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Apparent Molar Volumes of Strontium Nitrate and Copper(II) Chloride in Ethanol + Water at 298.15 K

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

Introduction

Volumetric characteristics of electrolyte solutions in solvent mixtures in a wide range of solute and solvent concentrations are of fundamental importance for the understanding of numerous physicochemical processes occurring in the process industry.

In previous papers we studied the vapor−liquid equilibrium of ethanol + water + inorganic salt systems, salt being strontium bromide (Vercher et al., 1994), cobalt(II) chloride (Peña et al., 1994), strontium chloride (Peña et al., 1995a), copper(II) chloride (Vercher et al., 1995), potassium nitrate (Vercher et al., 1996a), strontium nitrate (Vercher et al., 1996b), and sodium nitrate (Peña et al., 1996b). In these works, the composition of the ternary liquid phase was determined by a combined gravimetric and densimetric method. Therefore, we measured the density of ternary mixtures of ethanol, water, and salt at different compositions, and we have published some (Peña et al., 1995b, 1996a, 1997, 1998). In the present work, we report the densities of ethanol + water + strontium nitrate and ethanol + water + copper(II) chloride systems at 298.15 K and the apparent molar volumes of the strontium nitrate and the copper(II) chloride in ethanol + water mixtures.

Several papers concerning the densities of strontium nitrate (Sugden, 1926; Pesce, 1935; Doan and Sangster, 1981; Kuznetsov et al., 1983) and copper(II) chloride (Herz, 1914; Schumb, 1928; Dolian and Briscoe, 1937; Lo Surdo and Millero, 1980; Pogue and Atkinson, 1988a) in aqueous solutions, as well as apparent molar volumes at 298.15 K of strontium nitrate (Padova, 1977) and copper(II) chloride (Lo Surdo and Millero, 1980; Pogue and Atkinson, 1988a, 1988b), have appeared in the literature. Meyer (1931, 1960), Pietsch (1958), Millero (1971, 1972), Lobo and Quaresma (1981), and Krumgalz et al. (1996) have compiled experimental data on densities and apparent molar volumes for these salts in aqueous solutions. We have not found any reported density value for these salts in ethanol + water mixtures at 298.15 K.

Experimental Section

Table 1. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Water (2) + Strontium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Strontium Nitrate in Water at 298.15 K

x_3	d/kg·m^{-3}	V/cm^3·mol^{-1}	c/mol·L^{-1}	V_ϕ/cm^3·mol^{-1}
0.003 86	1032.56	18.170	0.2123	44.5 ± 0.5
0.005 45	1046.64	18.220	0.2990	45.9 ± 0.3
0.007 80	1067.61	18.289	0.4267	46.41 ± 0.25
0.010 88	1094.14	18.391	0.5917	47.68 ± 0.16
0.013 60	1117.29	18.481	0.7359	48.38 ± 0.12
0.016 37	1140.19	18.579	0.8809	49.29 ± 0.10
0.019 03	1162.00	18.674	1.0189	49.89 ± 0.09
0.022 27	1188.27	18.789	1.1852	50.44 ± 0.07
0.025 06	1210.27	18.894	1.3262	51.01 ± 0.07
0.028 39	1235.81	19.026	1.4923	51.79 ± 0.06
0.032 15	1264.73	19.166	1.6775	52.21 ± 0.05
0.035 33	1288.18	19.295	1.8311	52.79 ± 0.05
0.038 83	1313.78	19.434	1.9979	53.25 ± 0.04
0.042 80	1342.23	19.595	2.1841	53.74 ± 0.04
0.047 44	1373.83	19.798	2.3960	54.53 ± 0.04
0.050 54	1394.94	19.929	2.5359	54.89 ± 0.03
0.054 66	1422.00	20.111	2.7180	55.44 ± 0.03
0.057 98	1443.69	20.255	2.8627	55.78 ± 0.03
0.062 11	1470.97	20.423	3.0414	55.97 ± 0.03

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

x_3	d/kg·m^{-3}	V/cm^3·mol^{-1}	c/mol·L^{-1}	V_ϕ/cm^3·mol^{-1}
0.010 29	1064.85	18.043	0.5702	15.59 ± 0.18
0.012 43	1078.43	18.047	0.6889	16.36 ± 0.14
0.015 10	1095.25	18.054	0.8366	17.13 ± 0.12
0.017 85	1112.56	18.061	0.9885	17.65 ± 0.11
0.021 55	1135.07	18.082	1.1917	18.69 ± 0.08
0.025 85	1161.35	18.103	1.4277	19.43 ± 0.06
0.031 08	1192.34	18.144	1.7128	20.49 ± 0.06
0.038 41	1234.94	18.209	2.1093	21.73 ± 0.04
0.045 80	1276.65	18.288	2.5044	22.87 ± 0.04
0.053 60	1319.38	18.385	2.9157	23.97 ± 0.03
0.060 94	1359.07	18.476	3.2982	24.76 ± 0.03
0.069 20	1402.14	18.595	3.7216	25.68 ± 0.03
0.077 34	1444.24	18.709	4.1339	26.35 ± 0.02
0.084 37	1479.55	18.815	4.4839	26.92 ± 0.02
0.088 56	1501.44	18.866	4.6941	27.08 ± 0.02
0.093 58	1526.47	18.940	4.9410	27.38 ± 0.02
0.096 90	1542.86	18.989	5.1030	27.57 ± 0.02

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 mass %), distilled water, strontium nitrate (Probus, >99.5 mass %), and copper(II) chloride (Probus, >99.5 mass %). They were used without further purification. Ethanol density was (785.08 ± 0.01) kg·m^{-3} at 298.15

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Table 3. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Water (2) + Strontium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Strontium Nitrate 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}	V_ϕ/cm^3·mol^{-1}
0.023 45	0.916 56	0.059 999	0.024 94	1428.42	21.205	2.8295	56.15 ± 0.02
0.023 61	0.921 76	0.054 639	0.024 97	1395.52	20.964	2.6063	55.38 ± 0.03
0.047 37	0.897 62	0.055 006	0.050 13	1372.16	21.859	2.5164	56.11 ± 0.03
0.024 00	0.926 11	0.049 888	0.025 26	1364.40	20.776	2.4012	54.88 ± 0.03
0.047 54	0.902 46	0.049 997	0.050 04	1341.43	21.640	2.3104	55.43 ± 0.03
0.071 25	0.878 80	0.049 947	0.075 00	1316.88	22.541	2.2158	56.83 ± 0.03
0.023 93	0.931 11	0.044 962	0.025 05	1331.65	20.570	2.1858	54.37 ± 0.03
0.047 69	0.907 31	0.044 996	0.049 94	1308.70	21.445	2.0982	55.11 ± 0.03
0.071 47	0.883 45	0.045 080	0.074 84	1286.98	22.338	2.0181	56.32 ± 0.03
0.095 63	0.859 37	0.044 993	0.100 14	1267.08	23.210	1.9385	56.80 ± 0.03
0.047 89	0.912 10	0.040 002	0.049 89	1276.27	21.237	1.8836	54.35 ± 0.04
0.071 62	0.888 40	0.039 986	0.074 60	1255.05	22.123	1.8074	55.70 ± 0.04
0.096 44	0.863 57	0.039 992	0.100 46	1235.65	23.035	1.7361	56.55 ± 0.04
0.120 02	0.839 98	0.040 000	0.125 02	1217.55	23.922	1.6721	57.57 ± 0.04
0.144 08	0.815 87	0.040 054	0.150 09	1200.14	24.840	1.6125	58.49 ± 0.04
0.048 25	0.916 81	0.034 941	0.049 99	1242.28	21.037	1.6610	53.53 ± 0.04
0.072 22	0.892 85	0.034 929	0.074 84	1223.07	21.915	1.5938	54.58 ± 0.04
0.096 56	0.868 40	0.035 038	0.100 07	1205.38	22.821	1.5354	55.75 ± 0.04
0.120 47	0.844 52	0.035 012	0.124 84	1188.05	23.714	1.4764	56.79 ± 0.04
0.145 08	0.819 92	0.034 999	0.150 34	1171.42	24.638	1.4205	57.51 ± 0.05
0.168 78	0.796 33	0.034 896	0.174 88	1154.53	25.557	1.3654	58.68 ± 0.05
0.048 72	0.921 27	0.030 016	0.050 22	1207.25	20.868	1.4383	53.17 ± 0.05
0.072 71	0.897 27	0.030 013	0.074 96	1189.97	21.737	1.3807	54.02 ± 0.05
0.097 07	0.872 94	0.029 990	0.100 08	1173.65	22.617	1.3260	54.70 ± 0.05
0.121 21	0.848 81	0.029 979	0.124 96	1156.73	23.532	1.2740	56.32 ± 0.05
0.145 58	0.824 42	0.029 997	0.150 08	1141.88	24.440	1.2274	56.88 ± 0.05
0.169 61	0.800 40	0.029 986	0.174 86	1126.80	25.363	1.1823	57.86 ± 0.05
0.193 66	0.776 33	0.030 014	0.199 65	1112.14	26.309	1.1408	58.99 ± 0.06
0.218 35	0.751 64	0.030 012	0.225 11	1099.70	27.236	1.1019	58.23 ± 0.06
0.048 73	0.926 28	0.024 997	0.049 98	1172.45	20.659	1.2100	51.83 ± 0.06
0.072 82	0.902 10	0.025 078	0.074 69	1156.69	21.538	1.1643	53.04 ± 0.06
0.097 56	0.877 39	0.025 054	0.100 07	1140.58	22.447	1.1161	54.43 ± 0.06
0.121 88	0.853 06	0.025 066	0.125 01	1125.81	23.350	1.0735	55.61 ± 0.06
0.146 53	0.828 43	0.025 046	0.150 29	1110.56	24.290	1.0312	57.21 ± 0.06
0.170 18	0.804 87	0.024 950	0.174 54	1098.62	25.141	0.9924	56.18 ± 0.07
0.193 93	0.781 15	0.024 921	0.198 88	1085.01	26.065	0.9561	57.23 ± 0.07
0.219 23	0.755 80	0.024 972	0.224 85	1073.21	27.022	0.9241	56.51 ± 0.07
0.267 95	0.707 01	0.025 043	0.274 83	1049.40	28.951	0.8650	57.17 ± 0.07
0.048 99	0.930 99	0.020 013	0.049 99	1135.52	20.488	0.9768	51.21 ± 0.08
0.073 17	0.906 77	0.020 063	0.074 66	1122.15	21.345	0.9399	51.52 ± 0.08
0.098 16	0.881 86	0.019 974	0.100 16	1107.77	22.239	0.8981	52.20 ± 0.08
0.122 45	0.857 56	0.019 983	0.124 95	1094.79	23.127	0.8640	52.99 ± 0.08
0.146 98	0.832 95	0.020 071	0.149 99	1081.67	24.060	0.8342	54.66 ± 0.08
0.171 43	0.808 63	0.019 945	0.174 92	1069.33	24.956	0.7992	54.20 ± 0.08
0.195 79	0.784 19	0.020 026	0.199 79	1055.50	25.945	0.7719	57.37 ± 0.08
0.220 21	0.759 81	0.019 975	0.224 70	1045.42	26.841	0.7442	55.29 ± 0.09
0.244 69	0.735 28	0.020 030	0.249 69	1033.88	27.815	0.7201	56.19 ± 0.09
0.269 39	0.710 60	0.020 012	0.274 89	1024.83	28.734	0.6965	53.49 ± 0.09
0.293 97	0.686 07	0.019 953	0.299 96	1013.41	29.727	0.6712	54.41 ± 0.10
0.318 83	0.661 09	0.020 079	0.325 36	1004.63	30.705	0.6539	53.42 ± 0.10
0.049 98	0.935 04	0.014 980	0.050 74	1098.33	20.319	0.7372	48.77 ± 0.11
0.073 50	0.911 46	0.015 040	0.074 63	1085.86	21.171	0.7104	50.36 ± 0.11
0.098 49	0.886 57	0.014 940	0.099 99	1072.69	22.067	0.6770	51.36 ± 0.11
0.123 32	0.861 68	0.015 000	0.125 20	1062.72	22.940	0.6539	50.05 ± 0.11
0.147 99	0.837 02	0.014 996	0.150 24	1049.83	23.880	0.6280	52.65 ± 0.11
0.172 22	0.812 71	0.015 072	0.174 85	1037.38	24.836	0.6069	56.07 ± 0.11
0.221 45	0.763 38	0.015 162	0.224 86	1018.10	26.680	0.5683	53.49 ± 0.12
0.246 46	0.738 54	0.014 994	0.250 21	1006.80	27.644	0.5424	53.16 ± 0.12
0.270 72	0.714 13	0.015 152	0.274 88	997.57	28.613	0.5295	53.63 ± 0.12
0.295 38	0.689 64	0.014 974	0.299 87	989.38	29.514	0.5073	48.84 ± 0.13
0.319 84	0.665 15	0.015 007	0.324 71	980.25	30.496	0.4921	49.01 ± 0.13
0.344 19	0.640 84	0.014 967	0.349 42	969.96	31.516	0.4749	51.92 ± 0.14
0.368 28	0.616 77	0.014 944	0.373 87	962.60	32.454	0.4605	49.79 ± 0.14
0.049 53	0.940 43	0.010 045	0.050 03	1059.21	20.156	0.4983	49.13 ± 0.16
0.074 05	0.915 93	0.010 012	0.074 80	1047.89	21.024	0.4762	49.92 ± 0.16
0.098 90	0.891 14	0.009 958	0.099 89	1037.30	21.901	0.4547	49.89 ± 0.16
0.123 72	0.866 25	0.010 034	0.124 97	1027.33	22.805	0.4400	51.07 ± 0.16
0.148 70	0.841 29	0.010 010	0.150 20	1016.99	23.722	0.4220	51.53 ± 0.17
0.173 33	0.816 61	0.010 063	0.175 09	1006.33	24.670	0.4079	54.45 ± 0.17
0.197 89	0.792 10	0.010 004	0.199 89	998.24	25.549	0.3916	49.48 ± 0.17
0.222 85	0.767 07	0.010 086	0.225 12	986.54	26.577	0.3795	56.02 ± 0.18
0.247 37	0.742 65	0.009 979	0.249 86	979.42	27.452	0.3635	48.25 ± 0.18
0.272 04	0.717 96	0.009 995	0.274 79	971.18	28.401	0.3519	45.89 ± 0.19
0.296 71	0.693 18	0.010 116	0.299 74	963.35	29.374	0.3444	44.90 ± 0.19
0.321 10	0.668 79	0.010 107	0.324 38	954.22	30.370	0.3328	47.06 ± 0.20

Table 3. (Continued)

x_1	x_2	x_3	x'_1	d/kg·m^{-3}	V/cm^3·mol^{-1}	c/mol·L^{-1}	V_ϕ/cm^3·mol^{-1}
0.346 51	0.643 46	0.010 031	0.350 02	946.40	31.359	0.3199	44.12 ± 0.21
0.395 31	0.594 53	0.010 156	0.399 37	931.87	33.343	0.3046	45.20 ± 0.23
0.420 48	0.569 49	0.010 037	0.424 74	922.17	34.434	0.2915	52.62 ± 0.24
0.445 42	0.544 50	0.010 084	0.449 96	918.49	35.344	0.2853	42.12 ± 0.25
0.470 56	0.519 38	0.010 062	0.475 34	910.84	36.410	0.2763	46.3 ± 0.3
0.049 82	0.945 13	0.005 047	0.050 07	1019.31	20.004	0.2523	47.7 ± 0.3
0.074 39	0.920 58	0.005 030	0.074 76	1010.05	20.866	0.2411	47.7 ± 0.3
0.099 48	0.895 41	0.005 107	0.099 99	1001.62	21.759	0.2347	48.4 ± 0.3
0.124 27	0.870 75	0.004 982	0.124 89	991.73	22.653	0.2199	50.1 ± 0.3
0.149 62	0.845 34	0.005 033	0.150 38	983.17	23.584	0.2134	50.6 ± 0.3
0.174 15	0.820 67	0.005 173	0.175 06	974.92	24.517	0.2110	53.6 ± 0.3
0.198 65	0.796 23	0.005 121	0.199 68	966.47	25.432	0.2013	51.4 ± 0.3
0.224 06	0.771 03	0.004 910	0.225 17	956.25	26.407	0.1859	52.2 ± 0.4
0.248 85	0.746 19	0.004 953	0.250 09	947.94	27.381	0.1809	53.4 ± 0.4
0.273 88	0.721 06	0.005 055	0.275 28	940.90	28.353	0.1783	49.9 ± 0.4
0.298 03	0.696 97	0.005 003	0.299 53	932.58	29.322	0.1706	52.1 ± 0.4
0.323 04	0.671 89	0.005 074	0.324 69	926.38	30.290	0.1675	45.5 ± 0.4
0.347 97	0.647 04	0.004 991	0.349 72	918.69	31.287	0.1595	45.2 ± 0.4
0.372 67	0.622 36	0.004 968	0.374 53	911.59	32.286	0.1539	46.0 ± 0.5
0.397 93	0.597 06	0.005 012	0.399 93	905.34	33.301	0.1505	44.6 ± 0.5
0.424 30	0.570 67	0.005 031	0.426 45	898.49	34.383	0.1463	46.9 ± 0.5
0.447 74	0.547 26	0.004 999	0.449 99	892.44	35.346	0.1414	49.1 ± 0.5
0.471 70	0.523 21	0.005 088	0.474 12	887.99	36.299	0.1402	44.1 ± 0.5
0.497 47	0.497 56	0.004 978	0.499 96	882.10	37.337	0.1333	41.4 ± 0.6
0.523 32	0.471 67	0.005 010	0.525 96	876.70	38.401	0.1305	41.9 ± 0.6
0.546 79	0.448 24	0.004 968	0.549 52	871.62	39.371	0.1262	42.6 ± 0.6
0.572 60	0.422 46	0.004 939	0.575 45	866.13	40.450	0.1221	45.0 ± 0.7
0.597 23	0.397 70	0.005 066	0.600 27	861.37	41.505	0.1221	50.3 ± 0.7
0.495 02	0.494 99	0.009 985	0.500 02	903.21	37.462	0.2665	51.6 ± 0.3

K, indicating a maximum of 0.01 vol % of water, as reported by Marsh and Richards (1980). The density of pure water at 298.15 K was taken as 997.05 kg·m^{-3} (Marsh and Richards, 1980).

The water + electrolyte mixtures were prepared from a concentrated solution by successive dilution and were analyzed gravimetrically by evaporation to dryness. The accuracy of salt mole fractions in the samples was better than ±0.000 02. The ethanol + water + electrolyte 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 ensure 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. In both systems, the accuracy of ethanol and water mole fractions was better than ±0.000 05, and the accuracy of salt mole fractions was better than ±0.000 03.

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 ±0.08 kg·m^{-3}.

Results and Discussion

In Table 1 the densities, d, of the water (2) + strontium nitrate (3) mixtures are reported; in Table 2, we show the densities of the water (2) + copper(II) chloride (3) mixtures, where x_3 is the mole fraction of salt in the binary mixture. In Table 3, the density, d, of the ethanol (1) + water (2) + strontium nitrate (3) system is reported, where x_i is the mole fraction of component i in the ternary mixture and x'_1 is the mole fraction of ethanol in the salt-free solvent. In Table 4, we show the density of the ethanol (1) + water (2) + copper(II) chloride (3) system. From these results, the molar volume of solution, V, and the molar concentration of salt in the solution, c, were calculated. In Tables 1, 2, 3, and 4 we also report values of V and c.

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

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

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 apparent molar volume of the electrolyte in a ternary liquid mixture of ethanol + water + electrolyte can be calculated, for each composition, by using eq 1, once the density of the sample, the molar 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., 1995b) obtained from experimental data published by Marsh and Richards (1980).

The values of the apparent molar volume of strontium nitrate calculated at 298.15 K are also shown in Tables 1 and 3, and those of copper(II) chloride, in Tables 2 and 4.

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

$$V_\phi = V_\phi^\infty + S_{\mathrm{v}}^{\mathrm{e}} \cdot c^{1/2} \qquad (2)$$

where V_ϕ^∞ is the apparent molar volume of electrolyte at infinite dilution, which is the same as the partial molar volume of electrolyte at infinite dilution, and $S_{\mathrm{v}}^{\mathrm{e}}$ is the experimental slope. Both V_ϕ^∞ and $S_{\mathrm{v}}^{\mathrm{e}}$ depend on the solvent

Table 4. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Water (2) + Copper(II) Chloride (3) Mixtures and Apparent Molar Volumes V_ϕ of Copper(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}	V_ϕ/cm^3·mol^{-1}
0.019 99	0.969 99	0.010 018	0.020 19	1052.01	18.766	0.5339	14.99 ± 0.16
0.041 35	0.948 62	0.010 038	0.041 76	1041.80	19.528	0.5140	15.25 ± 0.16
0.087 97	0.901 95	0.010 072	0.088 87	1023.02	21.169	0.4758	15.32 ± 0.16
0.142 16	0.847 85	0.009 986	0.143 59	1001.25	23.137	0.4316	17.14 ± 0.16
0.204 38	0.785 61	0.010 011	0.206 45	977.05	25.500	0.3926	19.75 ± 0.17
0.278 09	0.711 89	0.010 025	0.280 90	950.78	28.381	0.3532	19.92 ± 0.18
0.366 42	0.623 53	0.010 049	0.370 14	923.77	31.896	0.3151	17.70 ± 0.21
0.473 53	0.516 43	0.010 036	0.478 33	895.83	36.244	0.2769	17.7 ± 0.3
0.604 21	0.385 71	0.010 073	0.610 36	868.37	41.617	0.2420	15.7 ± 0.3
0.873 95	0.115 92	0.010 123	0.882 89	822.59	53.139	0.1905	17.4 ± 0.6
0.019 52	0.960 49	0.019 988	0.019 92	1112.83	18.772	1.0648	17.65 ± 0.08
0.041 58	0.938 38	0.020 037	0.042 43	1100.00	19.559	1.0244	17.81 ± 0.08
0.087 56	0.892 42	0.020 013	0.089 35	1075.77	21.196	0.9442	18.77 ± 0.08
0.141 50	0.838 45	0.020 053	0.144 40	1049.59	23.170	0.8655	20.41 ± 0.08
0.203 47	0.776 49	0.020 041	0.207 63	1020.61	25.530	0.7850	21.98 ± 0.08
0.275 72	0.704 33	0.019 959	0.281 33	990.04	28.356	0.7039	22.12 ± 0.09
0.362 25	0.617 65	0.020 099	0.369 68	959.36	31.811	0.6318	21.51 ± 0.10
0.467 48	0.512 55	0.019 969	0.477 01	927.87	36.056	0.5538	20.25 ± 0.13
0.588 66	0.391 66	0.019 683	0.600 48	896.63	41.066	0.4793	21.03 ± 0.16
0.597 17	0.383 01	0.019 818	0.609 25	895.76	41.390	0.4788	19.45 ± 0.17
0.763 08	0.216 95	0.019 968	0.778 63	861.86	48.439	0.4122	20.88 ± 0.24
0.863 93	0.116 30	0.019 768	0.881 35	844.50	52.757	0.3747	19.0 ± 0.3
0.019 93	0.950 07	0.030 003	0.020 55	1170.92	18.846	1.5920	19.79 ± 0.05
0.041 06	0.928 86	0.030 080	0.042 33	1156.51	19.602	1.5346	19.94 ± 0.05
0.087 47	0.882 48	0.030 041	0.090 18	1127.10	21.264	1.4128	20.93 ± 0.05
0.139 14	0.830 74	0.030 113	0.143 46	1097.22	23.172	1.2995	22.51 ± 0.05
0.200 52	0.769 43	0.030 045	0.206 73	1062.27	25.548	1.1760	24.88 ± 0.05
0.272 28	0.697 66	0.030 058	0.280 72	1027.71	28.367	1.0596	25.41 ± 0.06
0.358 08	0.612 16	0.029 760	0.369 06	991.61	31.793	0.9361	25.13 ± 0.07
0.462 71	0.507 27	0.030 020	0.477 03	957.52	36.022	0.8334	24.48 ± 0.08
0.591 33	0.378 63	0.030 043	0.609 64	922.84	41.288	0.7277	23.14 ± 0.11
0.755 67	0.214 17	0.030 164	0.779 17	886.06	48.221	0.6255	22.43 ± 0.15
0.855 59	0.114 51	0.029 908	0.881 96	867.58	52.445	0.5703	19.37 ± 0.19
0.019 13	0.940 84	0.040 035	0.019 93	1227.78	18.907	2.1175	21.59 ± 0.04
0.040 20	0.919 75	0.040 049	0.041 88	1210.90	19.660	2.0371	21.69 ± 0.04
0.085 38	0.874 54	0.040 079	0.088 95	1177.99	21.288	1.8827	22.66 ± 0.04
0.137 77	0.822 26	0.039 972	0.143 51	1142.57	23.223	1.7212	23.92 ± 0.04
0.198 82	0.761 04	0.040 137	0.207 13	1105.39	25.571	1.5696	25.26 ± 0.04
0.269 50	0.690 32	0.040 182	0.280 78	1067.15	28.350	1.4173	25.70 ± 0.04
0.354 41	0.605 43	0.040 164	0.369 24	1028.20	31.739	1.2654	25.41 ± 0.05
0.457 34	0.502 64	0.040 019	0.476 40	988.83	35.906	1.1145	25.18 ± 0.06
0.586 26	0.373 56	0.040 180	0.610 81	950.04	41.199	0.9753	24.47 ± 0.08
0.747 71	0.212 26	0.040 028	0.778 89	910.96	47.919	0.8353	21.72 ± 0.11
0.846 87	0.112 81	0.040 317	0.882 45	890.74	52.168	0.7728	20.79 ± 0.13
0.018 83	0.931 19	0.049 977	0.019 82	1282.49	18.996	2.6309	22.89 ± 0.03
0.039 86	0.910 24	0.049 898	0.041 95	1262.63	19.755	2.5258	23.13 ± 0.03
0.084 03	0.865 97	0.050 005	0.088 45	1225.91	21.368	2.3402	24.30 ± 0.03
0.140 04	0.810 18	0.049 777	0.147 38	1183.53	23.438	2.1238	25.38 ± 0.03
0.136 42	0.813 46	0.050 123	0.143 62	1186.66	23.324	2.1489	25.71 ± 0.03
0.196 18	0.753 86	0.049 954	0.206 50	1145.94	25.599	1.9514	26.35 ± 0.03
0.267 05	0.682 97	0.049 980	0.281 10	1103.24	28.395	1.7602	26.89 ± 0.03
0.350 74	0.599 36	0.049 899	0.369 16	1059.74	31.767	1.5708	27.31 ± 0.04
0.454 05	0.495 86	0.050 087	0.478 00	1017.44	35.958	1.3929	27.23 ± 0.05
0.579 45	0.370 44	0.050 113	0.610 01	976.31	41.079	1.2199	26.16 ± 0.06
0.739 76	0.210 29	0.049 945	0.778 65	933.41	47.764	1.0457	24.23 ± 0.09
0.838 50	0.111 32	0.050 179	0.882 79	912.34	51.934	0.9662	22.27 ± 0.10
0.019 28	0.920 62	0.060 099	0.020 51	1335.74	19.131	3.1415	24.05 ± 0.02
0.039 23	0.900 70	0.060 068	0.041 74	1315.10	19.854	3.0255	24.29 ± 0.02
0.083 39	0.856 62	0.059 986	0.088 71	1273.38	21.470	2.7940	25.34 ± 0.02
0.145 02	0.793 86	0.061 124	0.154 46	1226.58	23.806	2.5676	27.01 ± 0.02
0.134 88	0.805 14	0.059 978	0.143 48	1230.01	23.400	2.5631	26.64 ± 0.02
0.193 59	0.746 36	0.060 049	0.205 95	1186.68	25.649	2.3411	27.38 ± 0.03
0.264 21	0.675 85	0.059 941	0.281 05	1139.64	28.436	2.1079	27.86 ± 0.03
0.346 25	0.594 12	0.059 633	0.368 20	1093.24	31.715	1.8803	27.82 ± 0.03
0.446 97	0.493 03	0.060 002	0.475 50	1049.68	35.764	1.6777	27.11 ± 0.04
0.571 86	0.368 21	0.059 932	0.608 32	1004.90	40.836	1.4676	25.80 ± 0.05
0.730 43	0.209 55	0.060 021	0.777 07	958.89	47.446	1.2650	24.14 ± 0.07
0.018 54	0.911 33	0.070 129	0.019 94	1387.37	19.246	3.6439	25.21 ± 0.02
0.038 85	0.891 11	0.070 035	0.041 78	1363.96	19.986	3.5043	25.49 ± 0.02
0.082 73	0.847 11	0.070 165	0.088 97	1319.92	21.596	3.2489	26.43 ± 0.02
0.133 85	0.796 14	0.070 006	0.143 93	1271.22	23.537	2.9743	27.89 ± 0.02
0.192 22	0.737 48	0.070 302	0.206 75	1225.56	25.779	2.7271	28.54 ± 0.02
0.261 35	0.668 81	0.069 833	0.280 98	1175.13	28.489	2.4513	28.75 ± 0.02
0.343 02	0.587 07	0.069 913	0.368 81	1127.27	31.739	2.2027	28.45 ± 0.03
0.443 15	0.486 80	0.070 050	0.476 53	1079.21	35.770	1.9583	27.96 ± 0.03

Table 4. (Continued)

x_1	x_2	x_3	x'_1	d/kg·m^{-3}	V/cm^3·mol^{-1}	c/mol·L^{-1}	V_ϕ/cm^3·mol^{-1}
0.566 78	0.363 21	0.070 007	0.609 45	1031.84	40.769	1.7172	26.51 ± 0.04
0.726 34	0.203 43	0.070 224	0.781 20	983.09	47.370	1.4825	24.32 ± 0.06
0.018 40	0.901 61	0.079 986	0.020 00	1437.20	19.374	4.1285	26.01 ± 0.02
0.038 39	0.881 65	0.079 958	0.041 73	1412.89	20.102	3.9776	26.23 ± 0.02
0.082 00	0.837 92	0.080 072	0.089 14	1366.09	21.696	3.6906	26.96 ± 0.02
0.131 95	0.788 04	0.080 015	0.143 42	1315.91	23.583	3.3929	28.09 ± 0.02
0.190 24	0.729 67	0.080 085	0.206 80	1263.73	25.857	3.0972	29.14 ± 0.02
0.258 12	0.661 81	0.080 067	0.280 59	1210.98	28.555	2.8040	29.71 ± 0.02
0.340 20	0.580 00	0.079 800	0.369 71	1158.38	31.812	2.5085	29.38 ± 0.02
0.438 83	0.481 13	0.080 039	0.477 01	1107.65	35.792	2.2362	29.06 ± 0.03
0.559 87	0.360 24	0.079 894	0.608 48	1056.89	40.708	1.9626	28.11 ± 0.04
0.715 73	0.204 29	0.079 979	0.777 95	1006.03	47.123	1.6973	25.86 ± 0.05
0.021 02	0.889 85	0.089 125	0.023 08	1477.66	19.613	4.5441	26.83 ± 0.02
0.018 07	0.891 91	0.090 025	0.019 86	1486.00	19.518	4.6124	26.85 ± 0.02
0.037 78	0.872 28	0.089 943	0.041 52	1459.84	20.240	4.4438	27.10 ± 0.02
0.080 59	0.829 50	0.089 909	0.088 55	1409.23	21.817	4.1211	27.89 ± 0.02
0.130 54	0.779 37	0.090 086	0.143 47	1355.73	23.726	3.7969	29.12 ± 0.02
0.187 96	0.722 07	0.089 970	0.206 54	1302.71	25.918	3.4713	29.53 ± 0.02
0.707 09	0.203 02	0.089 886	0.776 93	1030.92	46.868	1.9178	26.02 ± 0.04
0.701 95	0.198 00	0.100 049	0.779 99	1057.12	46.690	2.1428	25.38 ± 0.04
0.691 74	0.198 65	0.109 612	0.776 89	1078.50	46.531	2.3557	27.08 ± 0.04
0.683 88	0.196 21	0.119 915	0.777 06	1103.73	46.354	2.5869	27.43 ± 0.03
0.676 25	0.193 75	0.129 996	0.777 30	1131.92	46.048	2.8231	26.67 ± 0.03
0.669 07	0.191 14	0.139 791	0.777 80	1152.81	46.028	3.0371	27.96 ± 0.03
0.827 14	0.112 98	0.059 876	0.879 82	934.89	51.548	1.1616	22.92 ± 0.09
0.821 32	0.108 65	0.070 023	0.883 17	957.61	51.388	1.3626	23.12 ± 0.07
0.812 70	0.106 95	0.080 355	0.883 71	980.78	51.154	1.5708	23.84 ± 0.06
0.802 99	0.106 96	0.090 046	0.882 45	1003.67	50.840	1.7712	24.11 ± 0.05
0.793 77	0.105 99	0.100 242	0.882 20	1027.98	50.541	1.9834	24.21 ± 0.05
0.784 24	0.105 40	0.110 367	0.881 53	1051.40	50.282	2.1950	24.78 ± 0.04
0.776 06	0.103 70	0.120 242	0.882 13	1073.15	50.121	2.3990	25.60 ± 0.04
0.765 07	0.105 32	0.129 617	0.879 00	1098.91	49.658	2.6102	24.97 ± 0.03
0.757 82	0.102 12	0.140 063	0.881 25	1122.07	49.536	2.8275	25.61 ± 0.03
0.989 05	0.000 00	0.010 95	1.000 00	808.98	58.143	0.1883	9.2 ± 1.3
0.982 73	0.000 00	0.017 27	1.000 00	822.25	57.885	0.2984	12.3 ± 1.0
0.974 63	0.000 00	0.025 37	1.000 00	839.37	57.556	0.4408	14.2 ± 0.6
0.966 41	0.000 00	0.033 59	1.000 00	856.30	57.267	0.5865	16.5 ± 0.4
0.957 08	0.000 00	0.042 92	1.000 00	875.39	56.960	0.7535	18.5 ± 0.4
0.945 87	0.000 00	0.054 13	1.000 00	898.94	56.570	0.9569	19.60 ± 0.25
0.939 79	0.000 00	0.060 21	1.000 00	912.04	56.347	1.0686	19.85 ± 0.21
0.933 04	0.000 00	0.066 96	1.000 00	926.54	56.109	1.1934	20.21 ± 0.19
0.926 25	0.000 00	0.073 75	1.000 00	941.18	55.873	1.3199	20.55 ± 0.19
0.918 00	0.000 00	0.082 00	1.000 00	958.73	55.612	1.4746	21.20 ± 0.13
0.909 65	0.000 00	0.090 35	1.000 00	976.76	55.341	1.6327	21.66 ± 0.14
0.900 92	0.000 00	0.099 08	1.000 00	995.53	55.072	1.7990	22.21 ± 0.11
0.890 64	0.000 00	0.109 36	1.000 00	1018.52	54.721	1.9986	22.44 ± 0.12
0.878 33	0.000 00	0.121 67	1.000 00	1044.79	54.386	2.2371	23.35 ± 0.09
0.864 40	0.000 00	0.135 60	1.000 00	1076.13	53.947	2.5136	23.74 ± 0.08
0.851 46	0.000 00	0.148 54	1.000 00	1103.92	53.624	2.7700	24.61 ± 0.07
0.838 24	0.000 00	0.161 76	1.000 00	1132.20	53.317	3.0340	25.50 ± 0.06
0.992 31	0.000 00	0.007 69	1.000 00	801.81	58.303	0.1318	9.0 ± 1.5
0.987 42	0.000 00	0.012 58	1.000 00	811.92	58.110	0.2164	12.9 ± 0.9
0.981 12	0.000 00	0.018 88	1.000 00	825.12	57.855	0.3263	14.7 ± 0.6
0.973 75	0.000 00	0.026 25	1.000 00	840.46	57.574	0.4559	16.4 ± 0.5
0.964 88	0.000 00	0.035 12	1.000 00	858.87	57.253	0.6134	17.9 ± 0.3
0.956 12	0.000 00	0.043 88	1.000 00	877.29	56.933	0.7706	18.7 ± 0.3
0.945 63	0.000 00	0.054 37	1.000 00	899.50	56.559	0.9614	19.57 ± 0.23
0.935 00	0.000 00	0.065 00	1.000 00	922.42	56.172	1.1572	20.02 ± 0.17
0.925 99	0.000 00	0.074 01	1.000 00	941.85	55.858	1.3249	20.48 ± 0.14
0.916 05	0.000 00	0.083 95	1.000 00	962.29	55.585	1.5103	21.75 ± 0.12
0.904 66	0.000 00	0.095 34	1.000 00	986.77	55.226	1.7264	22.40 ± 0.11
0.892 87	0.000 00	0.107 13	1.000 00	1012.40	54.857	1.9529	22.95 ± 0.14
0.881 69	0.000 00	0.118 31	1.000 00	1036.85	54.516	2.1701	23.44 ± 0.09
0.872 96	0.000 00	0.127 04	1.000 00	1055.95	54.261	2.3413	23.86 ± 0.09
0.862 81	0.000 00	0.137 19	1.000 00	1079.11	53.928	2.5440	24.01 ± 0.09
0.852 74	0.000 00	0.147 26	1.000 00	1100.36	53.695	2.7425	24.80 ± 0.07
0.839 86	0.000 00	0.160 14	1.000 00	1129.26	53.329	3.0029	25.24 ± 0.06

composition and can be correlated using the following expressions:

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

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

From the V_ϕ values of strontium nitrate in water (given in Table 1) and of copper(II) chloride in water (given in Table 2) we have calculated the V_ϕ^∞ values. These values

Table 5. Apparent Molar Volume of Strontium Nitrate in Water at Infinite Dilution, at 298.15 K

reference	V_ϕ^∞/cm^3·mol^{-1}
this work	40.83
Sugden (1926)[c]	n. s.[a]
Pesce (1935)[d]	40.5[b]
Fajans and Johnson (1942)	40.4
Millero (1971, 1972)	39.84
Padova (1977)	41.50
Doan and Sangster (1981)	41.9[b]
Kuznetsov et al. (1983)	n. s.
Smirnova et al. (1989)	42.6
Krumgalz et al. (1996)	41.17

[a] n. s.: no satisfactory experimental values for fitting. [b] Value obtained from density data reported. [c] Referenced in Meyer (1931). [d] Referenced in Meyer (1960).

Table 6. Apparent Molar Volume of Copper(II) Chloride in Water at Infinite Dilution, at 298.15 K

reference	V_ϕ^∞/cm^3·mol^{-1}
this work	9.79
Herz (1914)	n. s.[a]
Schumb (1928)	n. s.
Dolian and Briscoe (1937)[c]	n. s.
Fajans and Johnson (1942)	9.4
Millero (1971, 1972)	9.4
Lo Surdo and Millero (1980)	10.14
Pogue and Atkinson (1988a)	10.1[b]
Pogue and Atkinson (1988b)	10.07
Krumgalz et al. (1996)	8.571

[a] n. s.: no satisfactory experimental values for fitting. [b] Value obtained from density data reported. [c] Referenced in Pietsch (1958).

Table 7. Parameters of Eqs 3 and 4

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
	Ethanol + Water + Strontium Nitrate System				
b_ν	39.109	93.326	−506.16	1293.9	−1498.5
c_ν	11.134	−114.74	1427.9	−5595.8	6915.1
	Ethanol + Water + Copper(II) Chloride System				
b_ν	5.836	97.810	−401.16	620.4	−314.8
c_ν	9.852	−39.268	247.41	−439.6	232.1

can be compared with the experimental values reported in the literature, shown in Tables 5 and 6.

We have found for strontium nitrate that $V_\phi^\infty = 40.83$ cm^3·mol^{-1}. This value is very similar to the values reported by Pesce (1935), Fajans and Johnson (1942), and Krumgalz et al. (1996). For copper(II) chloride, we have found that $V_\phi^\infty = 9.79$ cm^3·mol^{-1}. This value is in good agreement with those obtained by Lo Surdo and Millero (1980) and Pogue and Atkinson (1988a,b).

From the V_ϕ values of strontium nitrate in ethanol + water system 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 V_ϕ in the range $0.025 \le x'_1 \le 0.60$. These parameters are given in Table 7. The mean absolute deviation of the apparent molar volume for the strontium nitrate is 1.25 cm^3·mol^{-1}, and the standard deviation is 1.85 cm^3·mol^{-1}.

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 + strontium nitrate solutions. The mean absolute deviation of molar volume is 0.016 cm^3·mol^{-1}, and the corresponding standard deviation is 0.021 cm^3·mol^{-1}. The mean absolute deviation of the density is 0.65 kg·m^{-3}, and the standard deviation is 0.83 kg·m^{-3}.

From the V_ϕ values of copper(II) chloride in ethanol + water system, we have found the values of b_ν and c_ν in the range $0.020 \le x'_1 \le 1.0$. These parameters are given also in Table 7. The mean absolute deviation of the apparent molar volume for the copper(II) chloride is 0.60 cm^3·mol^{-1}, and the standard deviation is 0.82 cm^3·mol^{-1}.

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 + copper(II) chloride solutions. The mean absolute deviation of molar volume is 0.031 cm^3·mol^{-1}, and the corresponding standard deviation is 0.044 cm^3·mol^{-1}. The mean absolute deviation of the density is 0.88 kg·m^{-3}, and the standard deviation is 1.18 kg·m^{-3}.

Therefore, the apparent molar volumes of strontium nitrate and copper(II) chloride in pure water recalculated from the eqs 1−4 with the parameters of Table 7 agree well with the values obtained from the experimental binary data.

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