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Quaternary Liquid–Liquid Equilibrium. Water–Ethanol–1-Butanol–Chloroform at 25 °C. Experimental Determination and Graphical Representation of Equilibrium Data

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Mutual solubility and tie-line data at 25 °C and atmospheric pressure are presented for the ternary systems water–1-butanol–chloroform, water–ethanol–chloroform, and water–ethanol–1-butanol and the quaternary system water–ethanol–1-butanol–chloroform. Experimental results have been obtained by applying a systematic method of selection of the points to be measured. This method permits representation of the heterogeneous region to be fully characterized as well as allowing extraction computations.

Introduction

The applications of quaternary systems in liquid–liquid extraction processes have in recent years gained increased interest in chemical technology. However, the number of studies related to quaternary liquid–liquid systems in the literature is small. Sorensen and Arlt (*1*) and Prats (*2*) report about 60 quaternary systems. On the other hand, experimental data from only some of these systems permit one to obtain equilibrium relationships of the entire heterogeneous region.

In this work, equilibrium data for the quaternary system water–ethanol–1-butanol–chloroform at 25 °C and atmospheric pressure have been determined experimentally. This system contains two pairs of partly miscible compounds: water–1-butanol and water–chloroform.

Experimental Section

Reagents. All chemicals (analytical reagent grade) were supplied by Merck. The contents of volatile impurities were determined by chromatographic analysis. With the exception of chloroform, all the compounds contained negligible amounts of impurities (less than 0.1%). Chloroform was stabilized with ethanol in a percentage varying from 0.7% to 0.8%; the ethanol was removed by extraction with water.

Determination of the Saturation Surface. The cloud point method was used for determinations of the saturation surface in the quaternary system and of the binodal curves in the three ternary systems with limited miscibility of the components. The experimental device was the same as that used by Ruiz and Prats (*3*).

Determination of Liquid–Liquid Equilibrium. Data of the tie lines of the different systems were determined by an intensive stirring of known amounts of the constituents for at least 2 h at 25 °C; the phases then were allowed to settle and separate. Multicomponent samples were then analyzed by gas chromatography, using a Shimadzu chromatograph GCR1A, equipped with an electronic integrator RPR-G1. A good separation of the four components was obtained on a 2 m × $^1/_8$ in. column, packed with Chromosorb 101 100/120. The column temperature was 170 °C and the detection was carried out by thermal conductivity. The detector current was 100 mA at a helium flow rate of 40 mL/min. For the quantitative results we have applied the internal standard method, 1-propanol being the standard compound used for this purpose. The relative accuracy of weight fraction measurements is about 1%.

Table I. Mutual Solubility Data (Weight Percent) for Water (W)-1-Butanol (B)-Chloroform (C) at 25 °C

X_W	X_B	X_C	X_W	X_B	X_C
99.3	0.0	0.7	11.9	70.5	17.6
99.2	0.2	0.7	9.5	63.3	27.2
99.8	0.5	0.7	6.6	56.0	37.4
98.3	1.1	0.6	5.0	47.5	47.5
96.8	2.6	0.6	3.3	38.6	58.0
92.6	7.4	0.0	2.4	29.6	68.0
20.1	79.8	0.0	1.2	19.8	79.0
15.8	75.6	8.6	0.09	0.0	99.9

Table II. Mutual Solubility Data (Weight Percent) for Water (W)-Ethanol (E)-Chloroform (C) at 25 °C

X_W	X_E	X_C	X_W	X_E	X_C
3.9	21.1	75.0	33.3	39.4	27.3
7.3	27.0	65.7	36.4	39.3	24.3
10.3	31.8	58.0	39.6	39.1	21.3
13.1	34.5	52.4	42.9	38.7	18.4
16.0	36.0	48.0	46.1	38.5	15.4
18.7	37.6	43.7	49.8	37.7	12.5
21.7	38.1	40.2	53.7	36.8	9.5
24.5	38.7	36.8	58.3	35.2	6.5
27.4	39.1	33.5	65.1	31.5	3.4
30.4	39.3	30.4	89.1	10.0	0.9

Methodology Applied to the Selection of Points To Be Determined Experimentally. The quaternary system water (W)–ethanol (E)–1-butanol (B)–chloroform (C) is represented schematically in Figure 1, using a regular tetrahedron. To characterize the solubility surface fully, ternary solubility curves for the systems W–B–C, W–E–C, and W–E–B were determined experimentally, and also the four quaternary solubility curves which form the intersections of four equidistant planes (such as W–E–M) with the heterogeneous region. *M* represents the mixture 1-butanol–chloroform and its value is defined as $M = X_B/(X_B + X_C)$ where X_B and X_C are the weight percent of 1-butanol and chloroform, respectively. The four quaternary planes have values of M = 0.2, 0.4, 0.6, and 0.8, while M = 0.0 denotes the ternary plane water–ethanol–chloroform and M = 1.0 the ternary plane water–ethanol–1-butanol. The six resulting solubility curves may prove to be sufficient for the deduction of points over the solubility surface, by interpolation.

Initial mixtures were selected to determine tie lines providing regular variation of composition within the heterogeneous region. Initial mixtures were selected with the following conditions: (i) $X_W = X_B + X_C$ in each plane W–E–M (M = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0). (ii) The ethanol levels (L) were increased stepwise until the homogeneous region was reached.

This methodology is a modification of that used of Chang and Moulton (*4*) for type II quaternary systems and it is similar to that developed by Ruiz and Prats (*3*) for type I quaternary systems.

Results

Tables I–III, respectively, show the mutual solubility data for each of the ternary systems water–1-butanol–chloroform,

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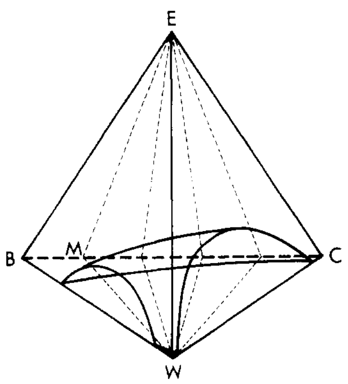

Figure 1. Schematic representation of quaternary system water (W)-ethanol (E)-1-butanol (B)-chloroform (C): section planes for the determination of the solubility surface.

Table III. Mutual Solubility Data (Weight Percent) for Water (W)-Ethanol (E)-1-Butanol (B) at 25 °C

X_W	X_E	X_B	X_W	X_E	X_B
23.7	5.2	71.1	56.2	13.6	30.2
27.6	8.3	64.1	60.6	13.4	26.0
31.2	10.6	58.1	66.2	13.0	20.8
35.1	12.2	52.7	70.3	12.1	17.6
39.1	13.3	47.6	75.4	11.3	13.3
43.1	13.7	43.2	82.1	8.7	9.1
47.3	14.0	38.7	87.6	4.7	7.7
51.7	13.8	34.5			

Table IV. Quaternary Solubility Data (Weight Percent) for Water (W)-Ethanol (E)-1-Butanol (B)-Chloroform (C) at 25 °C

X_W	X_E	X_B	X_C	X_W	X_E	X_B	X_C
	$M = 0.2$				$M = 0.4$		
4.3	14.1	16.3	65.3	4.7	5.5	35.9	53.8
7.7	22.5	14.0	55.8	8.5	15.5	30.4	45.6
10.9	27.3	12.4	49.4	11.7	21.9	26.6	39.8
14.0	30.5	11.1	44.5	15.0	24.8	24.1	36.1
16.9	32.1	10.2	40.7	18.1	27.7	21.7	32.5
19.9	33.9	9.2	37.0	21.2	29.2	19.8	29.8
22.9	34.5	8.5	34.1	24.4	30.2	18.1	27.2
26.0	35.0	7.8	31.2	27.6	30.9	16.6	24.9
28.8	35.3	7.2	28.7	31.0	31.2	15.1	22.7
32.3	35.5	6.5	25.8	34.3	31.5	13.7	20.5
35.5	35.6	5.8	23.1	37.6	31.5	12.3	18.5
38.7	35.5	5.2	20.6	41.1	31.4	11.0	16.4
41.9	35.4	4.5	18.2	44.8	31.1	9.6	14.5
45.5	35.0	3.9	15.6	48.4	30.9	8.3	12.4
49.0	34.8	3.2	13.0	51.9	30.8	6.9	10.4
52.8	34.0	2.6	10.6	55.5	30.6	5.6	8.3
56.6	33.4	2.0	8.0	59.2	30.3	4.2	6.3
60.9	32.3	1.4	5.4	64.1	28.8	2.9	4.3
67.5	28.9	0.7	2.8	70.8	25.4	1.5	2.3
78.1	20.2	0.3	1.4	88.0	10.0	0.8	1.2
88.8	10.0	0.2	1.0				
	$M = 0.6$				$M = 0.8$		
12.8	14.1	43.9	29.2	17.9	10.5	57.3	14.3
16.3	18.7	38.9	26.0	21.5	14.2	51.5	12.9
19.8	20.8	35.6	23.8	24.9	16.8	46.6	11.7
23.2	23.7	31.8	21.2	28.5	18.8	42.2	10.6
26.2	25.0	29.3	19.5	32.1	19.9	38.4	9.6
29.6	25.9	26.6	17.8	35.8	20.5	35.0	8.7
33.0	26.4	24.4	16.2	39.6	20.9	31.6	7.9
36.7	26.6	22.0	14.7	43.5	21.1	28.3	7.1
40.3	26.7	19.8	13.2	47.1	21.5	25.1	6.3
44.0	26.6	17.6	11.8	51.4	20.9	22.2	5.5
47.8	26.5	15.4	10.3	55.4	20.9	19.0	4.7
51.6	26.3	13.3	8.8	59.7	20.5	15.9	4.0
55.4	26.1	11.1	7.4	63.7	20.4	12.7	3.2
59.3	25.9	8.9	5.9	68.0	20.0	9.6	2.4
63.1	25.8	6.7	4.4	72.6	19.3	6.5	1.6
67.6	24.8	4.5	3.0	85.8	10.1	3.3	0.8
75.7	20.4	2.4	1.6				
87.1	10.0	1.7	1.2				

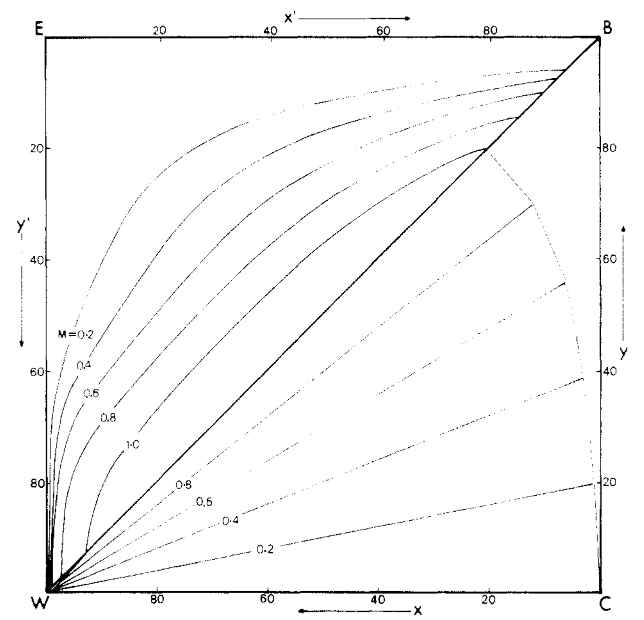

Figure 2. Solubility surface for the system water (W)-ethanol (E)-1-butanol (B)-chloroform (C) at 25 °C: method proposed by Frolov ($x = 100X_W/(100 - X_E)$, $y = 100X_B/(100 - X_E)$, $x' = 100X_B/(100 - X_C)$, and $y' = 100X_W/(100 - X_C)$).

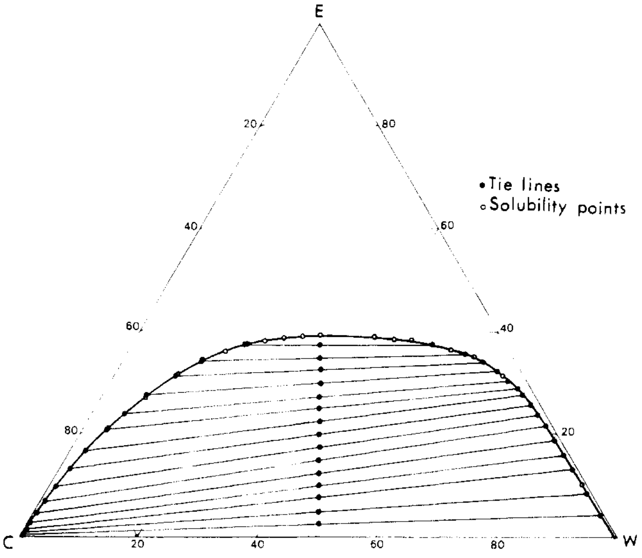

Figure 3. Phase diagram for the ternary system water (W)-ethanol (E)-chloroform (C) at 25 °C.

Table V. Tie-Line Data (Weight Percent) for Water (W)-1-Butanol (B)-Chloroform (C) at 25 °C

	aqueous phase			organic phase		
M(initial)	X_W	X_B	X_C	X_W	X_B	X_C
0.0	99.3	0.00	0.70	0.088	0.0	99.9
0.2	96.8	2.66	0.56	1.13	17.7	81.2
0.4	95.8	3.74	0.48	3.15	37.1	59.8
0.6	94.9	4.76	0.32	6.38	54.7	38.9
0.8	93.9	5.98	0.17	11.7	69.8	18.5
1.0	92.6	7.35	0.00	20.2	79.8	0.0

water-ethanol-chloroform, and water-ethanol-1-butanol. Quaternary solubility points concerning the planes $M = 0.2$, 0.4, 0.6, and 0.8 are shown in Table IV.

The quantitative representation of the solubility surface is shown in Figure 2. The representation proposed by Frolov (*5*) has been used in this figure. This representation is appropriate for the interpolation of solubility surface points.

The tie lines for the ternary systems water-1-butanol-chloroform, water-ethanol-chloroform, and water-ethanol-1-buta-

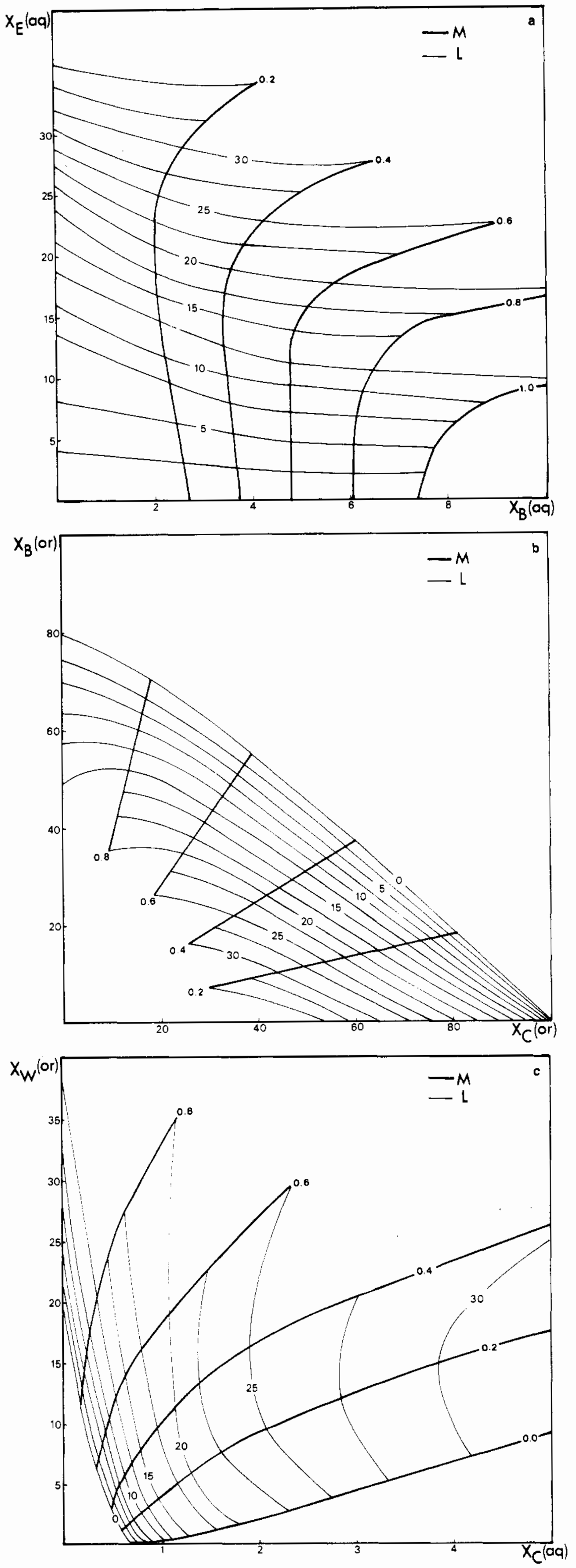

Figure 4. Distribution curves for the system water (W)–ethanol (E)–1-butanol (B)–chloroform (C) at 25 °C: (a) weight percentage of ethanol vs. weight percentage of 1-butanol, aqueous phase; (b) weight percentage of 1-butanol vs. weight percentage of chloroform, organic phase; (c) weight percentage of water in organic phase vs. weight percentage of chloroform in aqueous phase.

Table VI. Tie-Line Data (Weight Percent) for Water (W)-Ethanol (E)-Chloroform (C) at 25 °C

	aqueous phase			organic phase		
L(initial)	X_W	X_E	X_C	X_W	X_E	X_C
2.5	95.1	4.16	0.76	0.10	0.51	99.4
5.0	90.6	8.56	0.88	0.11	1.04	98.9
7.5	85.5	13.6	0.92	0.14	1.86	98.0
10.0	83.0	16.0	1.02	0.25	2.96	96.8
12.5	80.0	18.9	1.08	0.44	4.75	94.8
15.0	77.6	21.2	1.27	0.77	7.14	92.1
17.5	74.7	23.7	1.54	1.21	10.1	88.6
20.0	72.5	25.8	1.77	1.76	13.2	85.0
22.5	70.4	27.3	2.28	2.86	17.1	80.0
25.0	68.4	28.9	2.74	3.88	20.9	75.2
27.5	66.3	30.4	3.35	5.23	24.7	70.1
30.0	63.8	32.1	4.16	7.51	28.0	64.5
32.5	60.4	33.8	5.72	10.3	31.5	58.2
35.0	56.4	35.7	7.95	13.7	34.8	51.6
37.5	49.7	37.8	12.6	19.7	37.7	42.6

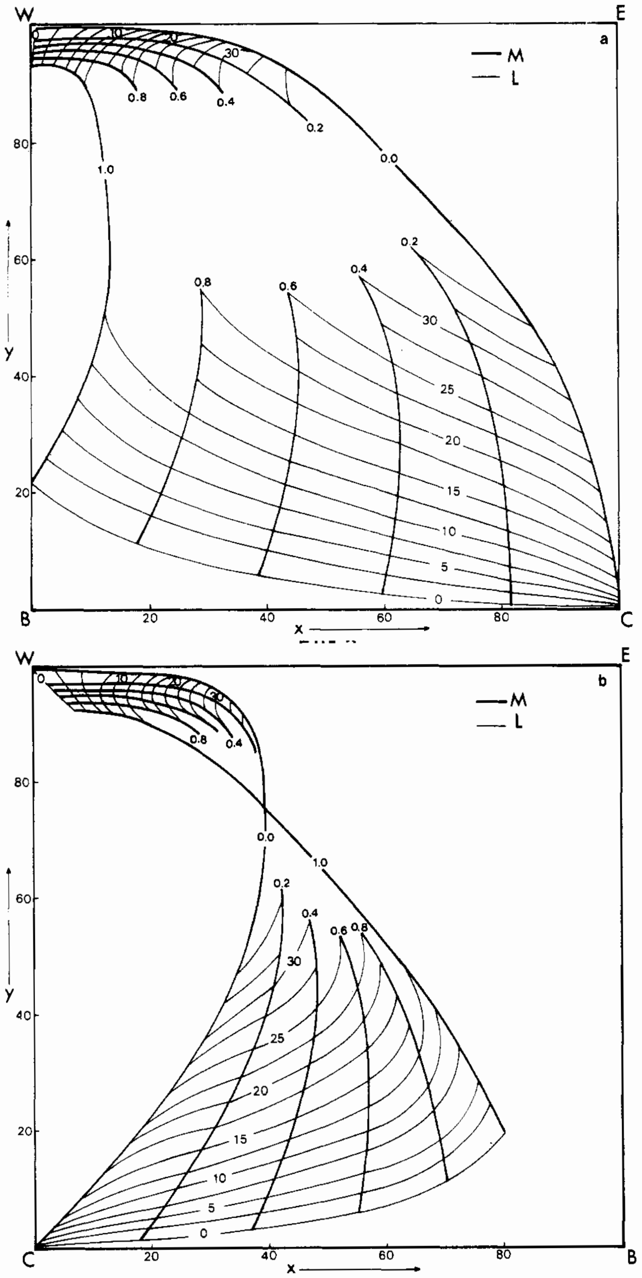

Figure 5. Equilibrium of the system water (W)–ethanol (E)–1-butanol (B)–chloroform (C) at 25 °C: (a) projection onto a plane parallel to the W–C and E–B edges ($x = X_E + X_C$ and $y = X_E + X_W$); (b) projection onto a plane parallel to the W–B and E–C edges ($x = X_E + X_B$ and $y = X_E + X_W$).

Table VII. Tie-Line Data (Weight Percent) for Water (W)-Ethanol (E)-1-Butanol (B) at 25 °C

	aqueous phase			organic phase		
L(initial)	X_W	X_E	X_B	X_W	X_E	X_B
1.25	91.5	1.06	7.48	21.0	1.34	77.7
2.50	90.5	1.95	7.55	22.7	2.68	74.6
3.75	89.5	2.96	7.58	23.4	4.18	72.4
5.00	88.4	3.94	7.64	24.6	5.49	69.9
6.25	87.1	5.01	7.90	26.8	6.83	66.4
7.50	85.7	6.11	8.21	27.9	8.29	63.8
8.75	84.8	6.93	8.27	29.6	9.36	61.1
10.00	83.5	7.72	8.78	31.9	10.6	57.5
11.25	81.0	8.55	10.4	34.6	11.9	53.5
12.50	79.4	9.46	11.1	38.1	12.9	49.1

nol appear in Tables V–VII. As an example, Figure 3 shows the phase diagram for the solutropic ternary system water–ethanol–chloroform. The data points plotted give an idea of the relative accuracies.

The compositions for the quaternary tie lines are shown in Table VIII. The values of M and L for the initial mixtures are also included.

The compositions of all tie lines may be correlated graphically by the Ruiz and Prats methods (*6*). Figure 4 shows a set of three graphs which define the equilibrium of the system. This method of representation is a modification of the method 1 suggested by Ruiz and Prats (*6*) and consists of representing, on the same graph, the percentages of two compounds as a function of the parameters M and L. Figure 5 is an application of method 2 (*6*) and consists of a graphical representation of the variations of two parameters (M and L) of the original mixture vs. the concentrations of the four components. In order to carry out the representation, a tetrahedral projection is made onto a plane parallel to the edges that do not meet.

These representations are appropriate for the interpolation of equilibrium data suitable for extraction computations.

Glossary

B	1-butanol
C	chloroform
E	ethanol
L	ethanol level; its value is defined as $L = X_E$ in the initial mixture

Table VIII. Tie-Line Data (Weight Percent) for Water (W)-Ethanol (E)-1-Butanol (B)-Chloroform (C) at 25 °C

	aqueous phase				organic phase			
L(initial)	X_W	X_E	X_B	X_C	X_W	X_E	X_B	X_C
M(initial) = 0.2								
2.5	93.7	3.18	2.54	0.63	1.36	1.67	17.3	79.6
5.0	90.5	6.40	2.45	0.65	1.64	3.45	17.0	77.9
7.5	87.4	9.56	2.30	0.72	2.06	5.62	16.7	75.6
10.0	85.2	11.7	2.24	0.84	2.53	8.14	16.4	72.9
12.5	82.1	14.9	2.07	0.88	3.08	10.4	15.8	70.7
15.0	80.1	17.4	1.97	0.95	3.87	13.2	15.1	67.8
17.5	78.2	18.6	2.02	1.19	4.92	16.4	14.5	64.2
20.0	76.0	20.7	2.02	1.31	6.12	19.3	13.8	60.8
22.5	73.8	22.6	2.06	1.62	7.67	22.4	12.9	57.1
25.0	70.9	24.9	2.08	2.06	9.50	25.1	12.1	53.2
27.5	68.0	26.8	2.28	2.85	12.0	28.2	11.1	48.7
30.0	64.8	28.7	2.62	3.83	15.0	31.0	10.0	44.0
32.5	59.9	31.0	3.08	6.00	19.1	33.3	8.95	38.6
35.0	50.0	34.2	4.19	11.5	28.1	35.2	7.10	29.6
M(initial) = 0.4								
2.5	93.3	2.62	3.65	0.53	3.62	2.36	35.7	58.4
5.0	90.5	5.38	3.58	0.54	4.22	4.65	34.6	56.5
7.5	88.0	7.92	3.50	0.56	5.01	7.14	33.5	54.3
10.0	85.6	10.3	3.48	0.64	5.83	9.65	32.1	52.4
12.5	83.4	12.5	3.41	0.70	6.79	12.5	30.6	50.1
15.0	80.5	15.3	3.38	0.80	8.00	15.3	29.1	47.6
17.5	78.9	16.6	3.51	0.96	9.95	18.6	27.4	44.0
20.0	76.5	18.7	3.66	1.16	11.4	21.1	25.9	41.7
22.5	74.0	20.8	3.80	1.37	13.4	23.8	23.8	39.0
25.0	71.1	22.8	4.24	1.92	16.5	26.3	21.9	35.2
27.5	67.2	24.9	4.92	3.03	20.5	28.7	19.5	31.3
30.0	60.6	27.5	6.45	5.43	27.3	30.7	16.4	25.6
M(initial) = 0.6								
2.5	92.6	2.30	4.82	0.37	7.29	2.65	53.1	37.1
5.0	90.1	4.71	4.75	0.42	8.21	5.26	50.4	36.1
7.5	87.8	7.11	4.69	0.43	9.30	7.91	48.3	34.5
10.0	85.5	9.27	4.76	0.49	10.6	10.7	46.0	32.8
12.5	83.6	11.1	4.79	0.54	12.2	13.5	43.4	30.9
15.0	80.7	13.8	4.82	0.62	14.1	16.0	40.8	29.0
17.5	78.3	15.6	5.23	0.85	16.2	19.0	37.9	26.9
20.0	75.5	17.7	5.73	1.07	19.1	21.4	34.8	24.7
22.5	71.4	20.0	7.09	1.48	22.9	23.8	31.1	22.2
25.0	66.3	22.4	9.00	2.36	29.5	25.6	26.4	18.5
M(initial) = 0.8								
2.5	91.6	2.09	6.09	0.19	12.8	2.81	76.7	17.7
5.0	89.3	4.36	6.08	0.22	14.1	5.46	63.4	17.0
7.5	87.2	6.51	6.10	0.23	15.9	8.25	59.9	15.9
10.0	84.9	8.60	6.21	0.28	17.9	11.0	56.0	15.1
12.5	82.7	10.5	6.52	0.34	20.4	13.7	52.1	13.8
15.0	79.3	13.2	7.04	0.44	23.7	16.0	47.7	12.6
17.5	76.1	15.1	8.09	0.65	27.5	18.4	42.9	11.2
20.0	71.0	16.9	11.0	1.18	35.1	20.5	35.3	9.09

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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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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