M	mixture 1-butanol-chloroform; its value is defined as $M = X_B/(X_B + X_C)$ in the initial mixture
W	water
X_i	weight percentage of component i
aq	aqueous phase
or	organic phase
x, y	coordinates
x', y'	coordinates

Registry No. Chloroform, 67-66-3; 1-butanol, 71-36-3; ethanol, 64-17-5.

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Received for review February 22, 1983. Accepted July 27, 1983.

Densities and Apparent Molal Volumes of Aqueous Manganese, Cadmium, and Zinc Chlorides at 25 °C

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Densities of aqueous solutions of $MnCl_2$ have been measured from 0.04 to 6.03 mol kg^{-1}, of $CdCl_2$ from 0.25 to 6.36 mol kg^{-1}, and of $ZnCl_2$ from 0.04 to 7.32 mol kg^{-1}. These densities were measured at 25 °C with very high purity chemicals by using 31-cm^3 single-stem pycnometers. For comparison, densities are also reported for low-purity $ZnCl_2$. Our experimental densities are compared to published literature data, and some discrepancies may be due to low-purity chemicals in certain other studies. Problems with hydrolytic precipitation of basic species from $ZnCl_2$ solutions above their equivalence pH values are discussed.

Introduction

Density data for aqueous electrolyte solutions are quite useful for a variety of purposes. They are required for buoyancy corrections when weighing samples, and for conversion of mass concentrations to volume concentrations. Density data for solutions yield partial molal volumes, and these are related to the pressure derivatives of solvent and solute activities (*1*).

In studying the diffusion coefficients of aqueous transition-metal chlorides, we require very accurate density data to high concentrations at 25 °C. Examination of published density data for these systems indicated significant discrepancies, especially at high concentrations. We therefore redetermined the densities of aqueous $MnCl_2$, $CdCl_2$, and $ZnCl_2$ at 25 °C from low to high concentrations. Since some literature discrepancies may be due to the use of low-purity chemicals, care was taken to guarantee that ours were of very high purity. For comparison, densities of low-purity $ZnCl_2$ were also measured.

Experimental Materials and Analyses

Preliminary experiments for chemical stability for $MnCl_2$ were performed with a test solution in contact with air by measuring its pH at several month intervals. This test solution had a concentration of 4.12 mol kg^{-1} and an initial pH of 2.57. After 13.5 months the pH had decreased to 1.81. This pH decrease with time indicates that oxidation by air and/or slow hydrolysis occurs at about 0.1% per year. Oxidation to form MnOOH(s) or Mn_3O_4(s) generates two hydrogen ions per Mn involved, as would the formation of $Mn(OH)_2$(s) by hydrolysis. If this pH change is due to slow oxidation, it occurs even at fairly acidic pH values (even though Mn^{2+} is reported to be stable in acid solution (*2*)).

Table I. Densities and Apparent Molal Volumes of Aqueous $MnCl_2$ at 25 °C

m, mol kg^{-1}	c, mol dm^{-3}	d, g cm^{-3}	ϕ_V, cm^3 mol^{-1}
0.044493	0.044323	1.001 75	19.75
0.090013	0.089584	1.006 51	20.25
0.16003	0.15903	1.013 75	20.86
0.24995	0.24789	1.022 96	21.37
0.36000	0.35614	1.034 09	21.89
0.48896	0.48224	1.046 95	22.43
0.63661	0.62562	1.061 46	22.95
0.80898	0.79161	1.078 15	23.46
1.0001	0.97388	1.096 34	23.96
1.2102	1.1720	1.115 94	24.47
1.4407	1.3867	1.137 04	24.96
1.6897	1.6155	1.159 36	25.44
1.9607	1.8607	1.183 12	25.91
2.2507	2.1187	1.207 98	26.36
2.5608	2.3899	1.234 01	26.77
2.8911	2.6732	1.261 02	27.17
3.2733	2.9939	1.291 40	27.61
3.6024	3.2642	1.316 87	27.94
3.9183	3.5186	1.340 80[a]	28.23
4.4054	3.9008	1.376 35	28.69
4.8581	4.2459	1.408 29	29.07
5.4244	4.6637	1.446 65	29.53
6.0292	5.0929	1.485 62	30.00

[a] This point given zero weight in the least-squares fits.

The $MnCl_2$ stock solution used for density measurements was therefore stored in a nitrogen atmosphere to reduce this problem to negligible amounts. All density experiments were made within 5.5 months after this stock solution was prepared, and neither colloid nor precipitate was present even after this period.

The $MnCl_2$ stock solution was prepared from filtered Mallinckrodt analytical reagent $MnCl_2$. X-ray fluorescence spectroscopy of the original material indicated that it contained small amounts of Ca, Fe, and Zn. However, Fe and Zn were absent from the final solution since they precipitate from all but extremely acid solutions. Direct current arc optical emission spectroscopic (DCAOES) analysis of an evaporated stock solution sample indicated the presence of only 30 ppm Ca, <20 ppm Si, 3 ppm Mg, and 3 ppm Na by weight.

The concentration of the $MnCl_2$ stock solution was determined to be 3.2746 ± 0.0026 mol kg^{-1} by mass titration with

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Table II. Densities and Apparent Molal Volumes of Aqueous $CdCl_2$ at 25 °C

m, mol kg^{-1}	c, mol dm^{-3}	d, g cm^{-3}	ϕ_V, cm^3 mol^{-1}
0.24987	0.24752	1.035 96	26.17
0.49994	0.49175	1.073 76	27.39
0.99934	0.96832	1.146 47	29.09
1.5093	1.4392	1.217 39	30.30
2.0004	1.8775	1.282 74	31.24
2.4884	2.2984	1.345 01	32.02
3.0042	2.7278	1.408 05	32.74
3.5665	3.1783	1.473 77	33.42
4.1037	3.5921	1.533 81	33.99
4.4980	3.8855	1.576 12	34.38
5.8582	4.8376	1.712 59	35.51
6.3608	5.1670	1.759 52	35.86

$AgNO_3$ solutions, and 3.2719 ± 0.0013 mol kg^{-1} by conversion to the anhydrous sulfate. Drying this $MnSO_4$ at 400 and 500 °C gave concordant results, but after 3 days at the higher temperature some oxidation occurred as evidenced by a pale gray coloration. Molecular weights used for calculations are 125.844 for $MnCl_2$ and 150.996 for $MnSO_4$. Table I contains the $MnCl_2$ solution densities.

$CdCl_2$ for our experiments was filtered Apache ACS grade. This grade could have contained up to 0.05% Zn, but DCAOES of the original material showed that Zn was below the detection limit. DCAOES results gave 20 ppm Si, ≤10 ppm Fe, 2 ppm Ca, ≤1 ppm Cu, and 1 ppm Mg. The stock solution concentration was determined to be 2.4888 ± 0.0005 mol kg^{-1} by dehydration at 220 °C, and 2.4880 ± 0.0003 mol kg^{-1} by conversion to the anhydrous sulfate at 450 °C. Molecular weights used were 183.316 for $CdCl_2$ and 208.468 for $CdSO_4$. Table II contains the $CdCl_2$ solution densities.

An attempt was made to prepare a $ZnCl_2$ stock solution by dissolving commercial analytical reagent $ZnCl_2$ in water. Concentrated solutions seemed to be stable and exhibited no Tyndall cone. However, upon dilution large amounts of a gelatinous white precipitate formed, which was presumably $Zn(OH)_2$ or a hydroxy or oxy chloride. The common way of avoiding this problem is that of Robinson and Stokes (*3*), i.e., acidification of the solution until dilution of it no longer causes precipitation. This procedure will be valid if the adjustment results in a stoichiometric solution. Reported chemical analyses indicate that solutions adjusted in this manner have a Cl-to-Zn ratio of 2:1 within the precision of the analyses (*4*). This implies that solutions that precipitate are chloride deficient.

Since this method of adjustment of the Cl-to-Zn ratio seemed rather arbitrary, we instead chose the method of Spedding et al. (*5*). In this approach, a sample of an original stock solution above its equivalence pH is titrated with dilute HCl, and the equivalence pH is obtained from the inflection point of the titration curve. The remainder of the stock solution is then adjusted to this pH with the same HCl concentration.

Unfortunately, there were also severe purity problems for commercial analytical reagent $ZnCl_2$. A sample of Mallinckrodt AR $ZnCl_2$ was analyzed for impurities by DCAOES and found to contain ≥2000 ppm K, 800 ppm Na, 1500–3900 ppm Ba, 600 ppm Ca, 500 ppm Mg, 700 ppm Si, 150 ppm Al, 80 ppm Sr, 160 ppm Rb, and other elements in lesser amounts. The variable Ba content presumably came from sample inhomogeneity. A sample of "Baker Analyzed" $ZnCl_2$ contained 1000 ppm Na, 800 ppm Ba, 600 ppm Ca, 600 ppm K, 100 ppm Mg, 30 ppm Sr, and other impurities in lesser amounts. We therefore prepared our solution from ZnO and HCl, which were available in much higher purity.

Our $ZnCl_2$ stock solution was thus prepared by reaction of Apache 99.999% ZnO with Mallinckrodt analytical reagent HCl. DCAOES analysis of the ZnO detected only 50 ppm Si, 3 ppm Ca, 3 ppm Mg, and 1 ppm Cu. The pH of this stock solution was adjusted to its equivalence point as determined by pH titration (*5*). Fairly concentrated HCl was required for the stock solution titration and pH adjustment owing to the large amount of hydrolyzed Zn^{2+} species present initially. Dilution of the freshly prepared pH-adjusted stock solution produced no precipitate. This stock had a concentration of 7.32 mol kg^{-1} and an equivalence pH of 1.3. When the solution pH was 0.1 unit higher, dilution of it resulted in slow (several minutes) colloid formation. If the solution pH was 0.3 unit above the equivalence pH, dilution produced rapid precipitation. Thus, the two methods of adjusting the solution pH (adjustment to the equivalence pH, or acidification until dilution no longer produces precipitation) have been verified as equivalent procedures or nearly so. All of these pH values are uncertain by at least 0.1 unit owing to drift in concentrated solutions.

The possibility was considered that hydrolysis in $ZnCl_2$ solutions might involve slow reaction kinetics when near their equivalence pHs. Consequently, our 7.32 mol kg^{-1} stock solution was adjusted to pH 1.0, which is below the equivalence pH 1.3. Unfortunately, after it had aged several months, dilution of samples of this stock solution much below 0.3 mol kg^{-1} resulted in a slow colloid formation. Colloid formation is consistent with the observation that upon aging for 6.5 months the stock solution pH had increased somewhat to 1.5. This small pH change should have no detectable effect on the experimental densities since the concentrations of these basic species are very small, but it did make it impossible to do measurements at lower concentrations. Hydroxy chlorides such as $Zn_5(OH)_8Cl_2{\cdot}H_2O$ or $Zn_5(OH)_8Cl{\cdot}H_2O$ are probably too soluble at our pH values to be causing this problem (*6*).

The concentration of the pH-adjusted high-purity $ZnCl_2$ stock solution was determined to be 7.3206 ± 0.0043 mol kg^{-1} by conversion to the anhydrous sulfate. Concordant results were obtained at 390 and 425 °C. Mass titration with $AgNO_3$ yielded a concentration of 7.3219 ± 0.0088 mol kg^{-1}. The solution was stoichiometric, since these two analyses gave an anion-to-cation ratio of 2.0004 ± 0.0027. Molecular weights used for the calculations are 136.286 for $ZnCl_2$ and 161.438 for $ZnSO_4$. Table III contains the experimental $ZnCl_2$ densities.

In order to do density measurements below 0.3 mol kg^{-1}, it was necessary to eliminate the colloid formation by acidifying a sample of the stock solution. The acidified sample used had 0.001 45 mol of HCl per mole of $ZnCl_2$ (ionic strength fraction of 0.000 48). This amount of acid was too small to affect the densities within the precision of their determination. This additional acidification might have been avoided had the stock solution been adjusted to its equivalence pH, allowed to age several months, and then readjusted to its equivalence pH. When we calculated concentrations and apparent molal volumes for these acidified solutions, the molecular mass of $ZnCl_2{\cdot}0.00145HCl$, 136.339 g mol^{-1}, was used. These densities are also listed in Table III.

Since both samples of commercial analytical reagent $ZnCl_2$ that were studied contained significant impurities, we measured some additional densities to determine how much error these impurities cause. The Mallinckrodt analytical reagent sample was used since it contained the larger amount of impurities and would emphasize the differences. However, the molecular weight for pure $ZnCl_2$ was used in calculating concentrations since we wanted to see the resulting error if the presence of impurities had not been known. This stock solution had a brownish-yellow color. In contrast, the high-purity stock solution was colorless.

Mass titration of the pH-adjusted Mallinckrodt AR $ZnCl_2$ stock solution with $AgNO_3$ gave a concentration of 17.258 ± 0.009 mol kg^{-1}. Conversion to the anhydrous sulfate at 480 °C resulted in a sample whose weight decreased with time. The samples of $ZnSO_4$ were weighed daily for 1 week and the

Table III. Densities and Apparent Molal Volumes of Aqueous High-Purity $ZnCl_2$ at 25 °C

m, mol kg^{-1}	c, mol dm^{-3}	d, g cm^{-3}	ϕ_V, cm^3 mol^{-1}
0.040010^a	0.039872	1.002 00	12.10
0.089958^a	0.089592	1.008 14	12.54
0.15994^a	0.15913	1.016 61	13.43
0.23987^a	0.23833	1.026 07	14.60
0.28986	0.28774	1.031 91	15.16
0.29985	0.29759	1.033 03	15.41
0.29985^a	0.29760	1.033 07	15.33
0.32790	0.32526	1.036 30	15.65
0.33191	0.32923	1.036 79	15.61
0.33194^a	0.32925	1.036 78	15.70
0.37981	0.37632	1.042 11^b	16.58
0.41978	0.41560	1.046 68	16.91
0.47991	0.47446	1.053 30	17.77
0.51976	0.51337	1.057 67	18.25
0.74978	0.73587	1.081 74	21.25
0.92673	0.90461	1.099 42	23.18
0.94975	0.92635	1.101 61	23.48
0.97261	0.94799	1.103 89	23.65
0.99563	0.96970	1.106 11	23.88
1.2275	1.1863	1.128 06	25.92
1.2711	1.2265	1.132 12	26.24
1.4733	1.4115	1.150 45	27.69
1.5253	1.4587	1.155 13	27.99
1.7505	1.6606	1.174 96	29.23
1.9309	1.8197	1.190 43	30.10
1.9693	1.8533	1.193 64	30.29
1.9893	1.8707	1.195 34	30.38
2.0298	1.9060	1.198 77	30.54
2.4998	2.3070	1.237 29	32.24
2.9664	2.6909	1.273 83	33.52
3.0332	2.7446	1.278 90	33.69
3.4979	3.1116	1.313 66	34.64
3.9653	3.4677	1.347 12	35.44
4.0332	3.5185	1.351 91	35.53
4.4945	3.8561	1.383 49	36.18
5.0018	4.2143	1.416 90	36.77
5.4975	4.5516	1.448 26	37.26
6.0010	4.8821	1.478 89	37.70
6.5043	5.2007	1.508 36^c	38.08
6.9026	5.4448	1.530 87^c	38.36
7.3213	5.6943	1.553 83^c	38.62

[a] Acidified solution corresponding to $ZnCl_2 \cdot 0.00145HCl$. [b] This point given zero weight in the least-squares fits. [c] These three densities are the average of duplicate measurements; the other densities in this table are single determinations.

weights extrapolated back to zero time to yield a concentration of 17.083 ± 0.009 mol kg^{-1}. In contrast, $ZnSO_4$ from the high-purity stock analysis showed no sign of decomposing. Table IV contains the densities of these solutions and the molalities based on both types of concentration analyses. Two experiments were performed with slightly acidified solutions to see whether acidification affects the densities.

The concentration differences for the low-purity stock solution are due to the effect of large amounts of impurities on the analyses. If $AgNO_3$ titration results are accepted, then the low-purity stock solution will yield apparent densities much below their correct values (maximum deviation 1.5 × 10^{-3} g cm^{-3} at 2.5 mol kg^{-1}). Had conversion to the sulfate been used, apparent densities would have been only slightly low. However, if EDTA titration of Zn^{2+} had been used, then the apparent densities probably would have been high. Consequently, impurities in commercial $ZnCl_2$ may be responsible for many discrepancies in published literature data.

Density Measurements

Densities were measured by using ~31-cm^3 single-stem pycnometers that had each been calibrated 7–9 times with pure water at 25.00 ± 0.005 °C (IPTS-68). Water used for these calibrations and for solution preparations was first deionized and then distilled. The pycnometers were wiped with 95% ethanol and then allowed to sit about 0.5 h before weighing. All weights were corrected to vacuum.

The uncertainty in each experimental density measurement is 3 × 10^{-5} g cm^{-3} or less. This uncertainty limit includes the 0.0003–0.0004-cm^3 uncertainty in the pycnometer volume calibrations. A H_2O density of 0.997 045 g cm^{-3} was assumed for volume calibrations (*7*). Duplicate density measurements were made for $MnCl_2$ and $CdCl_2$ and some of the concentrated high-purity $ZnCl_2$ solutions. The remaining $ZnCl_2$ densities are from single measurements.

Most of the concentrations in Tables I–IV were made up by mass dilution of the stock solutions. Concentrations of $MnCl_2$ and $CdCl_2$ greater than the stock concentrations were obtained either by concentrating samples in a desiccator or by gently warming samples at about 50 °C.

Results

Density data from Tables I–IV were represented by least-squares equations of the form

$$d = d^\circ + \sum_{i=2}^{n} B_i X^{i/2} \qquad (1)$$

where X denotes m in mol kg^{-1} or c in mol dm^{-3}. The density of pure water was set at 0.997 045 g cm^{-3} (*7*). Literature density data for these salts (*8–20*) were also included in these fits, and weights were assigned on the basis of internal consistency and upon agreement with other studies. Tables V and VI contain the least-squares coefficients and standard deviations σ for the molality fits and molarity fits, respectively. Density data for high-purity and low-purity $ZnCl_2$ solutions were treated separately.

Unit weights were assigned to our $MnCl_2$ data except for the point at 3.9183 mol kg^{-1}, to Lo Surdo and Millero's results (*8*) except for their point at 0.986 34 mol kg^{-1}, and to Spitzer et al.'s (*9*) values. Figure 1 illustrates the differences between the best molality and molarity fits and these three sets of data.

Three other low-accuracy data sets for $MnCl_2$ solutions (*10–12*) were assigned zero weights for these calculations. Phang's somewhat scattered results (*10*) show random devia-

Table IV. Densities and Apparent Molal Volumes of Aqueous Low-Purity $ZnCl_2$ at 25 °C

m,^{a} mol kg^{-1}	m,^{b} mol kg^{-1}	d, g cm^{-3}	m,^{a} mol kg^{-1}	m,^{b} mol kg^{-1}	d, g cm^{-3}
0.181 46	0.180 90	1.019 04	0.59826	0.59629	1.065 73
0.219 59	0.218 90	1.023 56	0.68053	0.67825	1.074 30
0.240 22	0.239 46	1.025 97	0.72338	0.72095	1.078 67
0.281 30	0.280 41	1.030 76	0.97647	0.97309	1.103 69
0.375 93^c	0.374 72	1.041 54	1.0295	1.0259	1.108 83
0.376 31	0.375 10	1.041 58	1.4783	1.4728	1.149 98
0.420 20^c	0.418 84	1.046 49	1.5318	1.5262	1.154 81
0.420 48	0.419 12	1.046 51	2.4744	2.4643	1.233 74
0.543 08	0.541 30	1.059 89	2.5437	2.5332	1.239 25

[a] Molalities calculated from mass titration with $AgNO_3$. [b] Molalities calculated from conversion to anhydrous sulfate. [c] Acidified solution corresponding to $ZnCl_2 \cdot 0.0014HCl$.

Table V. Molality Coefficients for Density Polynomials

B_i	$MnCl_2$	$CdCl_2$	$ZnCl_2$ [a]	$ZnCl_2$ [b]
B_2	0.106388	0.160110	0.1315768	0.114103
B_3	−0.00299169	−0.00689693	−0.0772948	0.049521
B_4	−0.00543261	−0.00316914	0.30968439	−0.099242
B_5	0.00152964	−0.000749266	−0.68225844	0.055419
B_6	−0.000217274	0.000230691	0.80218974	−0.010858
B_7	0.0	0.0	−0.56504064	0.0
B_8	0.0	0.0	0.24780300	0.0
B_9	0.0	0.0	−0.066581436	0.0
B_{10}	0.0	0.0	0.0100615706	0.0
B_{11}	0.0	0.0	−0.00065623834	0.0
max concn	6.0292	6.3608	7.3213	2.5437
σ	0.000016	0.000022	0.000025	0.000025

[a] High-purity $ZnCl_2$. [b] Low-purity $ZnCl_2$, concentrations based on mass titration with $AgNO_3$.

Table VI. Molarity Coefficients for Density Polynomials

B_i	$MnCl_2$	$CdCl_2$	$ZnCl_2$ [a]	$ZnCl_2$ [b]
B_2	0.106593	0.160342	0.127861	0.114428
B_3	−0.00252066	−0.00647478	−0.0381259	0.050264
B_4	−0.00420492	0.000375581	0.16058645	−0.100682
B_5	0.00247601	0.0	−0.37201666	0.059667
B_6	−0.000463146	0.0	0.41811156	−0.012021
B_7	0.0	0.0	−0.26140323	0.0
B_8	0.0	0.0	0.093884260	0.0
B_9	0.0	0.0	−0.018211594	0.0
B_{10}	0.0	0.0	0.001483429	0.0
max concn	5.0929	5.1670	5.6943	2.3408
σ	0.000015	0.000021	0.000024	0.000022

[a] High-purity $ZnCl_2$. [b] Low-purity $ZnCl_2$, concentrations based on mass titration with $AgNO_3$.

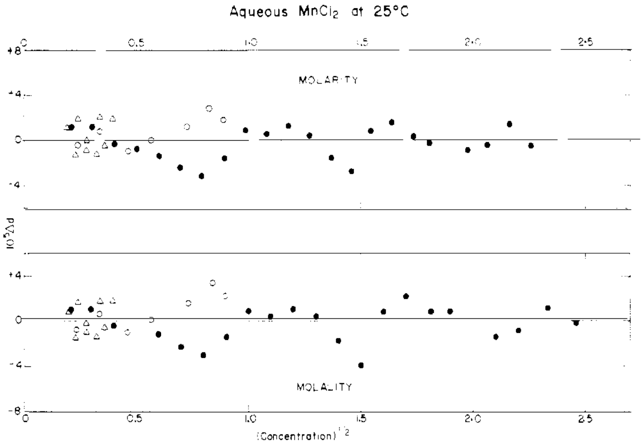

Figure 1. Differences between experimental densities and least-squares equations for $MnCl_2$ solutions in g cm^{-3} × 10^5: (●) this research; (○) Lo Surdo and Millero (*8*); (△) Spitzer et al. (*9*). Top curve is for molarity fit; bottom curve is for molality fit.

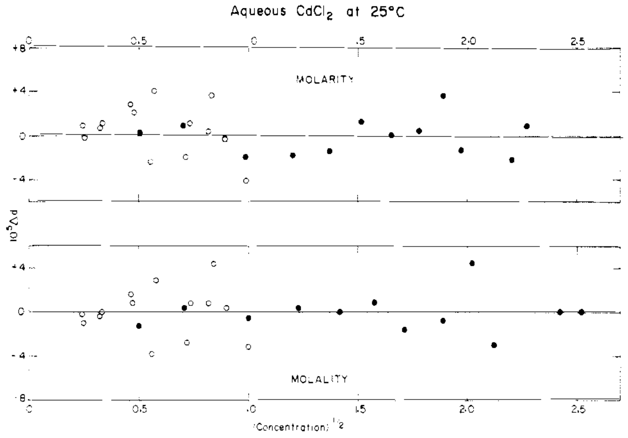

Figure 2. Differences between experimental densities and least-squares equations for $CdCl_2$ solutions in g cm^{-3} × 10^5: (●) this research; (○) Lo Surdo and Millero (*8*). Top curve is for molarity fit; bottom curve is for molality fit.

tions from eq 1 up to 1 mol kg^{-1}; they are fairly low from 1.5 to 2.4 mol kg^{-1}, but they are high at higher concentrations. Borovskaya's data (*11*) have gross negative deviations, whereas Kapustinskii's values (*12*) have gross positive deviations.

Unit weights were given to our $CdCl_2$ densities and the recent values of Lo Surdo and Millero (*8*), except for their point at 0.79698 mol kg^{-1}. Figure 2 compares these densities to the least-squares fits of eq 1. These two set of densities agree within their experimental scatter.

The badly scattered $CdCl_2$ density data of Dolian and Briscoe (*13*), Rabinowitsch (*14*), and Getman and Gilroy (*15*) were assigned zero weights in the least-squares fits, as were the slightly less scattered results of Lühdemann (*16*). Lühdemann's and Rabinowitsch's results tend to be higher than ours, whereas Getman and Gilroy's tend to be lower. Dolian and Briscoe's results exhibit random deviations from our values. Reilly and Stokes' densities (*17*) are within 1.6 × 10^{-4} g cm^{-3} of ours, but the differences show a sinusoidal type variation with concentration. They reported their densities at round concentrations, and the systematic variation may be due to inaccuracies in the smoothing rather than in their original data. Values given in the International Critical Tables (*18*), based on data published before 1928, are low over most of the concentration range.

As noted above, commercial $ZnCl_2$ samples were found to contain significant and variable amounts of impurities which affect the observed density values. The impurity content of the $ZnCl_2$ is unknown for most published studies. Consequently, only our data were included in the least-squares fits, and the high-purity and low-purity data were treated separately. Figure 3 compares the high-purity densities to the least-squares fit of eq 1. The scatter is slightly greater than for the other two salts, presumably because most of the $ZnCl_2$ points were single rather than duplicate determinations. The results with and without extra HCl are in agreement. A rather large number of terms were required for eq 1 to represent the $ZnCl_2$ data accurately. Least-squares coefficients for the low-purity $ZnCl_2$ were based on the $AgNO_3$ titration data.

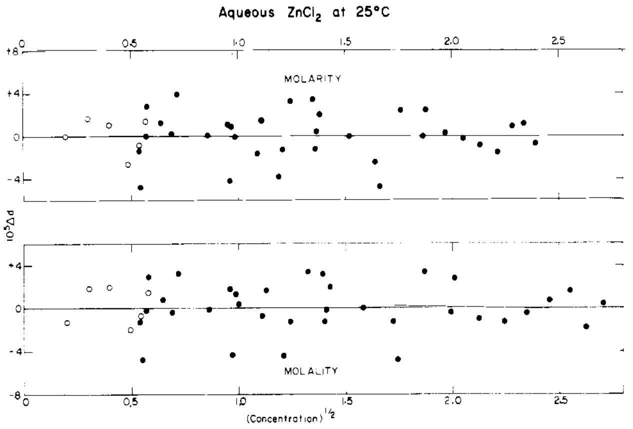

Figure 3. Differences between experimental densities and least-squares equations for high-purity $ZnCl_2$ solutions in g cm^{-3} × 10^5: (●) pH-adjusted stock solution; (○) acidified stock solution. Top curve is for molarity fit; bottom curve is for molality fit.

Rabinowitsch's results (*14*) exhibit large positive deviations from our high-purity $ZnCl_2$ densities. International Critical Tables values (*18*) are also high and are presumably based mainly on Rabinowitsch's data.

Lo Surdo and Millero's $ZnCl_2$ densities (*8*) are 1.8×10^{-5} g cm^{-3} higher than our high-purity results at 0.06 mol kg^{-1} but are 2.2×10^{-4} g cm^{-3} high at 1.028 mol kg^{-1}. This maximum discrepancy is 39% of the error for our low-purity solutions at 1.028 mol kg^{-1} (our $AgNO_3$ analysis results) but is opposite in sign. This indicates that the impurity content was less for their solution than ours. Dr. Millero (*21*) believes that their $ZnCl_2$ may have been Baker Analyzed, but the information is no longer available to him. If their concentration scale is normalized to our high-purity solution data at their highest concentration (0.222% molality increase), then their other densities are within 1.1×10^{-5} g cm^{-3} of our least-squares equations.

Two previous $ZnCl_2$ density studies (*19*, *20*) have been reported for high-purity $ZnCl_2$. The EDA results (*19*) differ by as much as 3×10^{-3} g cm^{-3} from the present results. This difference is not very surprising since the temperature was only controlled to 25.0 ± 0.2 °C in that study, and their data are scattered by 2×10^{-3} g cm^{-3}. Agnew and Paterson (*20*) reported their results only as a least-squares equation "valid" from 0.1 to 4.0 mol dm^{-3}. Their equation agrees very well with our data at the lower and higher concentration limits but shows cyclic deviations of up to 1.5×10^{-3} g cm^{-3} at intermediate concentrations. As was the case for one $CdCl_2$ data set (*17*), this may be a problem more with the published smoothing of their data rather than a real disagreement between experimental results.

Tables I–III also contain the apparent molar volumes of these transition-metal chlorides in aqueous solution. These values were calculated with the equation

$$\phi_v = \frac{10^3(d^\circ - d)}{m d^\circ d} + \frac{M_2}{d} \qquad (2)$$

where M_2 is the molecular weight of the electrolyte and ϕ_v is in cm^3 mol^{-1}. The experimental uncertainty of 3×10^{-5} g cm^{-3} in d yields values of ϕ_v reliable to 0.003 cm^3 mol^{-1} at high concentrations. However, at 0.04 mol kg^{-1}, this same uncertainty produces an uncertainty in ϕ_v of 0.7 cm^3 mol^{-1}. In principle these values can be extrapolated to yield the standard-state partial molal volume at infinite dilution, $\bar{V}_2^\circ$, for each salt. Ion-pairing, electrostriction, and other structural effects could give a slope at infinite dilution different from that observed at our lowest experimental concentrations. Consequently, no attempt was made to obtain $\bar{V}_2^\circ$ from extrapolation of our data. Since $ZnCl_2$ and $CdCl_2$ are highly associated electrolytes, data at much lower concentrations would be required to do a meaningful extrapolation for them.

Under favorable circumstances, vibrating densimeters can yield slightly more precise densities and therefore $\bar{V}_2^\circ$ values. However, when we ran moderately and highly concentrated transition-metal chloride solutions in our SODEV unit, the calibration parameters underwent a large drift and took several days to return to normal. Although this problem would probably be less at lower concentrations, the SODEV was not used for these solutions since we would have had less confidence in the resulting data. Similar problems have occurred at the Australian National University (*22*).

Solubilities listed in Linke (*23*, *24*) are 6.130 mol kg^{-1} for $MnCl_2$ and 6.574 mol kg^{-1} for $CdCl_2$. Thus, our densities extend to within 0.1–0.2 mol kg^{-1} of saturation. However, the solubility of $ZnCl_2$ (*23*) is much greater than the highest concentration studied here (≈32 mol kg^{-1}).

Note Added in Proof. In the text we speculated that the $ZnCl_2$ least-squares density equation of ref *20* was inaccurate. Professor Paterson (University of Glasgow, private communication, Oct 1983) supplied us with their actual data. Their density equation cycles around their data by 1.5×10^{-3} g cm^{-3}. However, their densities are still higher than ours ($<8 \times 10^{-4}$ g cm^{-3} below 3.2 mol dm^{-3}; 1.2×10^{-3} g cm^{-3} at 4.74 mol dm^{-3}).

Acknowledgment

We thank John G. Albright for the loan of his "Australian" pycnometers, and Richard Ryon, Beatrice Armstrong, and Theresa Duewer for the spectroscopic impurity analyses. The $MnCl_2$ and $CdCl_2$ data were measured with support from the Office of Basic Energy Sciences (Geosciences) of the U.S. Department of Energy; the $ZnCl_2$ measurements were supported by the Office of Energy Systems (Energy Storage Technology) of the U.S. Department of Energy. Thanks are also due to Sandy Auguadro, Susan Beighley, and Charlotte Stuart (LLNL Correspondence Center, A.D. Administrative) for the word processing/typing of this manuscript.

Glossary

d	density of solution, g cm^{-3}
d°	density of pure water, g cm^{-3}
m	molal concentration of solute, mol kg^{-1} (where kg refers to H_2O)
c	molar concentration of solute, mol dm^{-3}
ϕ_v	apparent molal volume of solute, cm^3 mol^{-1}
M_2	molecular weight of solute
$\bar{V}_2^\circ$	partial molal volume of solute at infinite dilution
B_i	least-squares coefficients for density polynomials
X	denotes m or c in fitting equations
σ	standard deviation of fitting equations

Registry No. $MnCl_2$, 7773-01-5; $CdCl_2$, 10108-64-2; $ZnCl_2$, 7646-85-7.

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Received for review March 10, 1983. Accepted August 30, 1983. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

Vapor–Liquid Equilibria for Three Aldehyde/Hydrocarbon Mixtures

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Isothermal vapor–liquid equilibrium (VLE) data were measured for the mixtures *n*-pentane/propionaldehyde, *n*-heptane/*n*-butyraldehyde, and isobutyraldehyde/*n*-heptane at low pressures (100–1000 mmHg) by using a dynamic still. The data reported here are thermodynamically consistent according to the point-to-point consistency test. These data are correlated with five activity coefficient models with parameters estimated from the maximum likelihood method. Also, UNIFAC parameters were estimated for the aldehyde/hydrocarbon functional-group interactions based on the new data.

Introduction

Reliable experimental vapor–liquid equilibrium (VLE) data are of importance in the design of separation processes based on phase equilibria, and also to the continuing development of group contribution methods for the semitheoretical prediction of VLE.

In this study, isothermal VLE data were measured for the following binary systems: *n*-pentane/propionaldehyde at 40.0 °C, *n*-butyraldehyde/*n*-heptane at 45.0 and 70.0 °C, and isobutyraldehyde/*n*-heptane at 45.0 °C. Accurate data for these aldehyde/hydrocarbon systems, which have not been previously available, will allow for the revision of the UNIFAC parameters for the aldehyde/hydrocarbon functional-group interactions. These data will also be useful in developing a better understanding of polar–nonpolar interactions.

Few vapor–liquid equilibrium data have been published for aldehydes, an industrially important and common class of chemicals. The lack of such data may be attributed to the difficulty involved in working with aldehydes, due to their chemical instability to oxidation and polymerization (*1*).

Experimental Section

A crucial step in the experimental procedure was ensuring that the materials used were pure. Three physical properties (density, refractive index, and normal boiling point) were measured as a criterion of purity (*2*). The normal boiling point and the pure-component vapor pressure data are the most important and sensitive properties for determining purity. The pure-component vapor pressures of the same batch of chemicals as were used in the mixture experiments were measured with the Stage-Muller still to be described shortly, which was also used for the binary VLE experiments. The vapor pressure data were correlated by using the Antoine equation

$$\log P = A - B/(T + C) \qquad (1)$$

where the constants were determined by using the maximum likelihood method (*3*). The pure-component vapor pressures at the temperatures of interest are included in the experimental data sets which follow, and the Antoine constants appear in Table I.

n-Pentane and *n*-heptane were available in relatively high purity (99+%) from Alfa Products. Further purification was not necessary since no secondary peaks were found from gas-chromatographic analysis and physical property measurements proved satisfactory (see Table II). The aldehydes, also obtained from Alfa Products, were distilled in a packed, all-glass rectification column in a nitrogen atmosphere and stored over molecular sieves (Fisher, Scientific, M-514). Traces of an oxidation inhibitor, hydroquinone (<0.05 wt %), were added to the distillation charge to minimize any oxidation. The physical property measurements of the aldehydes are summarized in Table II. There was no evidence of polymerization or oxidiation during the VLE experiments.

The vapor–liquid equilibrium experiments were the first that we have performed by using an all-glass, Stage-Muller dynamic equilibrium still (*4*), in which both the liquid and vapor phases are recirculated. The still was manufactured by Fischer Labor-und Verfahrenstechnik of West Germany. The essential features of the still, which have been described previously (*4*), are shown in Figure 1. The overall setup of the apparatus is shown in Figure 2. The important features of this still are the Cottrell pump, the silver-plated vacuum jacket, and the magnetic sampling valves. The jacket, which surrounds the equilibrium chamber, eliminates partial condensation of the vapor disengaging from the liquid at the exit from the Cottrell pump. The magnetic valves allow sampling without disruption of operation of the still. The still used in this study was further modified by adding condensers above the sampling points to recover any partially vaporized sample.

All experiments were carried out under an inert atmosphere of nitrogen (Matheson, purity greater than 99.99%) to avoid exposure to moisture and oxygen. The mixture was heated by immersing the boiling flask in a silicon oil bath. Mixing within the flask was accomplished by a magnetic stirrer. The temperature immediately outside the equilibrium chamber was maintained approximately 1 °C lower than the equilibrium temperature by using a thermostated heating jacket. Steady-state

0021-9568/84/1729-0156$01.50/0