Apparent Molar Volumes of Strontium Chloride in Ethanol + Water at 298.15 K

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Densities of ethanol + water + strontium 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 the electrolyte in these mixtures have been calculated, and partial molar volumes at infinite dilution have been evaluated.

Introduction

Density data on electrolyte solutions furnish some interesting information in elucidating the structural interactions occurring in solution. Most density measurements have been made on aqueous as well as nonaqueous electrolyte solutions. Comparatively, less attention has been devoted to densities of ternary mixtures (water + nonaqueous solvent + electrolyte), possibly due to the large quantity of experimental work necessary.

The effect of a salt dissolved in a mixed solvent has potential application in the recovery of organic liquids from aqueous solutions by distillation. The study of density data for a mixed solvent containing electrolytes provides some preliminary information concerning the salt effect on vapor−liquid equilibria.

In a previous work (Peña *et al.*, 1995a), we studied the vapor−liquid equilibrium of the ethanol + water + strontium chloride system. In the present work, we have determined the densities of this system at 298.15 K and have obtained the apparent molar volumes of the strontium chloride in ethanol + water mixtures.

Millero (1972) reported partial molar volumes at infinite dilution for the strontium chloride in water from Shedlovsky and Brown (1934), Kruis (1936), Redlich (1940), Wirth (1940), Fajans and Johnson (1942), and Ellis (1967). Furthermore, Herz (1914) published experimental density data of the water + strontium chloride binary system. Bateman (1949) gave apparent molar volume data for the strontium chloride in ethanol + water. The strontium chloride is not soluble in absolute ethanol.

Experimental Section

The chemicals were absolute ethanol (Baker analyzed reagent, >99.5 mass %), distilled water, and strontium chloride (Probus, >99.5 mass %). They were used without further purification. The density of ethanol was (785.08 ± 0.01) $kg\cdot m^{-3}$ at 298.15 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 $kg\cdot m^{-3}$ (Marsh and Richards, 1980).

The water + strontium chloride samples were analyzed gravimetrically, by evaporation to dryness. The accuracy of salt mole fractions in the samples was better than 0.000 01. The ethanol + water + strontium chloride mixtures were prepared one by one gravimetrically using a Sartorius analytical balance with a precision of ±0.0001 g. They were 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 ethanol and water mole fractions was better than 0.000 05, and the accuracy of salt mole fraction was better than 0.000 004.

Table 1. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Water (2) + Strontium Chloride (3) Mixtures and Apparent Molar Volumes V_ϕ of Strontium 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}
0.001 79	1010.77	18.073	0.0989	20.2 ± 0.8
0.004 84	1033.76	18.086	0.2678	21.6 ± 0.3
0.008 21	1058.79	18.105	0.4536	22.54 ± 0.17
0.013 86	1099.64	18.154	0.7633	24.23 ± 0.10
0.018 66	1133.87	18.202	1.0254	25.20 ± 0.08
0.022 09	1157.84	18.241	1.2109	25.84 ± 0.06
0.026 50	1188.37	18.293	1.4484	26.53 ± 0.05
0.030 19	1213.35	18.344	1.6458	27.20 ± 0.04
0.034 35	1241.22	18.404	1.8667	27.82 ± 0.04
0.039 06	1272.49	18.471	2.1147	28.37 ± 0.03
0.045 06	1311.07	18.571	2.4265	29.21 ± 0.03
0.054 72	1372.26	18.732	2.9214	30.19 ± 0.02
0.061 37	1413.31	18.849	3.2561	30.78 ± 0.02

The mole fraction solubility of strontium chloride in water at 298.15 K is 0.0596 (Menzies, 1936) and decreases almost linearly when the mole fraction of ethanol in the mixed solvent increases, to become practically zero when the mole fraction of alcohol in the ethanol + water mixed solvent is 0.80. Therefore, no samples were prepared with a mole fraction of alcohol in the ethanol + water mixed solvent greater than 0.80.

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 $kg\cdot m^{-3}$.

Results and Discussion

In Table 1 the densities, *d*, of the water (2) + strontium chloride (3) mixtures are reported, where x_3 is the mole fraction of strontium chloride in the binary mixture. In Table 2 the density, *d*, of the ethanol (1) + water (2) + strontium chloride (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. From these results, the molar volume of solution, *V*, and the molar concentration of salt in the solution, *c*, were

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Table 2. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Water (2) + Strontium Chloride (3) Mixtures and Apparent Molar Volumes V_ϕ of Strontium 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}
0.020 03	0.974 78	0.005 195	0.020 13	1026.04	18.818	0.2761	21.7 ± 0.3
0.041 29	0.953 62	0.005 091	0.041 50	1016.21	19.572	0.2601	21.6 ± 0.3
0.089 56	0.905 30	0.005 139	0.090 02	999.17	21.268	0.2416	21.1 ± 0.3
0.142 82	0.851 97	0.005 214	0.143 56	980.99	23.196	0.2248	23.2 ± 0.3
0.206 09	0.788 67	0.005 243	0.207 18	958.74	25.590	0.2049	26.5 ± 0.3
0.280 02	0.714 90	0.005 083	0.281 45	933.38	28.483	0.1784	27.6 ± 0.3
0.366 00	0.628 85	0.005 151	0.367 90	909.09	31.908	0.1614	24.0 ± 0.4
0.476 05	0.518 77	0.005 180	0.478 53	882.42	36.376	0.1424	24.2 ± 0.5
0.600 45	0.394 41	0.005 142	0.603 55	857.28	41.508	0.1239	24.6 ± 0.6
0.778 37	0.216 56	0.005 066	0.782 33	828.12	48.984	0.1034	14.9 ± 0.9
0.020 20	0.969 83	0.009 971	0.020 40	1059.99	18.853	0.5289	22.84 ± 0.15
0.041 18	0.948 85	0.009 976	0.041 59	1049.70	19.599	0.5090	22.94 ± 0.15
0.088 10	0.901 81	0.010 093	0.089 00	1030.77	21.252	0.4749	23.11 ± 0.15
0.142 78	0.847 23	0.009 989	0.144 22	1007.51	23.251	0.4296	26.22 ± 0.16
0.203 27	0.786 72	0.010 010	0.205 33	983.54	25.546	0.3919	28.62 ± 0.16
0.278 37	0.711 59	0.010 043	0.281 19	956.27	28.482	0.3526	28.92 ± 0.17
0.365 88	0.624 11	0.010 010	0.369 58	928.56	31.971	0.3131	27.39 ± 0.19
0.464 52	0.525 67	0.009 808	0.469 12	901.20	35.981	0.2726	28.47 ± 0.23
0.602 19	0.387 79	0.010 029	0.608 29	872.43	41.630	0.2409	25.5 ± 0.3
0.759 03	0.231 24	0.009 730	0.766 49	844.22	48.183	0.2019	18.1 ± 0.4
0.019 72	0.964 85	0.015 430	0.020 02	1097.94	18.887	0.8169	24.53 ± 0.10
0.041 43	0.943 13	0.015 443	0.042 08	1086.53	19.648	0.7860	23.84 ± 0.10
0.088 11	0.896 41	0.015 475	0.089 50	1063.75	21.304	0.7264	24.72 ± 0.10
0.141 85	0.842 67	0.015 489	0.144 08	1038.13	23.284	0.6652	27.65 ± 0.10
0.204 73	0.779 87	0.015 400	0.207 93	1009.12	25.689	0.5995	30.45 ± 0.10
0.365 29	0.619 25	0.015 459	0.371 03	949.74	32.047	0.4824	30.19 ± 0.12
0.472 49	0.511 93	0.015 572	0.479 97	919.34	36.395	0.4279	29.89 ± 0.15
0.603 38	0.381 20	0.015 427	0.612 83	888.72	41.758	0.3694	27.41 ± 0.19
0.019 43	0.960 52	0.020 048	0.019 83	1130.02	18.918	1.0597	25.10 ± 0.08
0.040 58	0.939 45	0.019 966	0.041 41	1116.73	19.665	1.0153	24.86 ± 0.08
0.086 71	0.893 33	0.019 960	0.088 48	1091.08	21.312	0.9366	26.11 ± 0.08
0.142 13	0.837 93	0.019 943	0.145 02	1062.14	23.354	0.8539	28.48 ± 0.08
0.201 80	0.778 23	0.019 976	0.205 91	1033.04	25.637	0.7792	30.54 ± 0.08
0.275 44	0.704 59	0.019 967	0.281 06	1000.38	28.538	0.6997	31.77 ± 0.08
0.362 08	0.617 93	0.019 988	0.369 46	969.01	31.973	0.6252	30.04 ± 0.09
0.467 36	0.512 66	0.019 978	0.476 89	935.57	36.272	0.5508	31.34 ± 0.11
0.019 76	0.954 39	0.025 855	0.020 28	1168.76	18.997	1.3610	26.12 ± 0.06
0.040 76	0.933 42	0.025 827	0.041 84	1154.38	19.741	1.3083	26.04 ± 0.06
0.087 20	0.886 94	0.025 853	0.089 52	1126.23	21.394	1.2084	26.79 ± 0.06
0.140 76	0.833 40	0.025 848	0.144 49	1094.87	23.379	1.1056	28.97 ± 0.06
0.202 44	0.771 75	0.025 810	0.207 81	1059.84	25.779	1.0012	32.18 ± 0.06
0.275 33	0.698 84	0.025 821	0.282 63	1025.52	28.638	0.9017	32.52 ± 0.06
0.363 14	0.610 95	0.025 915	0.372 80	990.75	32.142	0.8063	31.95 ± 0.07
0.019 74	0.950 28	0.029 979	0.020 35	1197.58	19.024	1.5759	25.91 ± 0.05
0.040 61	0.929 39	0.030 000	0.041 87	1181.15	19.786	1.5162	26.62 ± 0.05
0.086 46	0.883 55	0.029 991	0.089 13	1150.60	21.428	1.3996	27.60 ± 0.05
0.139 28	0.830 72	0.030 007	0.143 58	1116.31	23.416	1.2815	30.49 ± 0.05
0.200 51	0.769 53	0.029 957	0.206 70	1080.41	25.778	1.1621	32.59 ± 0.05
0.272 86	0.697 21	0.029 932	0.281 28	1043.71	28.626	1.0456	33.30 ± 0.05
0.358 60	0.611 39	0.030 006	0.369 69	1007.71	32.045	0.9364	32.80 ± 0.06
0.040 95	0.922 81	0.036 238	0.042 49	1219.17	19.896	1.8214	27.85 ± 0.04
0.086 71	0.877 20	0.036 085	0.089 96	1184.92	21.537	1.6755	28.74 ± 0.04
0.139 73	0.824 03	0.036 239	0.144 98	1149.38	23.515	1.5411	30.60 ± 0.04
0.201 58	0.762 17	0.036 242	0.209 16	1110.08	25.911	1.3987	32.55 ± 0.04
0.273 40	0.690 41	0.036 195	0.283 66	1071.40	28.721	1.2602	32.59 ± 0.04
0.019 14	0.940 92	0.039 942	0.019 93	1260.11	19.177	2.0828	28.35 ± 0.04
0.040 15	0.919 99	0.039 862	0.041 81	1242.01	19.922	2.0009	28.33 ± 0.04
0.085 53	0.874 45	0.040 024	0.089 09	1207.79	21.559	1.8565	29.31 ± 0.04
0.137 72	0.822 19	0.040 096	0.143 47	1169.14	23.533	1.7038	31.67 ± 0.04
0.198 16	0.761 80	0.040 044	0.206 42	1128.26	25.882	1.5472	33.68 ± 0.04
0.019 25	0.934 04	0.046 706	0.020 19	1303.35	19.272	2.4235	28.81 ± 0.03
0.040 15	0.913 13	0.046 724	0.042 12	1285.38	20.000	2.3362	28.49 ± 0.03
0.086 24	0.867 10	0.046 662	0.090 46	1244.52	21.689	2.1515	29.94 ± 0.03
0.090 87	0.862 89	0.046 244	0.095 27	1236.85	21.881	2.1135	30.65 ± 0.03
0.019 16	0.930 84	0.050 007	0.020 17	1324.88	19.307	2.5900	28.87 ± 0.03
0.040 31	0.909 49	0.050 200	0.042 44	1303.91	20.094	2.4983	29.53 ± 0.03
0.084 05	0.866 08	0.049 863	0.088 46	1263.47	21.671	2.3010	30.37 ± 0.03
0.019 09	0.923 69	0.057 216	0.020 25	1365.89	19.468	2.9390	30.36 ± 0.03

calculated. In Tables 1 and 2 we also report values of V and c.

The apparent molar volume, V_ϕ, of strontium 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.*, 1995b), by means of the expression

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

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 strontium chloride in a ternary liquid mixture of ethanol + water + strontium chloride 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 chloride calculated at 298.15 K are also shown in Tables 1 and 2. These values are significantly lower than the values reported by Bateman (1949).

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 equation (1929):

$$V_\phi = V_\phi^\infty + S_v^e c^{1/2} \qquad (2)$$

where V_ϕ^∞ is the apparent molar volume of strontium chloride at infinite dilution, which is the same as the partial molar volume of strontium chloride at infinite dilution, and S_v^e is the experimental slope. Both V_ϕ^∞ and S_v^e depend on the solvent composition and can be correlated using the following expressions:

$$V_\phi^\infty/\text{cm}^3\cdot\text{mol}^{-1} = \sum_{\nu=0}^{4} b_\nu (x_1')^\nu \qquad (3)$$

$$S_\nu^e/\text{cm}^3\cdot\text{mol}^{-3/2}\cdot\text{L}^{1/2} = \sum_{\nu=0}^{4} c_\nu (x_1')^\nu \qquad (4)$$

From the V_ϕ values of strontium chloride in water, given in Table 1, we have found that $V_\phi^\infty = 17.8$ cm^3·mol^{-1}. This value is in good agreement with the 17.94 cm^3·mol^{-1} value recommended by Millero (1972). The V_ϕ^∞ values obtained from density data reported by Herz (1914) and Bateman (1949) are respectively 20.7 cm^3·mol^{-1} and 29.2 cm^3·mol^{-1}. These values are out of the range suggested by Millero (1972).

From the V_ϕ 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 V_ϕ in the range $0.02 \le x_1' \le 0.8$. These parameters are given in Table 3. The mean absolute deviation of the apparent molar volume for the strontium chloride is 0.63 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 + strontium chloride solutions. The mean absolute deviation of molar volume is 0.011 cm^3·mol^{-1}, and the corresponding standard deviation is 0.015 cm^3·mol^{-1}. The mean absolute deviation of the density is 0.52 kg·m^{-3}, and the standard deviation is 0.67 kg·m^{-3}. However, the apparent molar volumes of strontium chloride in pure water recalculated from eqs 1−4 with the parameters of Table 3 do not agree well with the values obtained from the experimental binary data.

Table 3. Parameters of Eqs 3 and 4

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
b_ν	14.968	80.478	−376.42	736.7	−516.3
c_ν	8.827	−52.706	473.61	−1096.2	777.7

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