Partial Molar Volumes of Cobalt(II) Chloride in Ethanol + Water at 298.15 K

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Densities of ethanol + water + cobalt(II) chloride mixtures have been measured with an oscillating-tube densimeter over a large range of concentrations of salt, at 298.15 K. From these densities, apparent molar volumes of the electrolyte in these mixtures have been calculated, and partial molar volumes at infinite dilution have been evaluated, at different concentrations of alcohol in the solvent.

Introduction

The volumetric behavior of solutes has proved to be very useful in elucidating the different interactions present in a solution. Studies on the apparent and partial molar volumes of electrolytes can be used to examine the ion−ion, ion−solvent, and solvent−solvent interactions. However, little work has been carried out on experimental evaluation of the partial molar volumes of ions dissolved in aqueous mixed solvent systems.

In a previous work (Peña et al., 1994), we studied the vapor−liquid equilibrium of the ethanol + water + cobalt(II) chloride system. In the present work, we have determined the densities of this system at 298.15 K and we have obtained the apparent molar volumes of the cobalt(II) chloride in ethanol + water mixtures, as well as the partial molar volumes.

In the literature, we have found experimental density data of the water + cobalt(II) chloride (Phang, 1980; Herrington et al., 1986; Pogue and Atkinson, 1989) and ethanol + cobalt(II) chloride binary systems (Meyer *et al.*, 1960), but we have not found any reported density data of the ethanol + water + cobalt(II) chloride ternary system.

Experimental Section

The chemicals were absolute ethanol (Baker analyzed reagent, >99.5 mass %), distilled water, and cobalt(II) chloride (Probus, >99.5 mass %). They were used without further purification. Ethanol density was (785.08 ± 0.01) m^{-3} at 298.15 K, indicating a maximum of 0.01 vol % of water, as reported by Marsh and Richards (1980). Water density was (997.05 ± 0.01) kg·m^{-3} at 298.15 K.

The ethanol + water + cobalt(II) chloride mixtures were prepared one by one gravimetrically using a Sartorius analytical balance with a precision of ±0.0001 g. They were also stirred for sufficient time to assure dissolution of the salt and stored in vials prior to use. Samples were kept in a water bath at 303 K to prevent the formation of bubbles in the densimeter. The accuracy of sample molar fractions was also lower than 0.0001.

The sample densities were measured with an Anton Paar DMA 55 densimeter matched to a Julabo circulator with proportional temperature control and an automatic drift correction system that kept the samples at (298.15 ± 0.01) K. The densimeter was calibrated with distilled water and dry air. The accuracy of density values was ±0.01 kg·m^{-3}.

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Table 1. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Cobalt(II) Chloride (3) Mixtures and Apparent Molar Volumes Φ_v of Cobalt(II) Chloride in Ethanol at 298.15 K

x_3	d (kg·m^{-3})	V (cm^3·mol^{-1})	c (mol·L^{-1})	Φ_v (cm^3·mol^{-1})
0.0101	805.52	58.24	0.1729	14.66
0.0202	826.01	57.82	0.3493	16.09
0.0300	845.76	57.45	0.5228	17.49
0.0399	865.88	57.07	0.6995	18.23
0.0502	887.29	56.66	0.8865	18.49
0.0602	907.90	56.29	1.0686	18.96
0.0701	928.12	55.97	1.2530	19.96
0.0500	886.60	56.68	0.8813	18.62
0.0602	907.84	56.30	1.0693	19.14
0.0703	928.71	55.95	1.2564	19.75
0.0803	949.48	55.61	1.4446	20.41
0.0900	969.62	55.29	1.6285	21.03
0.1001	990.88	54.96	1.8212	21.44
0.1101	1013.98	54.53	2.0188	20.94
0.1200	1034.91	54.23	2.2131	21.59

Table 2. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Water (2) + Cobalt(II) Chloride (3) Mixtures and Apparent Molar Volumes Φ_v of Cobalt(II) Chloride in Water at 298.15 K

x_3	d (kg·m^{-3})	V (cm^3·mol^{-1})	c (mol·L^{-1})	Φ_v (cm^3·mol^{-1})
0.0100	1060.47	18.04	0.5542	15.51
0.0201	1122.34	18.06	1.1149	17.53
0.0300	1181.23	18.09	1.6589	18.89
0.0400	1238.46	18.16	2.2035	20.35
0.0500	1294.82	18.23	2.7410	21.28
0.0600	1349.38	18.32	3.2744	22.31
0.0700	1403.69	18.41	3.8034	23.00

Results and Discussion

In Tables 1 and 2 the density, d, of the ethanol (1) + cobalt(II) chloride (3) and the water (2) + cobalt(II) chloride (3) systems are reported, where x_3 is the molar fraction of cobalt(II) chloride in the binary mixture. In Table 3 the density, d, of the ethanol (1) + water (2) + cobalt(II) chloride (3) system is reported, where x_i is the molar fraction of component i in the ternary mixture and x'_1 is the molar fraction of ethanol in the salt-free solvent. From these results, the molar volume of solution, V, and the molar concentration of salt in the solution, c, were calculated. In Tables 1−3 we also report values of V and c.

The apparent molar volume, Φ_v, of cobalt(II) chloride in the ethanol + water mixture is defined from the molar volume of solution, V, as we deduced in a previous work (Peña et al., 1995), by means of the expression

$$V = V_1^\circ x_1 + V_2^\circ x_2 + V_{12}^E (x_1 + x_2) + \Phi_v x_3 \qquad (1)$$

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Table 3. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Water (2) + Cobalt(II) Chloride (3) Mixtures and Apparent Molar Volumes Φ_v of Cobalt(II) Chloride in Ethanol + Water Mixtures at 298.15 K

x_1	x_2	x_3	x'_1	d (kg·m^{-3})	V (cm^3·mol^{-1})	c (mol·L^{-1})	Φ_v (cm^3·mol^{-1})	x_1	x_2	x_3	x'_1	d (kg·m^{-3})	V (cm^3·mol^{-1})	c (mol·L^{-1})	Φ_v (cm^3·mol^{-1})
0.0498	0.9452	0.0050	0.0501	1007.66	19.82	0.2525	11.44	0.4237	0.5233	0.0530	0.4474	1039.82	34.46	1.5387	21.75
0.0995	0.8955	0.0050	0.1000	990.89	21.57	0.2334	10.40	0.5094	0.4378	0.0528	0.5378	1006.41	37.96	1.3896	21.68
0.1940	0.8011	0.0049	0.1950	957.89	25.06	0.1961	13.96	0.5904	0.3569	0.0527	0.6233	979.57	41.32	1.2753	21.49
0.2989	0.6960	0.0051	0.3005	924.93	29.16	0.1734	11.98	0.6575	0.2819	0.0605	0.6999	979.77	44.12	1.3718	20.51
0.3993	0.5957	0.0050	0.4013	897.53	33.18	0.1502	8.22	0.7527	0.1875	0.0597	0.8005	948.48	48.30	1.2365	22.50
0.4993	0.4958	0.0050	0.5017	874.93	37.24	0.1336	6.52	0.8460	0.0940	0.0600	0.9000	926.85	52.28	1.1469	21.37
0.5975	0.3977	0.0048	0.6004	855.35	41.29	0.1171	5.91	0.8891	0.0508	0.0601	0.9459	919.15	54.04	1.1112	19.13
0.0497	0.9403	0.0100	0.0502	1037.06	19.80	0.5060	12.78	0.0815	0.8545	0.0640	0.0870	1296.32	21.18	3.0218	21.46
0.1956	0.7945	0.0099	0.1975	979.56	25.13	0.3950	16.08	0.1616	0.7741	0.0642	0.1727	1227.41	24.22	2.6517	23.44
0.3953	0.5947	0.0100	0.3993	915.99	32.99	0.3023	10.67	0.2435	0.6922	0.0643	0.2603	1167.95	27.43	2.3435	24.21
0.5910	0.3991	0.0099	0.5969	870.99	40.99	0.2422	8.68	0.3252	0.6107	0.0641	0.3475	1118.54	30.67	2.0893	23.98
0.0484	0.9371	0.0145	0.0491	1063.45	19.75	0.7355	13.98	0.4072	0.5287	0.0641	0.4351	1077.19	33.98	1.8861	23.98
0.0949	0.8909	0.0142	0.0962	1041.36	21.39	0.6659	14.17	0.5585	0.3715	0.0699	0.6005	1030.37	40.28	1.7362	24.50
0.2870	0.6986	0.0145	0.2912	964.68	28.70	0.5044	16.77	0.6451	0.2852	0.0697	0.6934	1001.26	43.85	1.5891	23.55
0.3816	0.6040	0.0144	0.3872	933.87	32.48	0.4432	15.40	0.7434	0.1869	0.0697	0.7991	973.20	47.95	1.4540	22.28
0.4797	0.5058	0.0145	0.4868	908.11	36.45	0.3981	13.97	0.8356	0.0938	0.0705	0.8990	950.81	51.90	1.3589	21.44
0.6596	0.3261	0.0143	0.6692	869.13	43.86	0.3265	10.53	0.8829	0.0473	0.0698	0.9492	938.80	53.89	1.2951	20.16
0.8647	0.1209	0.0144	0.8773	833.16	52.67	0.2726	11.99	0.0787	0.8465	0.0748	0.0850	1347.56	21.22	3.5275	22.77
0.0491	0.9309	0.0200	0.0501	1094.12	19.77	1.0117	15.10	0.2340	0.6912	0.0748	0.2530	1209.52	27.24	2.7448	25.65
0.0896	0.8920	0.0184	0.0913	1065.49	21.20	0.8677	15.02	0.3123	0.6129	0.0748	0.3375	1157.94	30.35	2.4641	25.63
0.0980	0.8820	0.0200	0.1000	1070.36	21.49	0.9325	15.20	0.3907	0.5345	0.0749	0.4223	1114.87	33.50	2.2347	25.46
0.4896	0.4903	0.0201	0.4996	922.62	36.85	0.5455	14.82	0.4677	0.4573	0.0750	0.5057	1079.23	36.62	2.0473	25.16
0.5888	0.3912	0.0200	0.6008	898.62	40.92	0.4893	13.52	0.2759	0.6441	0.0800	0.2999	1196.45	29.00	2.7583	26.51
0.8817	0.0983	0.0200	0.8997	841.15	53.48	0.3738	16.49	0.3681	0.5520	0.0799	0.4000	1141.64	32.66	2.4479	25.83
0.9304	0.0498	0.0198	0.9492	832.97	55.62	0.3559	16.09	0.4604	0.4596	0.0799	0.5004	1093.07	36.48	2.1914	26.60
0.1835	0.7884	0.0281	0.1888	1064.64	24.71	1.1390	18.83	0.5503	0.3695	0.0802	0.5983	1056.71	40.15	1.9985	26.09
0.2743	0.6977	0.0280	0.2822	1021.05	28.25	0.9915	18.91	0.6407	0.2792	0.0800	0.6965	1024.60	43.86	1.8248	25.05
0.3673	0.6046	0.0281	0.3780	984.94	31.94	0.8793	17.68	0.7339	0.1863	0.0798	0.7975	995.96	47.72	1.6715	23.58
0.6409	0.3310	0.0280	0.6594	907.13	43.14	0.6501	15.51	0.8293	0.0909	0.0798	0.9012	970.88	51.71	1.5429	21.77
0.8738	0.0965	0.0297	0.9006	861.95	53.20	0.5589	18.01	0.8750	0.0452	0.0798	0.9509	959.00	53.69	1.4867	21.35
0.9245	0.0454	0.0301	0.9532	853.34	55.45	0.5428	18.50	0.3634	0.5468	0.0898	0.3993	1169.85	32.70	2.7467	27.47
0.0444	0.9148	0.0408	0.0463	1211.39	19.67	2.0754	18.22	0.4556	0.4540	0.0904	0.5009	1121.35	36.48	2.4782	27.69
0.0882	0.8710	0.0408	0.0920	1179.96	21.23	1.9228	18.82	0.5470	0.3631	0.0899	0.6010	1080.37	40.19	2.2371	26.97
0.1756	0.7835	0.0409	0.1831	1123.52	24.49	1.6711	20.40	0.6359	0.2739	0.0902	0.6990	1048.34	43.82	2.0575	25.81
0.2637	0.6954	0.0409	0.2750	1074.15	27.91	1.4639	20.48	0.7281	0.1817	0.0902	0.8003	1019.08	47.62	1.8942	24.34
0.3538	0.6054	0.0408	0.3688	1032.28	31.48	1.2950	19.66	0.8191	0.0910	0.0900	0.9000	993.07	51.41	1.7499	22.65
0.4391	0.5200	0.0409	0.4578	999.55	34.93	1.1716	19.24	0.8301	0.0834	0.0865	0.9087	984.25	51.80	1.6708	21.85
0.5297	0.4294	0.0409	0.5523	969.15	38.64	1.0584	19.27	0.3593	0.5404	0.1003	0.3994	1198.12	32.81	3.0565	29.12
0.6156	0.3434	0.0410	0.6419	944.45	42.21	0.9705	19.09	0.4495	0.4509	0.0997	0.4992	1147.65	36.40	2.7387	28.38
0.7647	0.1957	0.0396	0.7962	906.24	48.44	0.8178	16.60	0.5410	0.3586	0.1004	0.6014	1108.60	40.07	2.5053	27.19
0.8657	0.0947	0.0396	0.9014	882.91	52.93	0.7480	19.32	0.6289	0.2709	0.1002	0.6989	1073.83	43.64	2.2957	26.00
0.9144	0.0455	0.0402	0.9526	874.68	55.06	0.7295	18.89	0.7211	0.1790	0.0999	0.8012	1042.06	47.42	2.1069	24.54
0.6637	0.2865	0.0497	0.6985	951.10	44.37	1.1210	21.11	0.8116	0.0881	0.1003	0.9020	1015.77	51.19	1.9586	22.90
0.8559	0.0950	0.0491	0.9001	903.36	52.61	0.9339	20.64	0.5340	0.3560	0.1100	0.6000	1130.15	40.08	2.7447	29.04
0.9038	0.0456	0.0507	0.9520	896.44	54.70	0.9260	20.13	0.6212	0.2692	0.1096	0.6977	1094.73	43.57	2.5158	27.52
0.0423	0.9048	0.0529	0.0447	1276.10	19.68	2.6866	19.82	0.7116	0.1785	0.1099	0.7994	1063.63	47.26	2.3257	25.97
0.0831	0.8644	0.0525	0.0877	1240.96	21.13	2.4866	20.13	0.8016	0.0883	0.1101	0.9008	1036.95	50.94	2.1618	23.86
0.1687	0.7786	0.0527	0.1781	1177.17	24.33	2.1656	21.63	0.7921	0.0879	0.1200	0.9001	1059.17	50.66	2.3690	24.29
0.2533	0.6938	0.0529	0.2675	1123.21	27.63	1.9143	22.24	0.8365	0.0433	0.1201	0.9507	1046.48	52.48	2.2890	23.10
0.3355	0.6121	0.0524	0.3541	1078.11	30.87	1.6961	21.48								

where V_1° is the molar volume of pure ethanol, V_2° is that of pure water, and V_{12}^E is the excess molar volume of the binary ethanol + water mixture, which depends on the solvent composition.

The molar apparent volume of cobalt(II) chloride in a ternary liquid mixture of ethanol + water + cobalt(II) chloride can be calculated, for each composition, by using eq 1, once the density of the sample, the partial volumes of pure ethanol and pure water, and the dependence on composition of the excess molar volume of the binary ethanol + water mixture, at the same pressure and temperature conditions, are known.

The value of V_{12}^E, for each composition of the solvent mixture, was calculated by using a correlation (Peña et al., 1995) obtained from experimental data published by Marsh and Richards (1980).

The values of apparent molar volume of cobalt(II) chloride calculated at 298.15 K, are also shown in Tables 1−3.

Millero (1971) and Nomura et al. (1985) suggested that the apparent molar volume of a electrolyte in a mixed solvent, at constant solvent composition, can be fitted by the Masson equation (1929):

$$\Phi_v = \Phi_v^\circ + S_v^e c^{1/2} \qquad (2)$$

where Φ_v° is the apparent molar volume of cobalt(II) chloride at infinite dilution, which is the same as the partial molar volume of cobalt(II) chloride at infinite dilution, and S_v^e is the experimental slope. Both Φ_v° and S_v^e depend on the solvent composition and can be correlated using the following expressions:

$$\Phi_v^\circ/(\mathrm{cm^3{\cdot}mol^{-1}}) = \sum_{\nu=0}^{4} b_\nu\,(x'_1)^\nu \qquad (3)$$

$$S_v^e/(\mathrm{cm^3{\cdot}mol^{-3/2}{\cdot}L^{1/2}}) = \sum_{\nu=0}^{4} c_\nu (x'_1)^\nu \qquad (4)$$

From the Φ_v values of cobalt(II) chloride in water, given in Table 2, we have found that Φ_v° =10.9 cm^3·mol^{-1}. This value is in good agreement with the 11.66 cm^3·mol^{-1} value reported by Millero (1971), the 10.9 cm^3·mol^{-1} value

Table 4. Parameters of Equations 3 and 4

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
b_ν	1.744	114.971	−502.72	690.1	−291.1
c_ν	10.348	−55.305	311.95	−445.0	184.0

obtained from Phang (1980), the 11.5 $cm^3 \cdot mol^{-1}$ reported by Herrington et al. (1986), and the 10.2 $cm^3 \cdot mol^{-1}$ value reported by Pogue and Atkinson (1989).

From the Φ_v values of cobalt(II) chloride in ethanol, given in Table 1, we have found the partial molar volume at infinite dilution of cobalt(II) chloride in ethanol, 12.9 $cm^3 \cdot mol^{-1}$; the comparison with the values obtained from Meyer (1960) is poor, but Meyer's data are unreliable because they present a great dispersion.

From the Φ_v values and at a least-squares minimization, we have found the values of b_ν and c_ν that minimize the sum of the squares of deviations between experimental and calculated results of Φ_v in the range $0.04 \le x_1' \le 1$. These parameters are given in Table 4. The mean absolute deviation of the apparent molar volume for the cobalt(II) chloride is 0.57 $cm^3 \cdot mol^{-1}$, and the standard deviation is 0.75 $cm^3 \cdot mol^{-1}$.

All attempts to include in a single equation the apparent volume of cobalt(II) chloride in the entire range of ethanol water composition have failed. Therefore, eqs 1−4 with the parameters of Table 4 are not valid to recalculate the apparent volume of cobalt(II) chloride in pure water.

From the values of b_ν and c_ν and eqs 1−4, we have recalculated the molar volume and the density of the ethanol + water + cobalt(II) chloride solutions. The mean absolute deviation of molar volume is 0.026 $cm^3 \cdot mol^{-1}$, and the corresponding standard deviation is 0.035 $cm^3 \cdot mol^{-1}$. The mean absolute deviation of the density is 0.66 $kg \cdot m^{-3}$, and the standard deviation is 0.89 $kg \cdot m^{-3}$.

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