Partial Molar Volumes of Strontium Bromide in Ethanol + Water Mixtures at 298.15 K

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Densities of ethanol + water + strontium bromide 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

There is an increased interest in the thermodynamic behavior of solvent mixtures containing dissolved electrolytes. There is a shortage of measurements on such mixtures, and the complexity of interactions due to the presence of a dissociable electrolyte makes the physical properties difficult to correlate and predict.

In a previous work (Vercher et al., 1994), we studied the vapor–liquid equilibria of the ethanol + water + strontium bromide 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 strontium bromide in ethanol + water mixtures, as well as the partial molar volumes.

In the literature, we have found experimental density data of the water + strontium bromide (West and Hull, 1933; Meyer et al., 1960) and ethanol + strontium bromide (West and Hull, 1933) binary systems, but we have not found any reported density data of the ethanol + water + strontium bromide ternary system.

Experimental Section

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 mass %), distilled water, and strontium bromide (Probus, >99.5 mass %). They were used without further purification. Ethanol density was (0.785 08 ± 0.000 01) g·cm^{-3} at 298.15 K, indicating a maximun of 0.01 vol % of water, as reported by Marsh and Richards (1980). Water density was (0.997 05 ± 0.000 01) g·cm^{-3} at 298.15 K.

The ethanol + water + strontium bromide mixtures were prepared 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 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 accuracy of density values was ±0.00001 g·cm^{-3}. The densimeter was calibrated with distilled water and dry air. Furthermore, this apparatus was tested by measuring a set of standard aqueous solutions with known mass fractions of strontium bromide, and comparing them to results reported by West and Hull (1933). These results agree with ours over the entire range of compositions.

Results and Discussion

In Table 1 the density, d, of the ethanol (1) + water (2) + strontium bromide (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, was calculated using the equation

$$V = \frac{M_1x_1 + M_2x_2 + M_3x_3}{d} \quad (1)$$

where M_i is the molecular mass of component i. The molar concentration of salt in the solution, c, was obtained from the expression

$$c = x_3/V \quad (2)$$

In Table 1, we report values of V and c.

The apparent molar volume, Φ_v, of strontium bromide in the ethanol + water mixture is defined from the molar volume of solution, V, by means of the expression

$$V = V_{12}x_{12} + \Phi_v x_3 \quad (3)$$

where V_{12} is the molar volume of solvent (ethanol + water) and x_{12} is the molar fraction of solvent in the salt solution ($x_{12} = 1 - x_3 = x_1 + x_2$).

The molar volume of solvent can be calculated as the molar volume of a binary ethanol + water mixture with the same mole fraction of alcohol as the corresponding ternary mixture on a salt-free basis. This molar volume of solvent depends on the amount of ethanol and water present in its composition, and can be obtained from the molar volume of pure ethanol, $V_1°$, and that of pure water, $V_2°$, according to the equation

$$V_{12} = V_1°x'_1 + V_2°x'_2 + V^E_{12} \quad (4)$$

where x'_1 and x'_2 are the molar fractions of ethanol and water in the solvent, on a salt-free basis ($x'_1 = x_1/(x_1 + x_2)$; $x'_2 = x_2/(x_1 + x_2)$) and V^E_{12} is the excess molar volume of the binary ethanol + water mixture, which depends on the solvent composition.

Starting from eqs 3 and 4, the molar volume of solution can be expressed by

$$V = \left[V_1°\frac{x_1}{x_1 + x_2} + V_2°\frac{x_2}{x_1 + x_2} + V^E_{12}\right](x_1 + x_2) + \Phi_v x_3 \quad (5)$$

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Table 1. Densities of Ethanol (1) + Water (2) + Strontium Bromide (3) Mixtures and Apparent Molar Volumes of Strontium Bromide 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})
0.0198	0.9702	0.0100	0.0200	1099.96	18.97	0.5275	36.12	0.6308	0.3391	0.0300	0.6504	981.42	43.41	0.6921	38.84
0.0501	0.9398	0.0101	0.0506	1083.60	20.06	0.5023	37.10	0.6821	0.2887	0.0292	0.7026	963.67	45.50	0.6414	36.89
0.0744	0.9156	0.0100	0.0751	1071.25	20.91	0.4791	37.47	0.7229	0.2473	0.0298	0.7451	956.74	47.18	0.6321	34.59
0.0997	0.8904	0.0099	0.1007	1058.60	21.81	0.4556	38.44	0.7599	0.2107	0.0294	0.7830	946.16	48.70	0.6037	32.85
0.1494	0.8407	0.0100	0.1509	1036.24	23.64	0.4217	40.65	0.9698	0.0000	0.0302	1.0000	907.30	57.48	0.5256	18.94
0.1958	0.7937	0.0105	0.1979	1019.97	25.41	0.4137	42.70	0.0192	0.9408	0.0400	0.0200	1406.45	19.71	2.0272	41.65
0.2402	0.7499	0.0099	0.2426	996.48	27.12	0.3647	43.26	0.0487	0.9119	0.0395	0.0507	1369.53	20.76	1.9007	42.16
0.2977	0.6923	0.0101	0.3007	976.27	29.37	0.3428	41.31	0.0719	0.8881	0.0400	0.0749	1350.61	21.62	1.8479	42.86
0.3370	0.6529	0.0101	0.3404	962.45	30.95	0.3267	41.58	0.0950	0.8655	0.0394	0.0989	1323.71	22.46	1.7560	43.79
0.4456	0.5444	0.0100	0.4501	929.12	35.32	0.2838	39.22	0.1441	0.8159	0.0400	0.1501	1284.51	24.32	1.6450	45.48
0.5411	0.4487	0.0102	0.5466	905.86	39.23	0.2600	38.55	0.1925	0.7682	0.0394	0.2003	1240.54	26.16	1.5049	46.43
0.5906	0.3995	0.0099	0.5965	893.49	41.25	0.2401	36.21	0.2397	0.7204	0.0399	0.2497	1210.48	28.01	1.4255	46.56
0.6416	0.3483	0.0101	0.6482	883.82	43.37	0.2328	34.51	0.2883	0.6718	0.0399	0.3003	1179.19	29.91	1.3352	46.03
0.7430	0.2471	0.0098	0.7504	863.05	47.64	0.2064	32.51	0.3357	0.6244	0.0400	0.3496	1150.73	31.81	1.2566	46.12
0.8424	0.1475	0.0100	0.8510	847.66	51.84	0.1930	25.01	0.3847	0.5753	0.0400	0.4007	1126.41	33.72	1.1855	44.32
0.9900	0.0000	0.0100	1.0000	825.75	58.22	0.1711	12.31	0.4309	0.5291	0.0399	0.4489	1103.40	35.58	1.1214	44.06
0.0196	0.9603	0.0201	0.0200	1207.42	19.20	1.0473	38.65	0.4806	0.4795	0.0399	0.5005	1082.58	37.55	1.0625	42.66
0.0491	0.9310	0.0199	0.0501	1183.40	20.25	0.9834	39.17	0.5275	0.4325	0.0400	0.5495	1063.56	39.47	1.0123	42.43
0.0738	0.9063	0.0200	0.0753	1167.46	21.13	0.9452	39.83	0.5724	0.3879	0.0397	0.5961	1047.04	41.23	0.9618	40.07
0.1042	0.8760	0.0198	0.1063	1146.91	22.22	0.8910	40.51	0.6239	0.3361	0.0400	0.6499	1030.64	43.37	0.9223	39.34
0.1469	0.8331	0.0200	0.1499	1122.42	23.81	0.8408	42.75	0.9598	0.0000	0.0402	1.0000	947.12	57.19	0.7028	21.48
0.1950	0.7850	0.0199	0.1990	1094.07	25.65	0.7767	44.00	0.0191	0.9310	0.0500	0.0201	1501.45	19.99	2.4993	42.62
0.3429	0.6371	0.0201	0.3499	1024.00	31.48	0.6369	43.97	0.0475	0.9028	0.0497	0.0500	1462.28	21.03	2.3626	43.33
0.4400	0.5396	0.0204	0.4492	989.73	35.40	0.5760	43.09	0.0713	0.8787	0.0500	0.0751	1437.45	21.91	2.2825	44.03
0.5837	0.3965	0.0198	0.5955	944.51	41.22	0.4807	39.54	0.0946	0.8562	0.0492	0.0994	1405.53	22.74	2.1645	44.71
0.6389	0.3411	0.0201	0.6520	931.56	43.52	0.4607	38.45	0.1425	0.8076	0.0500	0.1500	1362.04	24.58	2.0328	46.38
0.6934	0.2867	0.0199	0.7075	918.33	45.77	0.4344	36.07	0.1899	0.7601	0.0500	0.1999	1319.30	26.39	1.8950	47.00
0.7369	0.2432	0.0199	0.7519	909.27	47.57	0.4185	33.71	0.2373	0.7128	0.0499	0.2497	1279.52	28.24	1.7683	47.24
0.7856	0.1948	0.0196	0.8013	898.40	49.59	0.3949	30.32	0.2857	0.6644	0.0499	0.3007	1245.08	30.10	1.6575	46.26
0.8319	0.1479	0.0202	0.8491	892.11	51.55	0.3920	28.30	0.3322	0.6177	0.0501	0.3497	1214.51	31.96	1.5659	46.14
0.8532	0.1267	0.0201	0.8707	888.18	52.43	0.3836	25.99	0.3762	0.5740	0.0497	0.3959	1186.76	33.69	1.4763	45.32
0.9800	0.0000	0.0200	1.0000	866.95	57.79	0.3460	13.76	0.4276	0.5224	0.0500	0.4501	1160.23	35.75	1.3981	44.73
0.0197	0.9503	0.0300	0.0203	1308.54	19.45	1.5430	40.29	0.4725	0.4779	0.0496	0.4972	1136.33	37.53	1.3210	43.84
0.0499	0.9203	0.0297	0.0514	1277.66	20.54	1.4481	40.95	0.4737	0.4767	0.0496	0.4984	1136.05	37.58	1.3207	43.84
0.0722	0.8978	0.0300	0.0744	1262.21	21.33	1.4071	41.26	0.5219	0.4282	0.0499	0.5493	1116.86	39.49	1.2635	42.27
0.1066	0.8639	0.0294	0.1099	1229.85	22.57	1.3042	42.32	0.5697	0.3803	0.0500	0.5997	1097.99	41.42	1.2080	41.14
0.1450	0.8252	0.0298	0.1494	1203.97	24.03	1.2420	44.09	0.0188	0.9212	0.0600	0.0200	1592.34	20.29	2.9566	43.66
0.2064	0.7644	0.0292	0.2126	1157.20	26.37	1.1091	45.54	0.0481	0.8924	0.0595	0.0512	1545.81	21.36	2.7851	44.36
0.2422	0.7278	0.0300	0.2497	1140.45	27.79	1.0788	45.60	0.0705	0.8695	0.0600	0.0750	1521.34	22.19	2.7042	44.98
0.2886	0.6818	0.0297	0.2974	1112.08	29.60	1.0020	45.21	0.0952	0.8454	0.0594	0.1012	1485.21	23.11	2.5711	45.91
0.3394	0.6306	0.0300	0.3499	1088.44	31.62	0.9478	44.33	0.1412	0.7988	0.0600	0.1502	1437.25	24.87	2.4121	47.21
0.4361	0.5340	0.0299	0.4495	1046.40	35.47	0.8441	42.51	0.1880	0.7531	0.0589	0.1998	1381.58	26.64	2.2103	47.94
0.4905	0.4796	0.0299	0.5056	1025.44	37.68	0.7939	42.03	0.9399	0.0000	0.0601	1.0000	1027.63	56.60	1.0610	24.00
0.5816	0.3887	0.0298	0.5994	995.19	41.36	0.7197	39.31	0.9300	0.0000	0.0700	1.0000	1066.31	56.42	1.2399	26.28

Table 2. Eq 7 Parameters

a_0	a_1	a_2	a_3	a_4	a_5	a_6
−4.235	−0.70	−1.26	−2.86	−1.9	3.87	3.6

Table 3. Parameters of Eqs 9 and 10

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
b_ν	27.786	89.541	−263.28	319.3	−170.1
c_ν	8.525	−19.707	79.42	−139.6	92.4

so it can be deduced that

$$\Phi_v = \frac{V - V_1^\circ x_1 - V_2^\circ x_2 - V_{12}^E(x_1 + x_2)}{x_3} \quad (6)$$

Therefore, the molar apparent volume of strontium bromide in a ternary liquid mixture of ethanol + water + strontium bromide can be calculated, for each composition, 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.

Marsh and Richards (1980) have reported experimental results of excess volumes of ethanol + water mixtures, expressed as $V_{12}^E/x'_1(1 - x'_1)$, at 298.15 K. We have correlated them according to the expression suggested, among different authors, by Mallu and Chalapati Rao (1990) and Mato et al. (1991):

$$V_{12}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x'_1(1 - x'_1)\sum_{\nu=0}^{6} a_\nu(1 - 2x'_1)^\nu \quad (7)$$

In Table 2, we report the values of a_ν obtained. The standard error of estimate is ±0.03 cm^3·mol^{-1}.

From eqs 6 and 7, we calculated the apparent molar volume of strontium bromide at 298.15 K, which depends on solvent composition and on the concentration of the salt. These values are also shown in Table 1.

The apparent molar volume of strontium bromide, at constant solvent composition, shows a linear dependence on the square root of the molar concentration of salt in the solution, according to the Masson equation (1929):

$$\Phi_v = \Phi_v^\circ + S_v^e c^{1/2} \quad (8)$$

where Φ_v° is the apparent molar volume of strontium bromide at infinite dilution, which is the same as the partial molar volume of strontium bromide 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

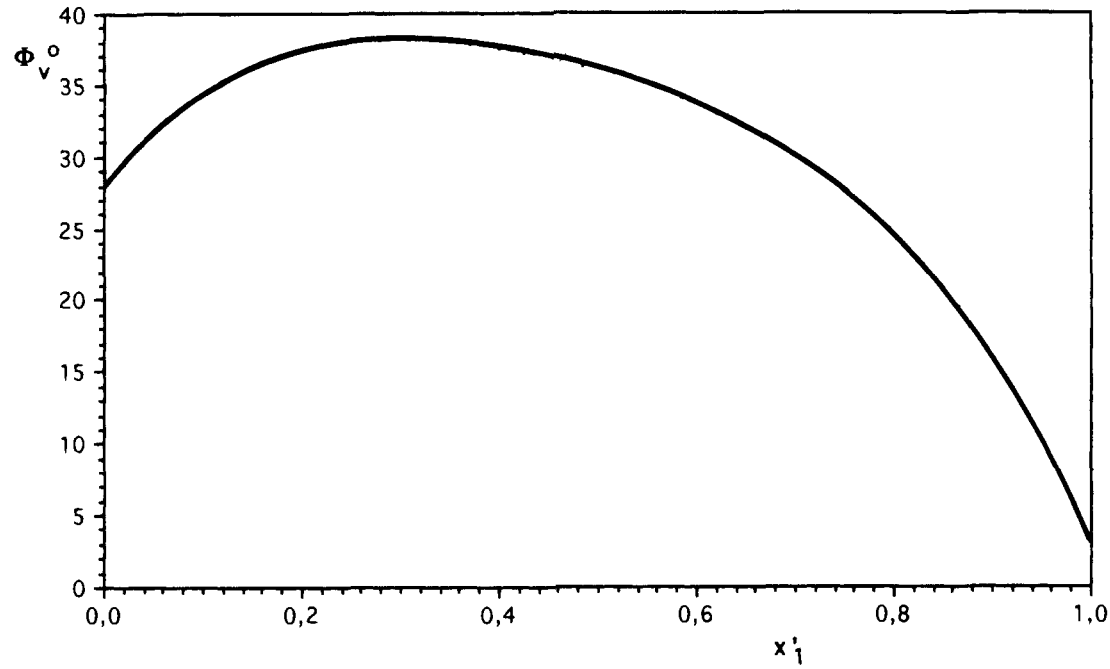

Figure 1. Partial molar volume of the strontium bromide in ethanol + water mixtures against the molar fraction of ethanol on a salt-free basis, at 298.15 K.

using the following expressions:

$$\Phi_v^\circ/(\mathrm{cm^3 \cdot mol^{-1}}) = \sum_{\nu=0}^{4} b_\nu (x'_1)^\nu \quad (9)$$

$$S_v^e/(\mathrm{cm^3 \cdot mol^{-3/2} \cdot L^{1/2}}) = \sum_{\nu=0}^{4} c_\nu (x'_1)^\nu \quad (10)$$

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. These parameters are given in Table 3. The mean absolute deviation of the apparent molar volume for the strontium bromide is 0.50 $\mathrm{cm^3 \cdot mol^{-1}}$, and the standard deviation is 0.61 $\mathrm{cm^3 \cdot mol^{-1}}$.

In Figure 1, we have plotted the partial molar volume of the strontium bromide in ethanol + water against the molar fraction of ethanol on a salt-free basis. There, it can be observed that Φ_v° has a maximum value for $x'_1 \approx 0.3$.

From the values of b_ν and c_ν and eqs 1−10, we have recalculated the molar volume and the density of the ethanol + water + strontium bromide solutions. The mean absolute deviation of molar volume is 0.013 $\mathrm{cm^3 \cdot mol^{-1}}$, and the standard deviation is 0.016 $\mathrm{cm^3 \cdot mol^{-1}}$. The mean absolute deviation of the density is 0.51 $\mathrm{kg \cdot m^{-3}}$, and the corresponding standard deviation is 0.64 $\mathrm{kg \cdot m^{-3}}$.

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