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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

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The densities and speeds of sound in aqueous solutions of $NiCl_2$ and $NiBr_2$ were measured at temperatures ranging from (291.15 to 297.15) K and over the concentration range (0.1 to 1.4) $mol\cdot kg^{-1}$. The dependences of the apparent molar volumes, V_Φ, apparent molar adiabatic compressibilities, $K_{s,\Phi}$, and the adiabatic compressibility coefficients, κ_s, on concentration and temperature were determined.

1. Introduction

The measurements on aqueous solutions of $NiCl_2$ and $NiBr_2$ were made as a part of our ultrasonic, volumetric and viscosimetric research program on aqueous and nonaqueous solutions of simple transition-metal salts. The measurement results for aqueous solutions of $CoCl_2$ and $CoBr_2$ have been reported in our previous paper (Ernst *et al.* 1996). Our interest in the nickel salts results from the role they play (particularly nickel chloride) in many industrial processes. The simple salts of nickel are often considered to be very useful subjects for testing experimental rules and theoretical hypotheses (Weingartner and Hertz, 1978; Powell and Neilson, 1990; Cordeiro *et al.*, 1993). From the results presented in this paper the apparent molar volumes and compressibilities were calculated. The corresponding partial molar quantities were found by extrapolation to infinite dilution.

2. Experimental Section

2.1. Chemicals. $NiCl_2\cdot 6H_2O$ of analytical grade (POCH, Gliwice, Poland) and $NiBr_2$ (Aldrich) were recrystallized from redistilled water. The stock solutions were prepared by mass using recrystallized salts and redistilled water having specific conductances lower than 1.5×10^{-4} $S\cdot m^{-1}$. The solution series used for the measurements were prepared from the stock solutions by weighing. The electrolyte concentrations in the stock solutions were controlled by gravimetric determinations of the Cl^- and Br^- concentrations (with an accuracy better than 0.2%) and by atomic emission spectroscopy (inductively coupled plasma, ICP) determination of the concentration of Ni^{2+} with an accuracy of 0.9% and a precision better than 0.2%.

2.2. Speed of Sound and Density Measurements. The speed of sound was measured by a sing-around measuring set as described in our previous paper (Ernst *et al.*, 1996) . The precision of the speed of sound measurements was ±0.05 $m\cdot s^{-1}$ within the calibration limits, i.e., for velocities ranging from (1472 to 1519) $m\cdot s^{-1}$, and decreased gradually for higher velocities, achieving a value of ±0.5 $m\cdot s^{-1}$ for 1780 $m\cdot s^{-1}$ (for the confidence level 95%). The repeatability was ±0.02 $m\cdot s^{-1}$ 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 thousandth of a degree (Ernst *et al.*, 1993).

The densities of the solutions were measured with a bicapillary pycnometer (Bauer and Lewin, 1959) calibrated as described previously (Ernst *et al.*, 1996). The temperature during the measurements was stabilized to ±0.005 K using two thermostats in a cascade arrangement. Buoyancy corrections were made taking into account the air density at the measured ambient temperature, the barometric pressure, and the relative humidity. The sensitivity, i.e., the smallest variation in density that can be determined taking into account the smallest measurable variations of the primary variables (mass, temperature, meniscus height in the picnometer capillary), is 5×10^{-3} $kg\cdot m^3$. According to Bauer and Lewin (1959), the highest attainable precision of density measurements carried out with capillary picnometers is 5×10^{-3} $kg\cdot m^3$, while the standard deviations of our measurements indicate a precision better than 5×10^{-2} $kg\cdot m^3$.

3. Measurement Results and Calculations

3.1. Speed of Sound and Densities. The speed of sound, *u*, and densities, *d*, were measured at 3-K intervals from 291.15 K to 297.15 K and for molalities, *m*, ranging from 0.21 $mol\cdot kg^{-1}$ to 1.44 $mol\cdot kg^{-1}$ for $NiCl_2$ and at 1-K intervals from 291.15 K to 297.15 K and for molalities of 0.09 $mol\cdot kg^{-1}$ to 1.23 $mol\cdot kg^{-1}$ for $NiBr_2$. 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 the following polynomial:

$$y = a_y + b_y m + c_y m^{1.5} \tag{1}$$

where $y = u$ or d, $a_u = u^0$ is the speed of sound in pure water (Del Grosso and Mader, 1972), and $a_d = d^0$ is the density of pure water (*Tabellenbuch Chemie*, 1975).

The coefficients of the polynomials, their standard deviations, *s*, 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 evidences that the dependence of the speed of sound shows only a very slight deviation from linearity and $NiCl_2$ affects the speed of sound much stronger than $NiBr_2$ does.

3.2. Adiabatic Compressibility. The speeds of sound and densities calculated from eq 1 were used for the

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Table 1. Speed of Sound in Aqueous Solutions of $NiCl_2$ and $NiBr_2$

	$u/(m\cdot s^{-1})$						
$m/(mol\cdot kg^{-1})$	291.15 K	292.15 K	293.15 K	294.15 K	295.15 K	296.15 K	297.15 K
				$NiCl_2$			
0.2075	1495.93			1504.86			1513.03
0.2564	1500.56			1509.36			1517.43
0.4356	1517.42			1525.74			1533.43
0.5156	1524.92			1532.97			1540.49
0.7707	1548.67			1555.83			1562.79
1.046	1573.83			1580.04			1586.39
1.4369	1609.12			1613.79			1619.26
				$NiBr_2$			
0.0912	1478.48	1481.60	1484.64	1487.61	1490.50	1492.31	1496.05
0.1573	1480.23	1483.28	1486.30	1489.15	1491.98	1494.73	1497.34
0.2701	1483.46	1486.41	1489.28	1492.08	1494.81	1497.47	1500.07
0.3552	1485.82	1488.70	1491.51	1494.24	1496.91	1499.51	1502.04
0.5015	1490.45	1493.24	1495.96	1498.61	1501.19	1503.70	1506.14
0.6251	1494.63	1497.27	1499.84	1502.35	1504.78	1507.15	1509.47
0.8830	1503.74	1506.13	1508.47	1510.74	1512.95	1515.12	1517.25
1.0901	1511.82	1514.03	1516.18	1518.27	1520.31	1522.29	1524.21
1.2330	1517.37	1519.43	1521.45	1523.42	1525.35	1527.24	1529.08

Table 2. Densities of Aqueous Solutions of $NiCl_2$ and $NiBr_2$

	$d/(kg\cdot m^{-3})$						
$m/(mol\cdot kg^{-1})$	291.15 K	292.15 K	293.15 K	294.15 K	295.15 K	296.15 K	297.15 K
				$NiCl_2$			
0.2075	1023.77			1023.05			1022.25
0.2564	1029.62			1028.88			1028.05
0.4356	1050.84			1050.04			1049.15
0.5156	1060.24			1059.38			1058.47
0.7707	1089.91			1088.90			1087.91
1.046	1121.16			1120.15			1119.13
1.4369	1164.75			1163.69			1162.66
				$NiBr_2$			
0.0912	1016.37	1016.15	1015.92	1015.68	1015.43	1015.17	1014.91
0.1573	1028.54	1028.33	1028.09	1027.84	1027.57	1027.29	1027.00
0.2701	1051.25	1051.01	1050.77	1050.51	1050.24	1019.96	1049.67
0.3552	1066.34	1066.11	1065.85	1065.56	1065.25	1064.91	1064.55
0.5015	1094.01	1093.71	1093.40	1093.10	1092.79	1092.48	1092.16
0.6251	1117.90	1117.54	1117.20	1116.88	1116.98	1116.31	1116.06
0.8830	1163.87	1163.52	1163.16	1162.80	1162.42	1162.05	1161.67
1.0901	1202.43	1202.04	1201.65	1201.26	1200.86	1200.45	1200.04
1.2330	1226.59	1226.22	1225.84	1225.44	1225.03	1224.60	1224.16

Table 3. Parameters of Eq 1 for Aqueous Solutions of $NiCl_2$ and $NiBr_2$

T/K	$u^0/(m\cdot s^{-1})$	$(b_u \pm s)/(m\cdot kg\cdot s^{-1})$	$(c_u \pm s)/m\cdot kg^{1.5}\cdot s^{-1}\cdot mol^{-1.5})$	$\delta_u/(m\cdot s^{-1})$	r
			$NiCl_2$		
291.15	1476.04	98.10 ± 0.15	−4.60 ± 0.14	0.05	0.999999
294.15	1485.37	96.78 ± 0.07	−6.17 ± 0.07	0.05	0.999999
297.15	1493.98	94.78 ± 0.07	−6.32 ± 0.07	0.05	1
			$NiBr_2$		
291.15	1476.04	21.0 ± 0.4	11.2 ± 0.5	0.14	0.99991
292.15	1479.23	20.2 ± 0.4	11.1 ± 0.4	0.14	0.99990
293.15	1482.34	19.5 ± 0.5	11.0 ± 0.5	0.14	0.99990
294.15	1485.34	18.7 ± 0.4	10.9 ± 0.4	0.13	0.99989
295.15	1488.32	18.0 ± 0.5	10.8 ± 0.5	0.14	0.99990
296.15	1491.19	16.6 ± 0.8	11.6 ± 0.9	0.26	0.9995
297.15	1493.98	16.5 ± 0.4	10.6 ± 0.4	0.15	0.99987

determination of the adiabatic compressibility, κ_s, using the Laplace's equation:

$$\kappa_s = 1/u^2 d \tag{2}$$

From Figure 2 one learns that $NiCl_2$ decreases the compressibility of water to a higher degree than $NiBr_2$ does, the dependence of the compressibility on molality being evidently nonlinear.

Table 4. Parameters of Eq 1 for Aqueous Solutions of $NiCl_2$ and $NiBr_2$

T/K	$d^0/(kg\cdot m^{-3})$	$(b_d \pm s)/(kg^2\cdot m^{-3}\cdot mol^{-1})$	$(c_d \pm s)/(kg^{2.5}\cdot m^{-3}\cdot mol^{-1.5})$	$\delta_u/(kg\cdot m^{-3})$	r
			$NiCl_2$		
291.15	998.59	125.5 ± 0.2	−8.2 ± 0.2	0.07	0.999998
294.15	997.99	124.7 ± 0.2	−7.8 ± 0.2	0.06	0.999998
297.15	997.30	123.9 ± 0.15	−7.4 ± 0.2	0.06	0.999999
			$NiBr_2$		
291.15	998.59	200.3 ± 1.7	−13.5 ± 2	0.54	0.99995
292.15	998.41	200.0 ± 1.7	−13.4 ± 1.7	0.53	0.99996
293.15	998.20	199.8 ± 1.7	−13.3 ± 1.7	0.52	0.99995
294.15	997.99	199.5 ± 1.7	−13.2 ± 1.7	0.53	0.99996
295.15	997.77	199.8 ± 2.0	−13.5 ± 1.9	0.60	0.99994
296.15	997.54	199.1 ± 2.0	−13.1 ± 1.8	0.58	0.99995
297.15	997.30	199.0 ± 1.8	−13.1 ± 1.9	0.58	0.99995

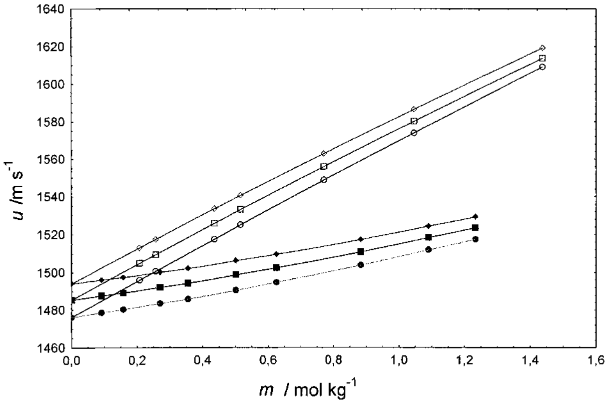

Figure 1. Speed of sound vs molality. $NiCl_2$: (◇) 297.15 K, (□) 294.15 K, (○) 291.15 K. $NiBr_2$: (◆) 297.15 K, (■) 294.15 K, (●) 291.15 K. Points from experiment; solid lines calculated from eq 1.

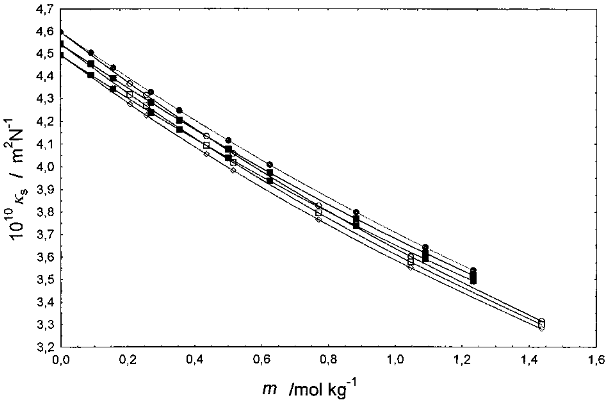

Figure 2. Adiabatic compressibility coefficient vs molality. Symbols as in Figure 1. Points calculated from eq 3; lines calculated by the spline function.

3.3. Apparent and Partial Molar Quantities. The apparent molar volumes, V_Φ, and apparent adiabatic compressibilities, $K_{s,\Phi}$, of the electrolytes were calculated using the densities and compressibility coefficients calculated from eqs 1 and 2:

$$V_\Phi = \frac{M}{d} - \frac{(d - d^0)}{mdd^0} \tag{3}$$

$$K_{s,\Phi} = \frac{\kappa_s d^0 - \kappa_s^0 d}{mdd^0} + \frac{M\kappa_s}{d} \tag{4}$$

where M is the molecular mass of the electrolyte and κ_s* is 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).

Table 5. Parameters of Eq 5 for Aqueous Solutions of $NiCl_2$ and $NiBr_2$

T/K	$10^6 \times (V_{\Phi}^{\infty} \pm s)/(m^3 \cdot mol^{-1})$	$10^6 \times (A_v \pm s)/(m^3 \cdot kg^{-0.5} \cdot mol^{-1.5})$	$10^6 \times (B_v \pm s)/(m^3 \cdot kg \cdot mol^{-2.5})$	r
		$NiCl_2$		
291.15	3.80 ± 0.05	9.0 ± 0.1	−1.97 ± 0.08	0.99996
294.15	4.60 ± 0.04	8.4 ± 0.1	−1.79 ± 0.07	0.99997
297.15	5.13 ± 0.09	8.4 ± 0.2	−2.07 ± 0.15	0.9998
		$NiBr_2$		
291.15	18.02 ± 0.02	13.85 ± 0.08	−5.32 ± 0.05	0.9998
292.15	18.16 ± 0.02	13.78 ± 0.08	−5.33 ± 0.05	0.99990
293.15	18.36 ± 0.02	13.68 ± 0.07	−5.32 ± 0.05	0.9998
294.15	18.58 ± 0.02	13.57 ± 0.07	−5.32 ± 0.05	0.9998
295.15	18.30 ± 0.02	13.99 ± 0.07	−5.38 ± 0.05	0.9998
296.15	18.94 ± 0.03	13.44 ± 0.08	−5.33 ± 0.05	0.99997
297.15	19.07 ± 0.03	13.42 ± 0.07	−5.33 ± 0.04	0.99998

Table 6. Parameters of Eq 5 for Aqueous Solutions of $NiCl_2$ and $NiBr_2$

T/K	$10^{13} \times (K_{s,\Phi}^{\infty} \pm s)/(m^5 \cdot N^{-1} \cdot mol^{-1})$	$10^{14} \times (A_{Ks} \pm s)/(m^5 \cdot kg^{-0.5} \cdot N^{-1} \cdot mol^{-1.5})$	$10^{15} \times (B_{Ks} \pm s)/(m^5 \cdot kg \cdot N^{-1} \cdot mol^{-2.5})$	r
		$NiCl_2$		
291.15	−1.202 ± 0.004	2.26 ± 0.09	5.4 ± 0.6	0.99993
294.15	−1.170 ± 0.003	2.29 ± 0.09	4.8 ± 0.5	0.99994
297.15	−1.134 ± 0.004	2.1 ± 0.1	4.9 ± 0.6	0.99994
		$NiBr_2$		
291.15	−0.987 ± 0.002	1.32 ± 0.07	6.3 ± 0.5	0.9997
292.15	−0.976 ± 0.002	1.31 ± 0.07	6.1 ± 0.5	0.9997
293.15	−0.965 ± 0.002	1.30 ± 0.06	6.1 ± 0.4	0.9998
294.15	−0.952 ± 0.002	1.27 ± 0.06	6.0 ± 0.4	0.9998
295.15	−0.949 ± 0.002	1.33 ± 0.06	5.7 ± 0.4	0.9998
296.15	−0.931 ± 0.002	1.21 ± 0.06	5.9 ± 0.4	0.9998
297.15	−0.927 ± 0.002	1.26 ± 0.06	5.7 ± 0.4	0.9998

Table 7. Comparison of Limiting Apparent Molar Volumes and Apparent Molar Compressibilities in 298.15 K Obtained in This Study and by Other Workers

	$10^6 \times V_{\Phi}^{\infty}/(m^3 \cdot mol^{-1})$		$10^{13} \times K_{s,\Phi}^{\infty}/(m^5 \cdot N^{-1} \cdot mol^{-1})$	
	eq 5	lit.	eq 5	lit.
$NiCl_2$	5.26[a]		−1.122[a]	
		6.18[b]		−1.0819[b]
		6.39[c]		−1.062[k]
		6.9[d]		
		11.6[e]		
		10.9,[f] 7.2[f]		
		11.6[g]		
		7.3[h]		
		6.2,[i] 6.34[j]		
		10.7[k]		
		6.84[l]		
$NiBr_2$	19.28[a]		−0.914[a]	
		25.42[e]		
		24.7,[f] 21.0[f]		
		25.4[g]		

[a] Our results extrapolated to 298.15 K. [b] Lo Surdo and Millero (1980). [c] Pogue and Atkinson (1988a,b). [d] Spitzer *et al.* (1978). [e] Millero (1971), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(H^+) = 0$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 17.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [f] Akitt (1980), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(H^+) = -5.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 23.6 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [g] Friedman and Krishnan (1973), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(H^+) = -5.4 \times 10^{-6}$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 23.2 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [h] Spitzer and Olofsson (1979), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(Ni^{2+}) = -28.3 \times 10^{-6}$ $m^3 \cdot mol^{-1}$ based on $Ni(NO_3)_2$. [i] Pogue and Atkinson (1989), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(H^+) = 0$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 17.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [j] Pogue and Atkinson (1989), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(H^+) = -3.9 \times 10^{-6}$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 21.7 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [k] Kawaizumi *et al.* (1987), assuming additivity of the limiting ionic apparent molar volumes and $V_{\Phi}^{\infty}(Ni^{2+}) = -24.9 \times 10^{-6}$ $m^3 \cdot mol^{-1}$, $V_{\Phi}^{\infty}(Cl^-) = 17.8 \times 10^{-6}$ $m^3 \cdot mol^{-1}$. [l] Perron *et al.* (1981).

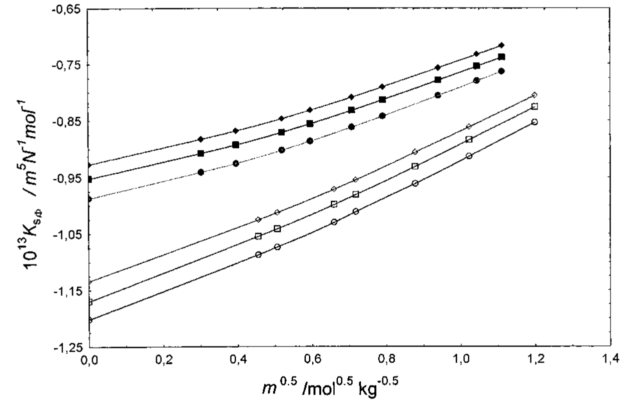

Figure 3. Apparent adiabatic molar compressibility vs $m^{0.5}$. Symbols as in Figure 1. Points calculated from eq 4; lines calculated from eq 5.

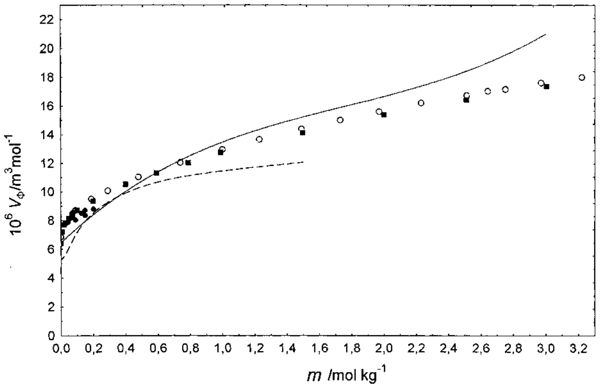

Figure 4. Apparent molar volume vs m from our results extrapolated to 298.15 K (− −) and from Lo Surdo and Millero (1980) (—), Spitzer *et al.* (1978) (■), Perron and Roux (1981) (○), and Pogue and Atkinson (1988a,b) (●).

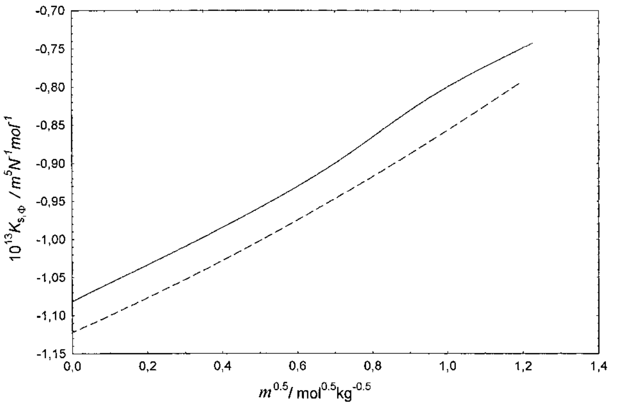

Figure 5. Apparent adiabatic molar compressibility of $NiCl_2$ vs $m^{0.5}$ from our results extrapolated to 298.15 K (− −) and from Lo Surdo and Millero (1980) (—).

The concentration dependences of the the apparent volume and apparent compressibility can be satisfactorily described by the following Redlich−Mayer type equation (Redlich and Meyer, 1964):

$$X_{\Phi} = X_{\Phi}^{\infty} + A_x m^{0.5} + B_x m \qquad (5)$$

where $x = V$ or K_s.

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

The Redlich−Mayer equation provides an effective method to determine the limiting values of V_{Φ}^{∞} and $K_{s,\Phi}^{\infty}$.

The dependences of $K_{s,\Phi}^{\infty}$on the molar concentration are shown for a few temperatures in Figure 3; they evidence that the deviations from Masson's rule become significant at higher electrolyte concentrations.

Table 7 gives a comparison of the values V_{Φ}^{∞} and $K_{s,\Phi}^{\infty}$ calculated from eq 5 and extrapolated to 298.15 K with the corresponding values found in the literature. The dependences of the literature and our apparent molar volumes and compressibilities on the molar concentration (after extrapolation to 298.15 K) are compared in Figures 4 and 5, respectively. To our best knowledge, there are no data in the literature for the apparent (or partial) compressibilities of aqueous $NiBr_2$ solutions.

The bromide anion, which is markedly larger than the chloride one, makes both the limiting coefficients, V_{Φ}^{∞} and $K_{s,\Phi}^{\infty}$, of $NiBr_2$ larger than the corresponding quantities of $NiCl_2$. The relation between the compressibilities of both the salts is most probably a consequence of a stronger electrostriction of water by the smaller Cl^- ion, similar to the case of the cobalt salts (Ernst *et al*., 1996).

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