the dependence of the apparent molar volumes and compressibilities on concentration could be expected to obey Masson's rule: $\Phi_x = \Phi_{x,0} + \Phi_{x,1} m^{0.5}$ (Owen and Simons, 1957). However, our attempts to fit the experimental values into the empirical Masson-type equation have failed; i.e., the approximation was rather poor. On the other hand, in spite of our findings, the Redlich–Mayer-type equation results in principle from polynomials similar to eq 2 but terminating with m^2 (Hall and Yeager, 1973), i.e., $+k_y m^2$. However, even when the $k_y m^2$ term in the latter polynomial is negligibly small, the $\Phi_{x,2}$ coefficient of eq 6, being a combination of k_u , k_d , κ , and d , may be comparable with $\Phi_{x,1} m^{0.5}$, which results in the Redlich–Mayer equation.

The parameters of eq 6 together with their standard deviations and the correlation coefficients are given in Tables 5 and 6.

The dependences of Φ_{KS} on the molar concentration are shown for a few temperatures in Figure 3, from which one learns that the deviations from Masson's rule become significant at higher electrolyte concentrations.

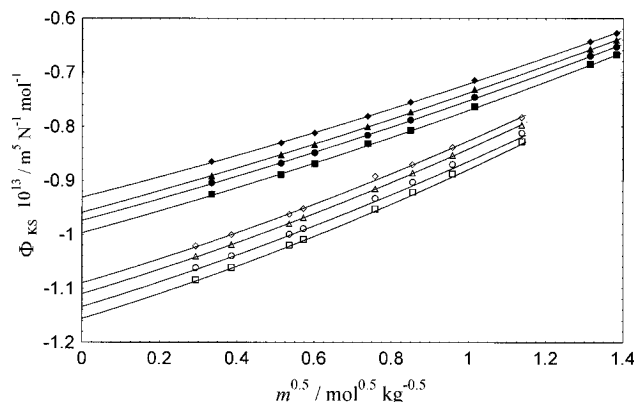


Figure 3. Apparent adiabatic molar compressibility vs $m^{0.5}$; symbols as in Figure 1, points calculated from eq 5, lines calculated from eq 6.

Table 5. Parameters of Eq 6 for Aqueous Solutions of CoCl_2 and CoBr_2

T/K	$(\Phi_{V,0} \pm s) \times 10^6 / (\text{m}^{-3} \cdot \text{mol}^{-1})$	$(\Phi_{V,1} \pm s) \times 10^6 / (\text{m}^3 \cdot \text{kg}^{0.5} \cdot \text{mol}^{-1.5})$	$(\Phi_{V,2} \pm s) \times 10^6 / (\text{m}^3 \cdot \text{kg} \cdot \text{mol}^{-2.5})$	r
CoCl_2				
291.15	7.22 ± 0.05	10.1 ± 0.17	-2.1 ± 0.1	0.9992
292.15	7.44 ± 0.05	10.1 ± 0.16	-2.2 ± 0.1	0.9992
293.15	7.51 ± 0.06	10.2 ± 0.2	-2.3 ± 0.1	0.9998
294.15	7.61 ± 0.06	10.2 ± 0.2	-2.3 ± 0.1	0.9998
295.15	7.75 ± 0.02	10.5 ± 0.05	-2.6 ± 0.03	0.9999
296.15	8.11 ± 0.08	9.9 ± 0.2	-2.2 ± 0.1	0.9998
297.15	8.15 ± 0.09	10.1 ± 0.3	-2.5 ± 0.2	0.9997
CoBr_2				
291.15	18.83 ± 0.07	15.1 ± 0.2	-5.36 ± 0.07	0.9998
292.15	19.00 ± 0.07	15.0 ± 0.2	-5.36 ± 0.07	0.9998
293.15	19.08 ± 0.07	15.1 ± 0.2	-5.4 ± 0.1	0.9998
294.15	19.37 ± 0.07	14.9 ± 0.2	-5.4 ± 0.1	0.9998
295.15	19.56 ± 0.07	14.8 ± 0.3	-5.3 ± 0.1	0.9998
296.15	19.79 ± 0.08	14.7 ± 0.2	-5.3 ± 0.1	0.9998
297.15	19.94 ± 0.09	14.6 ± 0.3	-5.3 ± 0.1	0.9997

Table 6. Parameters of Eq 6 for Aqueous Solutions of CoCl_2 and CoBr_2

T/K	$(\Phi_{KS,0} \pm s) \times 10^{13} / (\text{m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1})$	$(\Phi_{KS,1} \pm s) \times 10^{14} / (\text{m}^5 \cdot \text{kg}^{0.5} \cdot \text{N}^{-1} \cdot \text{mol}^{-1.5})$	$(\Phi_{KS,2} \pm s) \times 10^{15} / (\text{m}^5 \cdot \text{kg} \cdot \text{N}^{-1} \cdot \text{mol}^{-2.5})$	r
CoCl_2				
291.15	-1.156 ± 0.003	2.2 ± 0.1	5.7 ± 0.7	0.9998
292.15	-1.143 ± 0.003	2.2 ± 0.1	5.7 ± 0.7	0.9998
293.15	-1.134 ± 0.003	2.2 ± 0.1	5 ± 1	0.9991
294.15	-1.122 ± 0.003	2.21 ± 0.08	5.2 ± 0.7	0.9998
295.15	-1.110 ± 0.003	2.16 ± 0.08	5.3 ± 0.6	0.9998
296.15	-1.099 ± 0.003	2.13 ± 0.07	5.2 ± 0.6	0.9998
297.15	-1.090 ± 0.003	2.13 ± 0.08	5.1 ± 0.6	0.9998
CoBr_2				
291.15	-0.997 ± 0.003	1.98 ± 0.09	2.9 ± 0.5	0.9997
292.15	-0.985 ± 0.004	1.96 ± 0.09	2.8 ± 0.5	0.9998
293.15	-0.974 ± 0.004	1.94 ± 0.09	2.8 ± 0.5	0.9997
294.15	-0.962 ± 0.004	1.91 ± 0.09	2.7 ± 0.5	0.9997
295.15	-0.959 ± 0.004	1.96 ± 0.09	2.5 ± 0.5	0.9998
296.15	-0.940 ± 0.003	1.85 ± 0.08	2.7 ± 0.5	0.9998
297.15	-0.931 ± 0.003	1.84 ± 0.09	2.6 ± 0.5	0.9997

Table 7 gives a comparison of the values $\Phi_{V,0}$ and $\Phi_{KS,0}$ calculated from eq 6 with the apparent molar volumes and compressibilities for infinite dilution found in the literature. To the best of our knowledge, there are no data in the literature for the apparent (or partial) compressibilities of aqueous CoBr_2 solutions.

The bromide anion, markedly larger than the chloride one, makes both the limiting coefficients $\Phi_{V,0}$ ($\approx \Phi_{V^\infty}$ and $\Phi_{KS,0}$ ($\approx \Phi_{KS^\infty}$) of CoBr_2 larger than the corresponding quantities of CoCl_2 . The relation between the compress-

Table 7. Limiting Apparent Quantities of CoCl_2 , CoBr_2 , Co^{2+} , and Br^- from the Literature and $\Phi_{V,0}$ and $\Phi_{KS,0}$ Calculated from Eq 6

	$\Phi_{V,0} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ (eq 6)	$\Phi_{V^\infty} \times 10^6 / (\text{m}^3 \cdot \text{mol}^{-1})$ (lit.)	$\Phi_{KS,0} \times 10^{13} / (\text{m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1})$ (eq 6)	$\Phi_{KS^\infty} \times 10^{13} / (\text{m}^5 \cdot \text{N}^{-1} \cdot \text{mol}^{-1})$ (lit.)
CoCl_2	8.31^a	9.75^b 9.89^c 11.5^d 10.8^e 11.52^f 10.2^g 10.8^h	-1.079^a	-1.08^i -1.0379^j
CoBr_2	20.1^a		-0.920^a	
Co^{2+}	-27.4^c -38.1^e	-24.0^d -34.8^f -25.4^g -24.6^h -25.8^i		
Br^-	23.8^c 29.1^e	24.7^d 30.1^f		

^a From our results extrapolated to 298.15 K. ^b Pogue and Atkinson (1989). ^c Our results assuming additivity of the limiting ionic apparent volumes and, as cited by Millero (1971), $\Phi_{V^\infty}(\text{H}^+) = 0$ and $\Phi_{V^\infty}(\text{Cl}^-) = 17.8 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. ^d Millero (1971). ^e From our results extrapolated to 298.15 K assuming additivity of the limiting ionic apparent volumes and, as cited by Friedman and Krishnan (1973), $\Phi_{V^\infty}(\text{H}^+) = -5.4 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$ and $\Phi_{V^\infty}(\text{Cl}^-) = 23.2 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. ^f Friedman and Krishnan (1973). ^g Spitzer; quoted by Poque and Atkinson (1989). ^h Spitzer; quoted by Poque and Atkinson (1989). ⁱ Kawaizumi and Nomura (1987). ^j Lo Surdo and Milero (1980). ^k Couture; quoted by Kawaizumi and Nomura (1987). ^l Herrington; quoted by Kawaizumi and Nomura (1987). ^m Spitzer and Singh (1978). ⁿ Millero (1972).

ibilities of both the salts is most probably a consequence of a stronger electrostriction of water by the smaller Cl^- ion.

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