Apparent Molar Compressibilities of Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$ from 288.15 K to 313.15 K

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The speed of sound in aqueous solutions of $Cu(NO_3)_2$ and $CuSO_4$ was measured at concentrations from (0.06 to 2.9) mol kg^{-1} and temperatures from (288.15 to 313.15) K. Density measurements for the same solutions, and for aqueous solutions of $CuCl_2$, allowed the calculation of the apparent molar compressibilities from the speeds of sound measured for $Cu(NO_3)_2$ and $CuSO_4$ solutions and from those taken from the literature for the $CuCl_2$ ones. The dependences of the adiabatic compressibilities, κ_s, and the apparent molar compressibilities, $K_{S,\Phi}$, on concentration and temperature were determined. The limiting apparent compressibilities were determined by extrapolation to infinite dilution.

Introduction

Our earlier ultrasonic studies of simple transition metal salts (Ernst et al., 1996; Ernst and Manikowski, 1997) have been extended to aqueous solutions of $Cu(NO_3)_2$ and $CuSO_4$. The compressibilities of aqueous $CuCl_2$ solutions have been calculated from the speed of sound data of Onori (1990) and the densities measured in our laboratory. Copper salts play an important role in many industrial processes and biological systems. Contrary to the cobalt(II) and nickel(II) ions that form octahedral hydration complexes, the copper(II) ion is supposed to form with the weak field H_2O ligand a tetragonal $Cu(H_2O)_6$ complex because of Jahn−Teller distortion. This symmetry distortion should affect the acoustic and thermodynamic properties of the aqueous copper salt solutions. Furthermore, a comparison of the compressibilities of the three copper salts was expected to convey some insight into how the anions (particularly, the oxyanions) affect the hydration of the copper cation. Although there are in the literature relatively numerous reports concerning the apparent and partial molar volumes of aqueous copper salts, compressibility data of those solutions are scarce.

The adiabatic compressibilities and apparent molar compressibilities have been calculated from the ultrasound speeds and densities measured within the temperature range 288.15 K to 313.15 K for copper nitrate and sulfate and the data reported by Onori (1990) for copper chloride; the partial molar compressibilities at infinite dilution have been determined by extrapolation of the apparent compressibilities to infinite dilution.

Experimental Section

2.1. Chemicals. $CuCl_2\cdot 2H_2O$ (POCh, Gliwice), $Cu(NO_3)_2\cdot 3H_2O$ (POCh, Gliwice), and $CuSO_4$ (Hopkin & Williams) of analytical grade were recrystallized. The stock solutions in redistilled water of specific conductance lower than 5×10^{-4} S·m^{-1}, as well as the solution series used for the measurements, were prepared by weighing. The Cu^{2+} concentrations in the stock solutions determined iodometrically did not differ by more than 0.8% from those calculated from the weighed portions. Because of the undefined content of crystal water in the solid solutes and the good reproducibility of the titration results, concentration values determined analytically were used in the calculations.

Table 1. Speed of Sound in Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$ and $CuCl_2$

m/	u/(m·s^{-1}) for given temp (K)					
(mol·kg^{1})	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$Cu(NO_3)_2$			
0.0632	1469.1	1485.4	1499.7	1512.0	1522.4	1530.9
0.2758	1479.7	1494.5	1507.6	1518.9	1528.6	1536.5
0.6310	1499.5	1512.0	1523.1	1532.6	1540.7	1547.2
1.1536	1530.5	1539.8	1547.9	1554.8	1560.7	1565.3
2.0548	1582.3	1586.9	1590.8	1594.0	1596.5	1598.3
2.8676	1626.5	1627.7	1628.3	1628.3	1627.8	1626.8
			$CuSO_4$			
0.1162	1475.6	1490.9	1504.5	1516.5	1526.7	1535.3
0.2204	1483.1	1498.1	1511.4	1522.9	1532.8	1541.0
0.4279	1498.4	1512.3	1524.6	1535.5	1544.7	1552.4
0.6515	1515.6	1528.5	1539.8	1549.4	1557.3	1563.7
0.8596	1533.0	1544.9	1555.2	1563.9	1570.8	1576.2
1.0622	1551.4	1562.1	1571.2	1578.7	1584.6	1588.9
			$CuCl_2$[a]			
0.4743	1502.4	1516.5	1528.8	1540.1		
0.5534	1507.6	1521.5	1533.2	1543.6		
0.7351	1518.0	1530.8	1542.3	1553.3		
1.0129	1532.4	1544.7	1554.7	1562.7		
1.2098	1543.2	1553.5	1562.3	1570.0		
1.8575	1572.0	1579.4	1585.0	1590.6		

[a] Taken from Onori (1990).

2.2. Speed of Sound and Density Measurements. In the aqueous $Cu(NO_3)_2$ and $CuSO_4$ solutions, the speed of ultrasound was measured by a pulse−echo−overlap device designed and constructed in our laboratory (Zorbski et al., 1995). For the calibration of the measuring cell, water redistilled three times over NaOH and $KMnO_4$, and then degassed, was used (specific conductance, 1×10^{-4} S·m^{-1}). The speed of sound was measured at 5 K intervals for temperatures ranging from 288.15 K to 313.15 K and within the concentration limits (0.06−2.78) mol·kg^{-1} and (0.12−1.06) mol·kg^{-1} for $Cu(NO_3)_2$ and $CuSO_4$, respectively; the precision was better than ±0.15 m·s^{-1}, and the repeatability was 0.06 m·s^{-1}. The temperature inside the ultrasonic cell was controlled with an accuracy of ±0.01 K by a quartz thermometer of resolution ±0.001 K.

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Table 2. Densities of Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$

m/	d/(kg·m^{-3}) for given temp (K)					
(mol·kg^{-1})	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$Cu(NO_3)_2$			
0.0632	1008.63	1007.77	1006.54	1005.07	1003.37	1001.56
0.2758	1040.74	1039.43	1037.94	1036.26	1034.40	1032.36
0.6310	1092.60	1090.84	1088.93	1086.87	1084.67	1082.32
1.1536	1164.59	1162.49	1160.22	1157.78	1155.16	1152.37
2.0548	1279.34	1276.25	1273.11	1269.89	1266.62	1263.28
2.8676	1371.69	1368.24	1364.63	1360.86	1356.92	1352.81
			$CuSO_4$			
0.1293	1020.11	1019.07	1017.78	1016.26	1014.56	1012.69
0.1957	1031.02	1029.85	1028.51	1026.93	1025.16	1023.23
0.2641	1041.81	1040.63	1039.22	1037.59	1035.80	1033.76
0.4550	1071.91	1070.52	1068.93	1067.15	1065.22	1063.09
0.6182	1097.11	1095.58	1093.87	1091.91	1089.95	1087.75
0.7550	1118.07	1116.44	1114.61	1112.63	1110.46	1108.13
1.0620	1164.19	1162.31	1160.24	1158.07	1155.70	1153.20
			$CuCl_2$			
0.0403	1003.99	1003.05	1001.88	1000.49		
0.0518	1005.31	1004.37	1003.17	1001.75		
0.1586	1018.22	1017.15	1015.87	1014.40		
0.4095	1047.60	1046.47	1045.10	1043.49		
0.6789	1078.25	1076.79	1075.15	1073.35		
1.0555	1119.70	1118.02	1116.14	1114.10		
1.5722	1173.85	1171.74	1169.51	1167.15		
2.1262	1228.62	1226.18	1223.62	1220.94		

The densities of the solutions were measured with a bicapillary pycnometer (Bauer and Lewin, 1959) as described earlier (Ernst et al., 1996) (temperature stabilization, ±0.005 K by two thermostats in a cascade arrangement; precision, better than 5×10^{-2} kg·m^{-3}; sensitivity, i.e., the smallest variation in density that can be determined because of the smallest measurable variations of the primary variables, 5×10^{-3} kg·m^{-3}; buoyancy corrections taking into account the ambient temperature, barometric pressure, and relative humidity).

3. Measurement Results and Calculations

3.1. Speeds of Sound and Densities. The measured speeds of sound in the $Cu(NO_3)_2$ and $CuSO_4$ solutions are collected in Table 1 together with those reported by Onori (1990) and used in further calculations. The measured densities of the solutions under test are given in Table 2.

In our previous papers (Ernst et al., 1996; Ernst and Manikowski, 1997), the dependencies of the speed of sound

Table 4. Parameters of Equation 2 for Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$

T/K	d_0/ (kg·m^{-3})	($a_d \pm s_a$)/ (kg^2·m^{-3}·mol^{-1})	($b_d \pm s_b$)/ (kg^3·m^{-3}·mol^{-2})	δ_u/ (kg·m^{-3})	r
		$Cu(NO_3)_2$			
288.15	999.099	152.83 ± 0.12	−7.99 ± 0.05	0.12	0.999 999
293.15	998.203	151.48 ± 0.10	−7.83 ± 0.04	0.10	0.999 999
298.15	997.044	150.30 ± 0.11	−7.72 ± 0.04	0.11	0.999 999
303.15	995.646	149.31 ± 0.10	−7.66 ± 0.04	0.10	0.999 999
308.15	994.030	148.40 ± 0.08	−7.63 ± 0.03	0.08	0.999 999
313.15	992.219	147.61 ± 0.02	−7.63 ± 0.01	0.02	0.999 999
		$CuSO_4$			
288.15	999.099	163.51 ± 0.26	−7.66 ± 0.29	0.12	0.999 999
293.15	998.203	162.28 ± 0.23	−7.37 ± 0.26	0.10	0.999 999
298.15	997.044	161.33 ± 0.22	−7.33 ± 0.25	0.10	0.999 999
303.15	995.646	160.35 ± 0.23	−7.04 ± 0.27	0.11	0.999 999
308.15	994.030	159.70 ± 0.21	−7.10 ± 0.24	0.09	0.999 999
313.15	992.219	159.01 ± 0.21	−7.05 ± 0.24	0.10	0.999 999
		$CuCl_2$			
288.15	999.099	120.64 ± 0.09	−5.99 ± 0.05	0.08	0.999 9998
293.15	998.203	119.80 ± 0.11	−5.93 ± 0.06	0.09	0.999 9997
298.15	997.044	119.11 ± 0.14	−5.92 ± 0.08	0.11	0.999 9996
303.15	995.646	118.53 ± 0.15	−5.93 ± 0.09	0.13	0.999 9995

and density on the molality of the solutions of cobalt and nickel salts were represented by a polynomial suggested by Owen and Simons (1957) and Owen and Kronick (1961) (although these authors have applied molar concentrations instead of molalities). Since it turned out that this polynomial leads to unsatisfactory results for the speed of sound in the $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$ solutions, it was replaced by the following one:

$$u = u_0 + a_u m + b_u m^{1.5} + c_u m^2 \qquad (1)$$

where u_0 is the speed in pure water taken from Del Grosso and Mader (1972).

The densities of the solutions studied can be reproduced satisfactorily by the following polynomial:

$$d = d_0 + a_d m + b_d m^2 \qquad (2)$$

where d_0 is the density of water taken from the *Tabellenbuch Chemie* (1975).

The coefficients of the above polynomials, their standard deviations, and their mean deviations from the regression line are given in Tables 3 and 4.

The concentration dependencies of the speed of sound in the solutions studied are shown in Figure 1.

Table 3. Parameters of Equation 1 for Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$

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$^{1.5}$·s^{1}·mol$^{-1.5}$)	($c_u \pm s_c$)/ (m·kg^2·s^{-1}·mol^{-2})	δ_u/ (m·s^{-1})	r
			$Cu(NO_3)_2$			
288.15	1465.931	40.27 ± 1.73	23.28 ± 2.66	−8.26 ± 0.99	0.29	0.999 997
293.15	1482.343	35.12 ± 2.02	21.02 ± 3.11	−6.98 ± 1.16	0.34	0.999 995
298.15	1496.687	31.55 ± 2.73	17.84 ± 4.20	−5.53 ± 1.57	0.46	0.999 989
303.15	1509.127	28.30 ± 3.36	15.38 ± 5.17	−4.46 ± 1.93	0.56	0.999 990
308.15	1519.808	24.38 ± 3.49	14.83 ± 5.37	−4.11 ± 2.00	0.58	0.999 974
313.15	1528.864	18.88 ± 2.91	17.26 ± 4.48	−4.86 ± 1.67	0.49	0.999 978
			$CuSO_4$			
288.15	1465.931	98.35 ± 1.44	−63.92 ± 3.56	45.24 ± 2.17	0.09	0.999 9992
293.15	1482.343	85.28 ± 0.75	−46.53 ± 1.85	35.59 ± 1.13	0.05	0.999 9998
298.15	1496.687	77.90 ± 1.36	−39.41 ± 3.38	30.38 ± 2.06	0.09	0.999 9990
303.15	1509.127	73.76 ± 2.19	−38.02 ± 5.43	29.13 ± 3.30	0.14	0.999 9970
308.15	1519.808	70.73 ± 3.76	−38.34 ± 9.34	28.02 ± 5.68	0.24	0.999 9903
313.15	1528.864	65.20 ± 3.31	−35.62 ± 8.12	26.40 ± 4.94	0.21	0.999 9939
			$CuCl_2$			
288.15	1465.931	110.52 ± 1.64	−58.44 ± 3.06	14.02 ± 1.39	0.15	0.999 998
293.15	1482.343	103.06 ± 2.00	−52.53 ± 3.73	11.13 ± 1.69	0.18	0.999 997
298.15	1496.687	98.49 ± 2.07	−51.71 ± 3.87	10.65 ± 1.75	0.19	0.999 996
303.15	1509.127	98.22 ± 2.39	−59.50 ± 4.47	14.23 ± 2.02	0.22	0.999 994

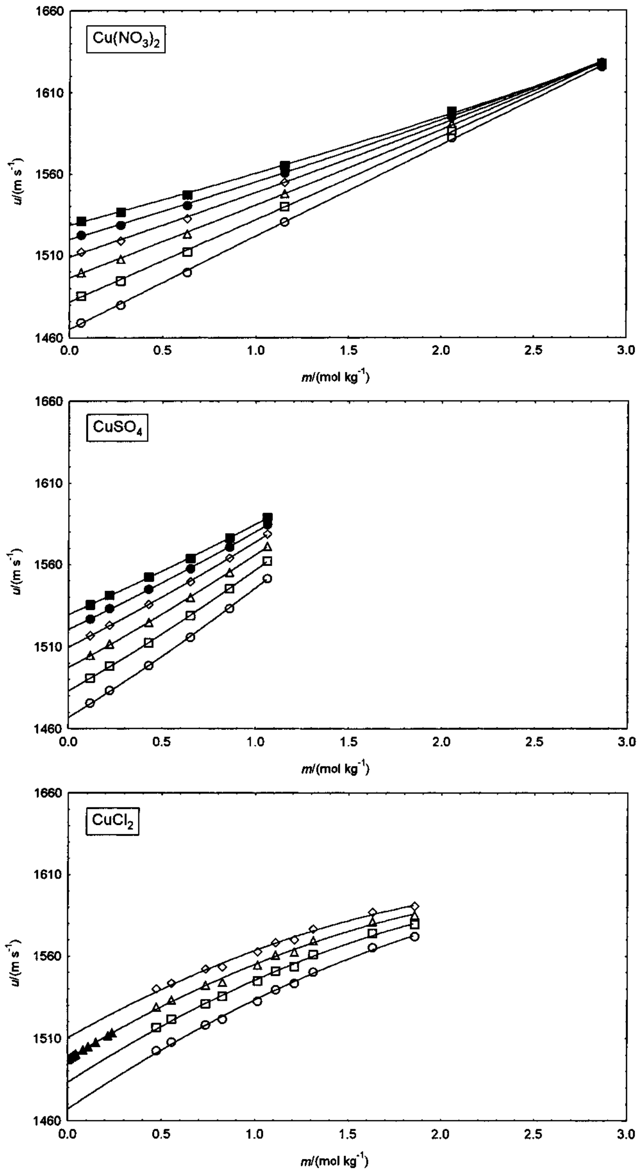

Figure 1. Speed of sound vs molality. $Cu(NO_3)_2$ and $CuSO_4$ (this work): (○) 288.15 K; (□) 293.15 K; (△) 298.15 K; (◇) 303.15 K; (●) 308.15 K; (■) 313.15 K. $CuCl_2$ (Onori, 1990): (○) 288.15 K; (□) 293.15 K; (△) 298.15 K; (◇) 303.15 K. $CuCl_2$ (Kawaizumi, 1987): (▲) 298.15 K. Points from experiment solid lines calculated from eq 1.

As in most of the aqueous electrolyte solutions, the speed of sound increases, although clearly nonlinearly, with increasing electrolyte concentration which indicates that the decrease of the adiabatic compressibility with increasing concentration prevails over the density increase. However, the dependence of the speed of sound in the $CuCl_2$ solutions, reported earlier (Onori, 1990; Kawaizumi et al., 1987) differs from those found for the copper sulfate and copper nitrate solutions in that they are depicted by convex curves $[(\partial^2 u/\partial m^2) < 0]$, while for most of the aqueous electrolyte solutions, similarly to the other two copper salts under test, the $u(m)$ curves are concave shaped. It is also worthwhile noting that the speeds of sound in the $Cu(NO_3)_2$ solutions are converging to a common value at about $m \approx 2.9$, which suggests that at higher concentrations the temperature dependence of the speed should become reversed. A similar weak convergence of the $u(m)$ curves is observed for the $CuCl_2$ and $CuSO_4$ solutions.

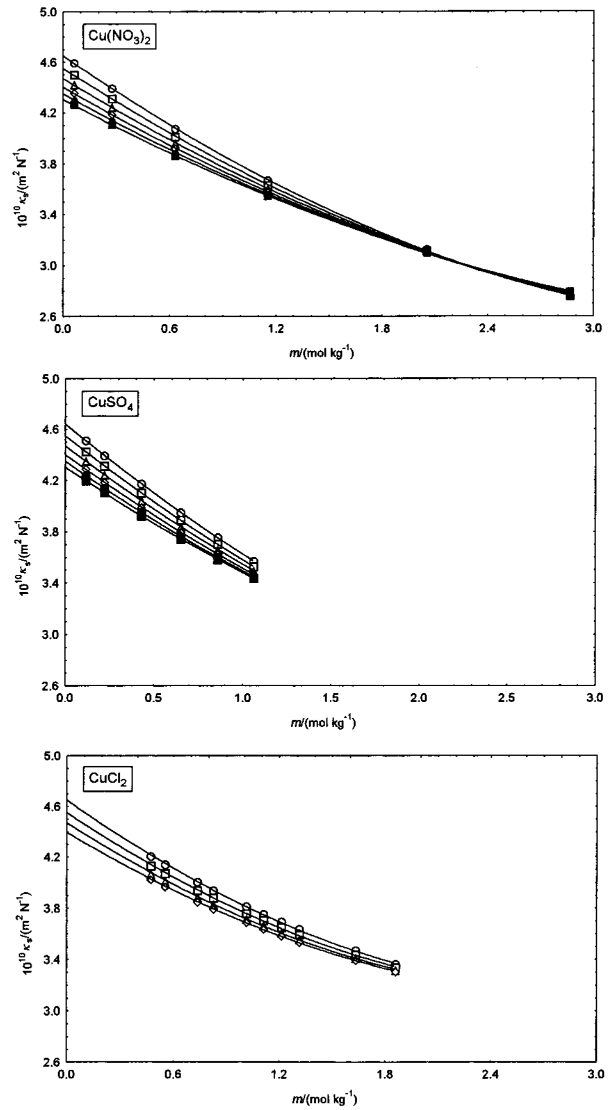

Figure 2. Adiabatic compressibility vs molality for $CuCl_2$, $Cu(NO_3)_2$, and $CuSO_4$. Symbols as in Figure 1. Points calculated from eq 3; lines calculated by the spline function.

3.2. Adiabatic Compressibility. The adiabatic compressibilities, $\kappa_s = -(1/V)(\partial V/\partial P)_S$, determined from the speeds of sound and densities 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), are shown as functions of molality in Figure 2. The speed of sound data reported by Onori (1990) were used for the $CuCl_2$ solutions. As expected, the compressibilities of the relatively dilute solutions decrease with increasing concentration and temperature; however, for the $Cu(NO_3)_2$ solutions, the temperature dependence of the adiabatic compressibility becomes reversed at $m \approx 2$. The convergence of the $\kappa_s(m)$ curves for the other two copper salts suggests a similar reversal of the temperature dependence of κ_s at higher concentrations.

3.3. Apparent Molar Compressibilities. The apparent molar compressibilities,

$$K_{S,\Phi} \equiv \frac{1}{n_s}(K_S - n_0 K_{S,0}) = \frac{V\kappa_S - n_0 \bar{V}_0 \kappa_{S,0}}{n_s}$$

Table 5. Apparent Molar Compressibilities of Aqueous $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$ Calculated from Equation 4

m/(mol·kg^{-1})	10^{14} $K_{S,\Phi}$/(m^5·N^{1-}·mol^{-1}) for given temp (K)					
	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
			$Cu(NO_3)_2$			
0.0632	−8.89	−8.10	−7.61	−7.00	−6.63	−6.34
0.2758	−8.49	−7.80	−7.25	−6.79	−6.40	−6.10
0.6310	−7.93	−7.30	−7.80	−6.38	−6.03	−5.74
1.1536	−7.21	−6.67	−6.22	−5.85	−5.53	−5.27
2.0548	−6.21	−5.77	−5.40	−5.09	−4.81	−4.59
2.8676	−5.50	−5.12	−4.80	−4.53	−4.29	−4.09
			$CuSO_4$			
0.1162	−12.13	−10.32	−10.80	−10.34	−9.99	−9.70
0.2204	−11.89	−10.14	−10.61	−10.12	−9.80	−9.51
0.4279	−11.41	−10.73	−10.22	−9.79	−9.43	−9.12
0.6515	−10.92	−10.30	−9.81	−9.39	−9.05	−8.73
0.8596	−10.50	−9.93	−9.46	−9.05	−8.71	−8.40
1.06218	−10.10	−9.57	−9.12	−8.74	−8.39	−8.09
			$CuCl_2$			
0.4743	−9.90	−9.28	−8.84	−8.33		
0.5537	−9.57	−8.97	−8.54	−8.04		
0.7351	−8.83	−8.26	−7.85	−7.38		
0.8259	−8.46	−7.90	−7.50	−7.05		
1.0129	−7.69	−7.17	−6.78	−6.37		
1.1103	−7.28	−6.79	−6.41	−6.02		
1.2098	−6.88	−6.39	−6.02	−5.65		
1.3114	−6.46	−5.99	−5.63	−5.28		
1.6308	−5.14	−4.73	−4.40	−4.12		
1.8575	−4.20	−3.84	−3.53	−3.29		

(where $K_S = -(\partial V/\partial P)_S$ is the total compressibility of the solution at its constant entropy S, $K_{S,0} = -(\partial V_0/\partial P)_{S_0}$ is the molar compressibility of pure water at its constant entropy S_0, V is the total volume of the solution, $\bar{V}_0$ is the molar volume of pure water, n_0 and n_S are the numbers of water and solute in the solution of volume V, respectively, $\kappa_S = -(1/V)(\partial V/\partial P)_S$ is the adiabatic compressibility of the solution, and $\kappa_{S,0} = -(1/V)(\partial \bar{V}_0/\partial P)_{S_0}$ is the adiabatic compressibility of pure water), have been calculated from the following equation:

$$K_{S,\Phi} = \frac{\kappa_S d_0 - \kappa_{S,0} d}{m d d_0} + \frac{M \kappa_S}{d} \tag{4}$$

where M is the molecular mass of the salt, d and d_0 are the densities of the solution and pure water, respectively, and m is the molality of the solution. They have been collected in Table 5.

As in our previous papers, the concentration dependencies of the apparent compressibility has been described by the following Redlich−Mayer type equation (Redlich and Mayer, 1964):

$$K_{S,\Phi} = K^{\infty}_{S,\Phi} + A_{K_S} m^{0.5} + B_{K_S} m \tag{5}$$

The parameters of eq 5 are given in Table 6. The dependencies of $K_{S,0}$ on $m^{0.5}$ shown in Figure 3 indicate significant deviations from the Masson rule.

The temperature dependence of the limiting apparent compressibilities, shown in Figure 4, can be described by the following simple polynomial:

$$K^{\infty}_{S,\Phi} = A + BT + CT^2 \tag{6}$$

with the coefficients given in Table 7. Distinct from the limiting apparent compressibilities of the $Cu(NO_3)_2$ and $CuSO_4$ solutions, the copper chloride one shows a linear temperature dependence. The partial molar compressibilities at infinite dilution become more positive with increasing temperature; as suggested in the literature (Hall and Yeager, 1973), this fact is probably due to a decrease of

Table 6. Parameters of Equation 5 for Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$

T/K	$10^{13}(K^{\infty}_{S,\Phi} \pm s)$/(m^5·N^{-1}·mol^{-1})	$10^{14}(A_{K_S} \pm s)$/(m^5·kg$^{-0.5}$·N^{-1}·mol$^{-1.5}$)	$10^{14}(B_{K_S} \pm s)$/(m^5·kg·N^{-1}·mol$^{-2.5}$)	r
		$Cu(NO_3)_2$		
288.15	−0.93 ± 0.009	0.56 ± 0.12	1.31 ± 0.21	0.9995
293.15	−0.84 ± 0.010	0.59 ± 0.11	0.97 ± 0.23	0.9930
298.15	−0.79 ± 0.005	0.64 ± 0.06	0.81 ± 0.13	0.9970
303.15	−0.72 ± 0.009	0.57 ± 0.11	0.65 ± 0.20	0.9910
308.15	−0.69 ± 0.007	0.51 ± 0.08	0.67 ± 0.16	0.9940
313.15	−0.66 ± 0.006	0.45 ± 0.07	0.71 ± 0.13	0.9960
		$CuSO_4$		
288.15	−1.26 ± 0.004	1.65 ± 0.10	0.70 ± 0.13	0.99995
293.15	−1.18 ± 0.006	1.71 ± 0.13	0.21 ± 0.18	0.99990
298.15	−1.11 ± 0.004	1.51 ± 0.10	0.37 ± 0.14	0.99991
303.15	−1.06 ± 0.006	1.42 ± 0.13	0.37 ± 0.18	0.99984
308.15	−1.03 ± 0.003	1.36 ± 0.07	0.47 ± 0.09	0.99996
313.15	−1.01 ± 0.005	1.24 ± 0.12	0.65 ± 0.17	0.99986
		$CuCl_2$		
288.15	−1.18 ± 0.003	−0.12 ± 0.04	4.17 ± 0.07	0.9999
293.15	−1.11 ± 0.004	−0.11 ± 0.04	3.99 ± 0.09	0.9999
298.15	−1.06 ± 0.003	−0.14 ± 0.03	3.91 ± 0.06	0.9999
303.15	−1.00 ± 0.003	−0.13 ± 0.03	3.71 ± 0.07	0.9999

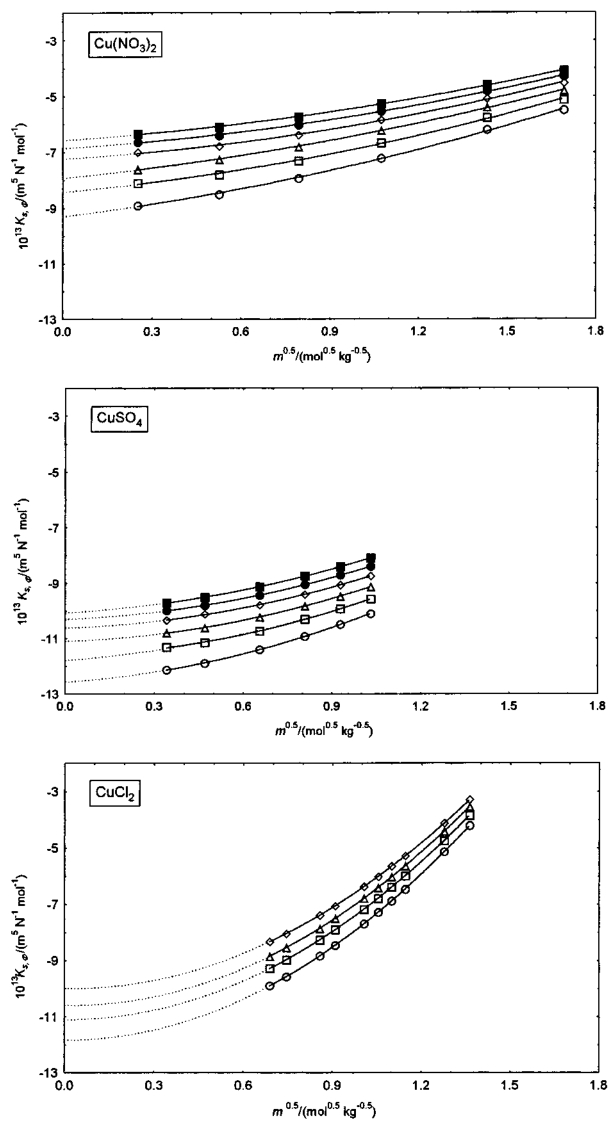

Figure 3. Apparent adiabatic molar compressibility vs $m^{0.5}$ for $CuCl_2$, $Cu(NO_3)_2$, and $CuSO_4$. Symbols as in Figure 2; points calculated from eq 4; lines calculated from eq 5.

the ability of the ions to electrostrict the solvent at higher temperatures, which may be offset partially by some

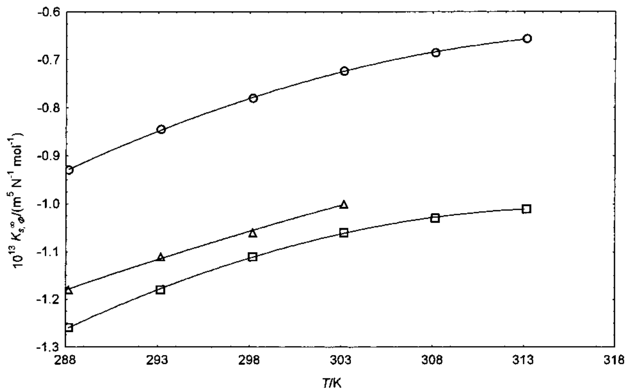

Figure 4. Limiting apparent adiabatic molar compressibility vs temperature: (○) $Cu(NO_3)_2$; (□) $CuSO_4$; (△) $CuCl_2$. points calculated from eq 5; lines calculated from eq 6.

Table 7. Parameters of Equation 6 for Aqueous Solutions of $Cu(NO_3)_2$, $CuSO_4$, and $CuCl_2$

	$10^{13}(A \pm s_A)$/ ($m^5 \cdot N^{-1} \cdot mol^{-1}$)	$10^{14}(B \pm s_B)$/ ($m^5 \cdot N^{-1} \cdot mol^{-1} \cdot K^{-1}$)	$10^{16}(C \pm s_C)$/ ($m^5 \cdot N^{-1} \cdot mol^{-1} \cdot K^{-2}$)	r
$Cu(NO_3)_2$	−29.06 ± 1.09	1.78 ± 0.07	0.30 ± 0.01	0.999 90
$CuSO_4$	−33.79 ± 1.29	2.08 ± 0.09	0.30 ± 0.01	0.999 90
$CuCl_2$	−4.58 ± 0.16	0.12 ± 0.01		0.998 0

Table 8. Comparison of Limiting Apparent Molar Compressibilities at 298.15 K Obtained in This Study and Reported in the Literature

	$K_{S,\Phi}^{\infty} \times 10^{14}/(m^5 \cdot N^{-1} \cdot mol^{-1})$	
	eq 5	lit.
$Cu(NO_3)_2$	−7.9[a]	
$CuSO_4$	−11.1[a]	
$CuCl_2$	−10.6[a]	−10.7[b]
		−9.9[c]
$CoCl_2$		−10.79[d]
		−10.8[c]
		−10.379[b]
$NiCl_2$		−11.22[e]
		−10.819[b]
		−10.62[c]

[a] This work. [b] Lo Surdo and Millero (1980). [c] Kawaizumi et al. (1987). [d] Ernst et al. (1996). [e] Ernst and Manikowski (1997).

decrease of the structure breaking effect.

The limiting adiabatic apparent molar compressibilities found for the copper salt solutions under test, $K_{S,\Phi}^{\infty}$, together with those reported in the literature for aqueous $CuCl_2$, are collected in Table 8. For comparison, the corresponding compressibilities of the $CoCl_2$ and $NiCl_2$ solutions reported earlier are given too. There is evidently no correlation between the possible geometry of the hydration complexes (slightly distorted octahedron for $Co(H_2O)_6^{2+}$, regular octahedron for $Ni(H_2O)_6^{2+}$, and strongly tetragonally distorted octahedron for $Cu(H_2O)_6^{2+}$) and the partial adiabatic compressibilities although a lower electrostriction of the water molecules by the copper cation could be expected because of the elongated poles in the D_{4h} structure of the $Cu(H_2O)_6^{2+}$ complex (Pogue and Atkinson, 1989). Also the size and the ability of the interactions of the anions with water molecules (stronger hydrogen bonds of oxyanions with the surrounding water molecules) does not affect markedly the limiting apparent compresssibilities of the solutions studied; however, some effect of the anions upon the concentration dependences of the speed of sound (Figure 1) and the apparent compressibility (Figure 3), as well as on the temperature dependence of the limiting apparent compressibility (Figure 4), can be noted (probably because of the possible association equilibria).

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