Densities of Aqueous Electrolytes $MnCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, and $CdCl_2$ from 25 to 72 °C at 1 atm

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A weight dilatometer has been used to measure the densities of aqueous solutions of $MnCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, and $CdCl_2$ up to 3 *m* at 10-deg intervals in the range 25–75 °C at 1.013 bar. The precision of the densities is $\pm 1 \times 10^{-5}$ g cm^{-3}. The data are compared with literature values where applicable.

Introduction

Density data on aqueous electrolytes at high temperatures and pressures are required for the nuclear power industry. Our apparatus designed to obtain this data required calibration at ambient temperatures. A literature search revealed little data on these systems except at 25 °C and then principally confined to dilute solutions. Density measurements were made on solutions of five electrolytes of the MX_2 type ($MnCl_2$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, and $CdCl_2$) at 10-deg intervals from 25 to 75 °C. The results have been used for calculation of apparent molar volumes of the various electrolytes.

Experimental Section

Materials. AR grades of the salts were recrystallized 3 times from conductivity water made slightly acid with AR hydrochloric acid and dried in a stream of air at <50 °C. The purity values of the original of the original salts are given in Table XVI. All solutions were prepared by using demineralized water which was first distilled and then passed through a nuclear-grade mixed-bed ion-exchange resin, followed by a filter column, until its conductivity was less than 0.02 μS cm^{-1}. All mercury used was recovered and cleaned by a four-stage process, dried by passing air through it in contact with AR grade acetone and stored under nitrogen in plastic containers until use. All solutions were degassed before standardization. Weighed amounts of chloride solution were standardized by mass titration against silver nitrate solutions using a Metrohm 636 Titroprocessor in conjunction with a Metrohm E635 Dosimat unit. The silver nitrate was made up freshly for each standardization and was itself standardized against potassium chloride solution. All titrations were done at 25 °C under nitrogen and the precision was better than 0.01%. Solutions of each salt were also analyzed by EDTA titration, as described by Schwarzenbach and Flaschka (*1*). Both methods agreed within the precision of the analyses. Each stock solution of a given molality (enough for duplicate runs and analysis) was made and analyzed within a day of the density measurements. The pH of the solutions was checked to confirm that the recrystallized salts did not contain adsorbed acid. A pH $\simeq$4.0 was considered optimal; if the pH is too high hydrolysis to species such as MOH^+ may occur, but if the pH is too low the contribution of HCl to the properties of the solution may not be negligible.

Dilatometer. The dilatometer used was similar in design to the weight dilatometer of Gibson and Loeffler (*2*). The opening for filling the dilatometer was made as narrow as possible and the flange was sealed by a flat plate clamped against a silicone rubber seating. The principle of operation is that mercury is displaced through a capillary from the dilatometer and collected in a preweighed pot. The advantage of this method is that it allows a large number of measurements to be made over several temperatures without refilling the dilatometer, to give a precision of $\pm 1 \times 10^{-5}$ g cm^{-3}. Values for the density of water were taken from Kell (*3*) and for the density of mercury from ref *4*. The temperature of the water thermostat was monitored with a National Physical Laboratory calibrated platinum resistance thermometer, in conjunction with an Automatic Systems Laboratories precision ac double transformer ratio bridge (Model H6), to $\pm 1 \times 10^{-3}$ K. Temperature control was better than $\pm 2 \times 10^{-3}$ K.

A day's run was 25–75 °C; the water bath was left to cool overnight and the 25 °C run repeated next morning. The repeat values at 25 °C agreed well within the quoted experimental error, confirming that no hydrolysis had occurred at the higher temperatures. In each density run six dilatometers were used giving three sets of duplicate measurements.

Results and Discussion

Values for the density of each electrolyte were obtained at 10-deg intervals between 25 and 75 °C and up to about 3 *m*. The results are given in Tables I–V. The apparent molar volume of each solution was calculated from these data by using eq 1.

$$^{\phi}V = \frac{1}{m}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right) + \frac{M_2}{\rho} \qquad (1)$$

Measurements were not carried out at very low molality as a precision of $\pm 1 \times 10^{-5}$ g cm^{-3} in the density gives an error of ± 0.02 cm^3 mol^{-1} in $^{\phi}V$ at 0.5 *m* but ± 0.1 cm^3 mol^{-1} at 0.1 *m*. The apparent molar volume data were smoothed by fitting to an extended form of the Debye–Hückel equation of the type derived by Pitzer (*5*) for 2:1 electrolytes

$$^{\phi}V - [^{\phi}V^{st} - {}^{\phi}V^{\infty}] = {}^{\phi}V^{\infty} + 4RTm\left(\frac{\partial\beta^0}{\partial p}\right)_T + \frac{8RTm}{3\alpha^2}\left(\frac{\partial\beta^1}{\partial p}\right)_T[1 - (1 + \alpha 3^{1/2}m^{1/2})e^{-\alpha 3^{1/2}m^{1/2}}] + 2(2^{1/2})RTm^2\left(\frac{\partial C^{\phi}}{\partial p}\right)_T$$

where

$$^{\phi}V^{st} - {}^{\phi}V^{\infty} = (3/b)A_v \ln (1 + b(3m)^{1/2}) \qquad (2)$$

$b = 1.2$ kg$^{1/2}$ and $\alpha = 2.0$ kg$^{1/2}$ mol$^{-1/2}$. A_v is the Debye–Hückel slope: the values were taken from Bradley and Pitzer (*6*). The values of the fitting parameters were obtained by nonlinear regression and are given in Tables VI–X.

Values of $^{\phi}V$ (smoothed) at very low molality were calculated from the fitting parameters. The relative apparent molar volume $^{\phi}V^{rel}$ ($^{\phi}V^{rel} = {}^{\phi}V$ (smoothed) $- {}^{\phi}V^{\infty}$) is plotted against $m^{1/2}$ at 25 °C in Figure 1. As $m^{1/2} \rightarrow 0$, the slope approaches $3A_v/b$. The transition-metal chlorides studied all show a negative deviation from linearity except $ZnCl_2$. Millero (*7*) points

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Table I. Density of Aqueous Manganous Chloride at 1.013 bar

	ρ/(g cm^{-3})					
m/(mol kg^{-1})	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.5292	1.050 50	1.047 22	1.043 26	1.038 68	1.033 57	1.027 78
0.8038	1.077 08	1.073 68	1.069 66	1.065 04	1.059 95	1.054 18
1.0684	1.102 01	1.098 49	1.094 41	1.089 77	1.084 70	1.078 96
1.3397	1.126 91	1.123 27	1.119 14	1.114 47	1.109 41	1.103 73
1.6251	1.152 43	1.148 68	1.144 49	1.139 79	1.134 74	1.129 12
1.9287	1.178 89	1.175 03	1.170 77	1.166 03	1.160 97	1.155 41
2.2401	1.205 36	1.201 37	1.197 03	1.192 25	1.187 17	1.181 66
2.5142	1.228 14	1.224 05	1.219 63	1.214 80	1.209 68	1.204 20
2.8098	1.252 24	1.248 03	1.243 50	1.238 62	1.233 44	1.227 94
3.1178	1.276 88	1.272 54	1.267 88	1.262 93	1.257 67	1.252 10

Table II. Density of Aqueous Cobaltous Chloride at 1.013 bar

	ρ/(g cm^{-3})					
m/(mol kg^{-1})	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.2419	1.024 88	1.021 70	1.017 76	1.013 15	1.007 96	1.002 16
0.4640	1.049 86	1.046 53	1.042 50	1.037 85	1.032 65	1.026 82
0.6948	1.075 27	1.071 79	1.067 69	1.063 01	1.057 81	1.052 00
0.9215	1.099 71	1.096 10	1.091 94	1.087 22	1.082 03	1.076 27
1.1498	1.123 82	1.120 10	1.115 88	1.111 13	1.105 96	1.100 24
1.3886	1.148 53	1.144 70	1.140 42	1.135 65	1.130 49	1.124 83
1.6373	1.173 74	1.169 81	1.165 46	1.160 65	1.155 50	1.149 88
1.8878	1.198 62	1.194 60	1.190 18	1.185 32	1.180 15	1.174 55
2.1320	1.222 41	1.218 31	1.213 80	1.208 88	1.203 68	1.198 05
2.3727	1.245 44	1.241 26	1.236 66	1.231 65	1.226 39	1.220 68
2.6227	1.268 95	1.264 69	1.259 98	1.254 85	1.249 49	1.243 61
2.8825	1.292 97	1.288 64	1.283 78	1.278 48	1.272 97	1.266 83

Table III. Density of Aqueous Nickel Chloride at 1.013 bar

	ρ/(g cm^{-3})					
m/(mol kg^{-1})	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.3001	1.032 77	1.029 51	1.025 56	1.020 89	1.015 69	1.009 95
0.4677	1.052 28	1.048 90	1.044 88	1.040 15	1.034 94	1.029 21
0.6996	1.078 78	1.075 24	1.071 14	1.066 36	1.061 13	1.055 43
0.9188	1.103 33	1.099 65	1.095 48	1.090 66	1.085 43	1.079 76
1.1590	1.129 69	1.125 88	1.121 62	1.116 79	1.111 55	1.105 93
1.4107	1.156 75	1.152 80	1.148 47	1.143 63	1.138 38	1.132 81
1.6526	1.182 23	1.178 16	1.173 77	1.168 91	1.163 67	1.158 14
1.8985	1.207 64	1.203 46	1.199 01	1.194 14	1.188 89	1.183 39
2.1480	1.232 95	1.228 66	1.224 15	1.219 25	1.214 00	1.208 52
2.3916	1.257 23	1.252 85	1.248 28	1.243 33	1.238 06	1.232 59
2.6336	1.280 97	1.276 49	1.271 88	1.266 86	1.261 56	1.256 07
2.8917	1.305 88	1.301 30	1.296 63	1.291 50	1.286 17	1.280 62

Table IV. Density of Aqueous Zinc Chloride at 1.013 bar

	ρ/(g cm^{-3})					
m/(mol kg^{-1})	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.2348	1.025 39	1.021 87	1.017 52	1.012 49	1.006 79	1.000 34
0.4654	1.051 55	1.047 52	1.042 68	1.037 17	1.031 03	1.024 08
0.6969	1.076 35	1.071 82	1.066 52	1.060 59	1.054 06	1.046 77
0.9333	1.100 33	1.095 31	1.089 59	1.083 27	1.076 41	1.068 89
1.1759	1.123 71	1.118 24	1.112 11	1.105 45	1.098 31	1.090 64
1.4209	1.146 27	1.140 36	1.133 89	1.126 93	1.119 56	1.111 79
1.6722	1.168 51	1.162 25	1.155 45	1.148 22	1.140 65	1.132 79
1.9317	1.190 75	1.184 19	1.177 12	1.169 66	1.161 91	1.153 92
2.2667	1.218 77	1.211 95	1.204 61	1.196 92	1.188 96	1.180 67
2.4457	1.233 57	1.226 69	1.219 25	1.211 46	1.203 39	1.194 84
2.6199	1.247 97	1.241 07	1.233 56	1.225 69	1.217 51	1.208 64
2.9867	1.278 58	1.271 84	1.264 27	1.256 27	1.247 83	1.237 93

out that for most 2:1 electrolytes positive deviations occur at 0 °C, while at 50 °C, negative deviations occur.

The values for the apparent molar volume at infinite dilution, $^{\phi}V^{\infty}$, at 25 °C were compared where possible with existing literature data, as several modern measurements have been done in this very dilute region; the highest molalities used are lower than our most dilute solution. It can be seen from Tables XI–XV that there is considerable discrepancy between the $^{\phi}V^{\infty}$ values of different workers, even where the same method (vibrating tube) has been used from the same low molality. The precision of our density values gives an error of ±0.02 cm^3 mol^{-1} in $^{\phi}V$ at 0.5 mol kg^{-1}, whereas the vibrating tube densitometer should be capable of a precision at least a factor of 10 better than this. Thus the V_2^{∞} values quoted from our data are within ±2 cm^3 mol^{-1} of the true values, but are to be regarded as fitting parameters. Data fitting using the Pitzer equation gave a better fit for the same number of parameters than other commonly used forms of smoothing equations. Where sufficient density data were available in the literature, the quoted results were ffitted to eq 2. Whereas for the 1:1 electrolyte, HCl, extrapolation of our high-molality data to infinite dilution gave excellent agreement with low-molality data (*8*), for

Table V. Density of Aqueous Cadmium Chloride at 1.013 bar

m/(mol kg^{-1})	ρ/(g cm^{-3})					
	298.15 K	308.15 K	318.15 K	328.15 K	338.15 K	348.15 K
0.2288	1.032 66	1.029 36	1.025 25	1.020 49	1.015 12	1.009 13
0.4453	1.065 55	1.061 99	1.057 60	1.052 59	1.047 01	1.040 77
0.9005	1.132 33	1.128 22	1.123 26	1.117 74	1.111 68	1.104 98
1.3618	1.197 00	1.192 35	1.186 87	1.180 82	1.174 29	1.167 16
1.6270	1.232 95	1.228 01	1.222 24	1.215 90	1.209 11	1.201 73
1.8475	1.262 22	1.257 04	1.251 05	1.244 48	1.237 49	1.229 90
2.1395	1.300 19	1.294 69	1.288 44	1.281 58	1.274 34	1.266 46
2.3412	1.325 93	1.320 22	1.313 81	1.306 75	1.299 37	1.291 28
2.6401	1.363 40	1.357 40	1.350 78	1.343 46	1.335 89	1.327 47
2.8474	1.388 97	1.382 78	1.376 03	1.368 55	1.360 88	1.352 20

Table VI. Aqueous Manganous Chloride—Parameters for the Pitzer Equation

T/K	$^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	$10^5(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	std dev of fit
298.15	20.513 ± 0.139	−11.142 ± 0.813	69.964 ± 4.649	−1.007 ± 0.067	0.008
308.15	20.740 ± 0.135	−12.659 ± 0.765	76.915 ± 4.371	−0.380 ± 0.063	0.008
318.15	20.656 ± 0.158	−14.071 ± 0.869	83.371 ± 4.965	0.345 ± 0.072	0.010
328.15	20.207 ± 0.217	−14.948 ± 1.156	87.099 ± 6.608	0.868 ± 0.096	0.013
338.15	19.653 ± 0.262	−16.898 ± 1.353	96.857 ± 7.731	1.580 ± 0.112	0.016
348.15	19.492 ± 0.287	−19.757 ± 1.438	110.217 ± 8.222	3.005 ± 0.119	0.017

Table VII. Aqueous Cobaltous Chloride—Parameters for the Pitzer Equation

T/K	$^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	$10^6(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	std dev of fit
298.15	11.517 ± 0.022	−74.747 ± 1.569	52.305 ± 0.942	−1.430 ± 0.045	0.005
308.15	11.680 ± 0.030	−79.172 ± 2.058	52.496 ± 1.236	−0.705 ± 0.059	0.007
318.15	11.781 ± 0.048	−98.402 ± 3.143	61.104 ± 1.888	0.447 ± 0.090	0.011
328.15	11.740 ± 0.039	−124.981 ± 2.490	74.038 ± 1.495	1.664 ± 0.071	0.009
338.15	11.363 ± 0.050	−147.657 ± 3.086	84.523 ± 1.853	3.054 ± 0.089	0.012
348.15	11.196 ± 0.072	−176.040 ± 4.349	96.577 ± 2.612	5.548 ± 0.125	0.017

Table VIII. Aqueous Nickel Chloride—Parameters for the Pitzer Equation

T/K	$^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	$10^6(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	std dev of fit
298.15	6.886 ± 0.021	−64.769 ± 1.435	49.589 ± 0.851	−2.307 ± 0.031	0.004
308.15	7.322 ■ 0.031	−81.518 ± 2.051	56.612 ± 1.216	−1.459 ± 0.045	0.006
318.15	7.255 ± 0.034	−95.553 ± 2.175	62.829 ± 1.290	−0.844 ± 0.048	0.006
328.15	7.272 ± 0.060	−116.300 ± 3.646	71.453 ± 2.162	0.716 ± 0.080	0.010
338.15	6.849 ± 0.059	−139.103 ± 3.509	82.569 ± 2.081	1.565 ± 0.077	0.010
348.15	6.324 ± 0.073	−166.491 ± 4.205	95.777 ± 2.494	2.831 ± 0.092	0.013

Table IX. Aqueous Zinc Chloride—Parameters for the Pitzer Equation

T/K	$^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	$10^6(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	std dev of fit
298.15	9.252 ± 0.078	93.834 ± 5.470	13.266 ± 3.279	−28.409 ± 0.152	0.019
308.15	10.838 ± 0.073	84.476 ± 4.953	15.241 ± 2.970	−28.515 ± 0.138	0.018
318.15	12.674 ± 0.056	62.092 ± 3.705	23.186 ± 2.221	−27.351 ± 0.103	0.014
328.15	14.263 ± 0.031	47.849 ± 1.990	25.793 ± 1.193	−25.647 ± 0.055	0.008
338.15	16.354 ± 0.031	7.873 ± 1.905	41.594 ± 1.142	−22.843 ± 0.053	0.008
348.15	19.722 ± 0.014	−58.065 ± 0.845	66.082 ± 0.507	−15.814 ± 0.023	0.004

Table X. Aqueous Cadmium Chloride—Parameters for the Pitzer Equation

T/K	$^{\phi}V^{\infty}$/ (cm^3 mol^{-1})	$10^6(\partial\beta^0/\partial P)$/ (kg mol^{-1} atm^{-1})	$10^5(\partial\beta^1/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	$10^6(\partial C^{\phi}/\partial P)$/ (kg^2 mol^{-2} atm^{-1})	std dev of fit
298.15	23.665 ± 0.004	−64.252 ± 0.294	48.053 ± 0.177	−3.732 ± 0.008	0.001
308.15	24.419 ± 0.015	−79.509 ± 1.068	54.832 ± 0.644	−3.166 ± 0.030	0.003
318.15	25.028 ± 0.019	−87.766 ± 1.337	57.639 ± 0.807	−2.779 ± 0.038	0.004
328.15	25.253 ± 0.028	−93.564 ± 1.872	59.698 ± 1.130	−2.538 ± 0.053	0.006
338.15	25.441 ± 0.023	−111.254 ± 1.517	68.786 ± 0.915	−2.479 ± 0.043	0.005
348.15	25.835 ± 0.045	−130.792 ± 2.871	77.051 ± 1.732	−1.095 ± 0.081	0.010

Table XI. Values of $^{\phi}V^{\infty}$/(cm^3 mol^{-1}) for $MnCl_2$ at 25 °C

no.	method of measurement	concn range/ (mol kg^{-1})	m/(mol kg^{-1}) 0.0	0.5	1.0	1.5	2.0	2.5	3.0	source
1	weight dilatometer	0.5–3.0	20.51	23.28	24.61	25.74	26.65	27.38	27.95	this work
2	pycnometer	0.04–6.03	18.00	22.50	23.95	25.03	25.92	26.67	27.32	Rard and Miller (*9*)
3	vibrating tube	0.05–0.99	18.56	22.39	23.87					Lo Surdo and Millero (*10*)
4	vibrating tube	0.04–0.16	18.3							Spitzer et al. (*11*)
5	calcd from ICT (*13*)		22.0							Fajans and Johnson (*12*)

Table XII. Values of $^{\phi}V^{\infty}$/(cm^3 mol^{-1}) for $CoCl_2$ at 25 °C

no.	$^{\phi}V^{\infty}$/(cm^3 mol^{-1})	method of measurement	concn range/(mol kg^{-1})	source
1	11.52	weight dilatometer	0.25–3.0	this work
2	10.8	calcd from ICT (*13*)		Couture and Laidler (*16*)
3	10.2	vibrating tube	0.05–0.24	Spitzer et al. (*17*)
4	9.95	vibrating tube	0.05–1.0	Lo Surdo and Millero (*10*)
5	10.94	pycnometer	0.08–4.0	Phang (*18*)

Table XIII. Values of $^{\phi}V^{\infty}$/(cm^3 mol^{-1}) for $NiCl_2$ at 25 °C

no.	method of measurement	concn range/(mol kg^{-1})	m/(mol kg^{-1}) 0.0	0.5	1.0	1.5	2.0	2.5	3.0	source
1	weight dilatometer	0.3–3.0	6.89	10.74	12.60	14.15	15.44	16.52	17.41	this work
2	vibrating tube	0.1–5.4	6.41	11.05	12.92	14.41	15.65	16.71	17.61	Perron et al. (*19*)
3	pycnometer	0.004–4.2	5.2	11.41	13.27	14.60	15.72	16.80	17.73	Stokes et al. (*20*)
4	pycnometer	0.04–5.0	6.24	11.10	12.99	14.47	15.71	16.78	17.71	Rard (*21*)
5	vibrating tube	0.04–0.92	6.26	10.93	12.83					Lo Surdo and Millero (*10*)
6	vibrating tube	0.01–0.2	6.9							Spitzer et al. (*17*)

Table XIV. Values of $^{\phi}V^{\infty}$/(cm^3 mol^{-1}) for $ZnCl_2$ at 25 °C

no.	method of measurement	concn range/(mol kg^{-1})	m/(mol kg^{-1}) 0.0	0.5	1.0	1.5	2.0	2.5	3.0	source
1	weight dilatometer	0.2–3.0	9.25	18.34	23.59	27.52	30.30	31.99	32.62	this work
2	pycnometer	0.04–3.0	9.81	18.09	23.62	27.84	30.43	32.25	33.02	Rard and Miller (*9*)
3	pycnometer	0.1–4.0	17.51	22.38	25.98	29.30	32.41	35.31	38.02	Agnew and Paterson (*22*)
4	vibrating tube	0.06–1.03	10.24	17.82	23.73					Lo Surdo and Millero (*10*)

Table XV. Values of $^{\phi}V^{\infty}$/(cm^3 mol^{-1}) for $CdCl_2$ at 25 °C

no.	method of measurement	concn range/(mol kg^{-1})	m/(mol kg^{-1}) 0.06	0.5	1.0	1.5	2.0	2.5	3.0	source
1	weight dilatometer	0.23–2.9	23.67	27.43	29.12	30.44	31.45	32.20	32.72	this work
2	pycnometer	0.25–6.4	22.13	27.47	29.09	30.24	31.18	32.00	32.72	Rard and Miller (*9*)
3	pycnometer	0.05–1.0	25.23	27.32	29.18					Reilly and Stokes (*23*)
4	vibrating tube	0.06–1.00	22.61	27.36	29.07					Lo Surdo and Millero (*10*)
5	calcd from ICT (*13*)		23.24							Longsworth (*24*)
6	calcd from ICT (*13*)		22.8							Fajans and Johnson (*12*)

these 2:1 electrolytes ion-pairing and other structural effects undoubtedly play a dominant role at the lowest molalities studied here.

(a) Manganous Chloride. The only modern data over the same concentration range are those of Rard and Miller (*9*). In Table XI smoothed values of $^{\phi}V$ at rounded values of the molality are compared. Our data are some 0.6–0.8 cm^3 mol^{-1} higher than theirs. It is interesting that the extrapolated $^{\phi}V^{\infty}$ value of Rard and Miller (*9*), with a precision of only 3×10^{-5} g cm^{-3} in the density, agrees well with the vibrating tube results of Lo Surdo and Millero (*10*) and Spitzer et al. (*11*). Measurement 5 was calculated from density data tabulated in International Critical Tables (*13*). Only four measurements are reported at 25 °C (these are only to four decimal places and are based mainly on the work of Heydweiller (*14*) and Wagner (*15*)), insufficient to reanalyze by using the Pitzer equation.

(b) Cobaltous Chloride. Three values of $^{\phi}V^{\infty}$ have been reported and are given in Table XII. Measurement 2 was calculated from ICT (*13*); only four measurements are given and quoted to only four decimal places: these density data are mainly based on the work of Heydweiller (*14*). Measurements 3 and 4 should be the most accurate and our value lies rather higher than these. Smoothing the data of Lo Surdo and Millero (*10*) to eq 2 gives a value for $^{\phi}V$ of 14.59 cm^3 mol^{-1} at 0.5 mol kg^{-1} compared with 15.06 cm^3 mol^{-1} in this work. The data of Phang (*18*) smoothed to eq 2 give $^{\phi}V^{\infty}$ in between the values of methods 1 and 4.

(c) Nickel Chloride. The $^{\phi}V^{\infty}$ value of Spitzer et al. (*17*) is in excellent agreement with our extrapolated value (Table XIII). The disagreement in $^{\phi}V^{\infty}$ between the different workers (*10*, *17*, and *20*) using the vibrating tube method is surprising although Perron et al. (*19*) did not do measurements in very dilute solution. There is a consistent discrepancy between our values of $^{\phi}V$ and those of Perron et al. (*19*); our values are less by some 0.2–0.3 cm^3 mol^{-1}, whereas the values of Stokes et al. (*20*) are larger by 0.1–0.3 cm^3 mol^{-1}. The pycnometric data of Rard (*21*) fall between those of Stokes (*20*) and Perron (*19*).

Table XVI. Maximum Limits of Impurities Given by the Manufacturer (BDH, England) for the Salts Used in This Work

	$MnCl_2$	$CoCl_2$	$NiCl_2$	$ZnCl_2$	$CdCl_2$
min assay, %	98	99	98	98	99.5
water insol matter, %	0.003	0.003	0.005	0.005	0.003
N		0.003		0.001	0.004
SO_4	0.002	0.005	0.005	0.002	0.005
Ba	0.005				
Ca	0.005	0.005	0.005	0.001	0.002
Cd				0.0005	
Co			0.005		
Cu	0.0005	0.0005	0.001	0.001	0.0005
Fe	0.0005	0.002	0.002	0.0005	0.0005
Pb	0.0002	0.001	0.002	0.001	0.002
Mg	0.005	0.002			
Mn		0.001			
Ni	0.002	0.01			
K	0.005	0.005		0.001	0.002
Na	0.005	0.01	0.01	0.001	0.002
Zn	0.001	0.002	0.001		0.001

(d) Zinc Chloride. The values of $^{\phi}V$ (Table XIV) are in good agreement with those of Lo Surdo and Millero (*10*) but cycle about those of Rard and Miller (*9*) by −0.5–0.2 cm^3 mol^{-1}. The latter's data could not be fitted by eq 2 over their full molality range of 0.04–7.3 mol kg^{-1} to within experimental error, so the upper limit was set at the same as in this work; in the report of the work (*9*), 10 parameters were required to fit the densities for $ZnCl_2$ but only 5 for $MnCl_2$ and $CdCl_2$ over a similar concentration range. The data of Agnew and Paterson (*22*) are

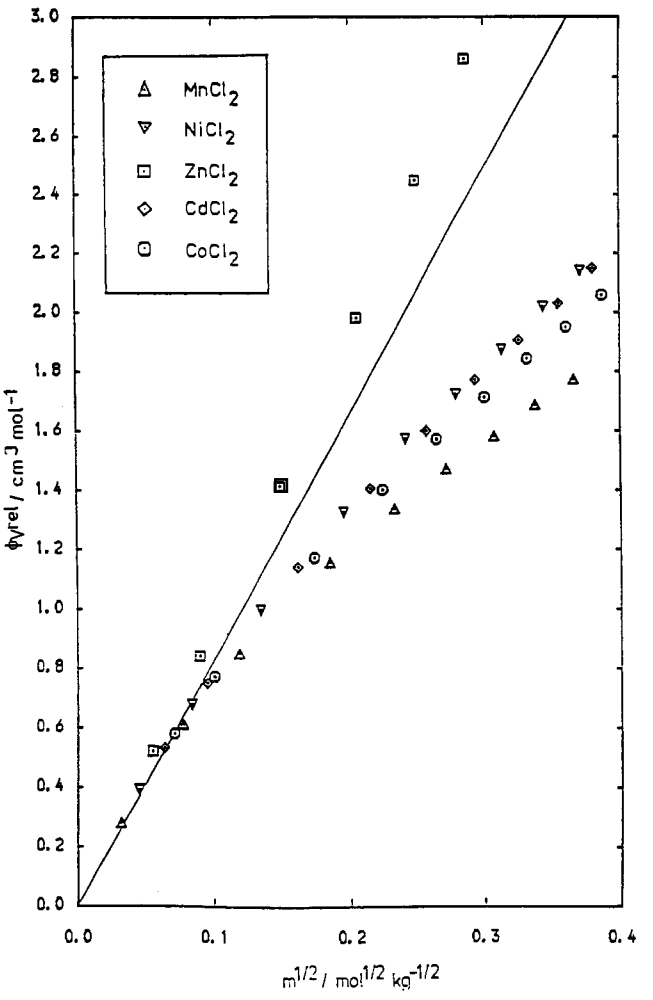

Figure 1. Comparison of $^{\phi}V^{rel}$ for the transition-metal chlorides at 25 °C.

considerably higher than other reported values.

(e) Cadmium Chloride. The reported values are shown in Table XV. There is excellent agreement between the results of the present work and those of Rard and Miller (*9*), Reilly and Stokes (*23*), and Lo Surdo and Millero (*10*), except for $^{\phi}V^{\infty}$ which simply reflects the lowest molality at which densities were obtained and the accuracy. Both measurements 5 and 6 were calculated from data tabulated in ICT (*13*) by Longsworth (*24*) and Fajans and Johnson (*12*), respectively. The density data are reported from 0 to 40 wt % and only to four decimal places: the data are mainly based on the work of Biron (*25*), Heydweiller (*14*), and Kremers (*26*). The inaccuracies in these data are reflected by the two different results for $^{\phi}V^{\infty}$ calculated from the same basic data.

Glossary

A_v	Debye–Hückel slope
M_2	molar mass of solute
m	molality of solute
$^{\phi}V$	apparent molar volume
$^{\phi}V^{\infty}$	apparent molar volume at infinite dilution
$^{\phi}V^{rel}$	$^{\phi}V$(smoothed) − $^{\phi}V^{\infty}$
ρ	density of solution
ρ_0	density of water

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Registry No. $MnCl_2$, 7773-01-5; $CoCl_2$, 7646-79-9; $NiCl_2$, 7718-54-9; $ZnCl_2$, 7646-85-7; $CdCl_2$, 10108-64-2.

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