Apparent Molar Volumes of Potassium Nitrate and Sodium Nitrate in Ethanol + Water at 298.15 K

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Densities of ethanol + water + potassium nitrate and ethanol + water + sodium nitrate 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

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). In the present work, we report the densities of ethanol + water + potassium nitrate and ethanol + water + sodium nitrate systems at 298.15 K and the apparent molar volumes of the potassium nitrate and the sodium nitrate in ethanol + water mixtures.

Several papers concerning the densities of potassium nitrate and sodium nitrate in aqueous solutions, as well as apparent molar volumes at 298.15 K of these electrolytes, have appeared in the literature. Millero (1971, 1972), Meyer (1928, 1966), Pietsch (1936), 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

The chemicals were absolute ethanol (Baker-analyzed reagent, >99.5 mass %), distilled water, potassium nitrate (Merck GR, >99 mass %), and sodium nitrate (Merck GR, >99.5 mass %). They were used without further purification. Ethanol density was (785.08 ± 0.01) kg·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·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

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Table 1. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Water (2) + Potassium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Potassium 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}
0.008 51	1025.64	18.255	0.4661	39.94 ± 0.20
0.012 17	1037.68	18.336	0.6637	40.05 ± 0.13
0.016 20	1050.56	18.430	0.8792	40.39 ± 0.10
0.020 40	1063.81	18.529	1.1012	40.63 ± 0.08
0.024 34	1075.97	18.623	1.3067	40.85 ± 0.07
0.028 10	1087.42	18.714	1.5013	41.05 ± 0.06
0.033 76	1104.31	18.854	1.7904	41.33 ± 0.05
0.037 59	1115.59	18.949	1.9837	41.48 ± 0.04
0.042 45	1129.61	19.071	2.2260	41.69 ± 0.04
0.048 50	1146.83	19.223	2.5228	41.87 ± 0.03
0.052 09	1156.83	19.315	2.6969	41.99 ± 0.03
0.056 33	1168.33	19.426	2.8995	42.16 ± 0.03
0.062 48	1184.93	19.585	3.1902	42.34 ± 0.02
0.066 00	1194.23	19.678	3.3542	42.45 ± 0.02

Table 2. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Water (2) + Sodium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Sodium 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 71	1008.40	18.112	0.2047	29.8 ± 0.4
0.008 36	1022.44	18.168	0.4599	29.94 ± 0.19
0.012 27	1034.12	18.217	0.6738	30.11 ± 0.13
0.016 67	1047.06	18.272	0.9120	30.28 ± 0.10
0.021 10	1059.75	18.334	1.1508	30.63 ± 0.08
0.025 86	1073.12	18.402	1.4051	30.97 ± 0.06
0.031 35	1088.29	18.484	1.6959	31.30 ± 0.05
0.036 92	1103.64	18.565	1.9888	31.51 ± 0.04
0.042 47	1118.63	18.648	2.2773	31.71 ± 0.04
0.048 01	1133.00	18.739	2.5619	32.03 ± 0.03
0.053 10	1146.51	18.816	2.8221	32.14 ± 0.03
0.059 09	1162.08	18.909	3.1250	32.29 ± 0.03
0.064 08	1174.74	18.990	3.3744	32.44 ± 0.02
0.069 19	1187.29	19.077	3.6267	32.64 ± 0.02
0.075 15	1201.81	19.179	3.9185	32.84 ± 0.02
0.081 41	1216.62	19.290	4.2203	33.07 ± 0.02
0.086 58	1229.17	19.375	4.4686	33.15 ± 0.02
0.091 40	1240.18	19.463	4.6961	33.32 ± 0.02
0.097 42	1253.72	19.575	4.9770	33.53 ± 0.02
0.104 13	1268.76	19.697	5.2868	33.70 ± 0.01
0.109 05	1280.38	19.775	5.5144	33.72 ± 0.01
0.114 62	1292.22	19.883	5.7647	33.90 ± 0.01
0.119 31	1302.42	19.969	5.9751	33.99 ± 0.01
0.124 82	1313.77	20.077	6.2173	34.16 ± 0.01
0.130 14	1324.31	20.186	6.4472	34.34 ± 0.01
0.136 73	1338.34	20.304	6.7340	34.42 ± 0.01
0.142 97	1350.90	20.425	6.9999	34.55 ± 0.01
0.152 26	1368.60	20.615	7.3859	34.79 ± 0.01
0.160 70	1385.38	20.774	7.7359	34.90 ± 0.01
0.168 74	1401.39	20.921	8.0658	34.97 ± 0.01

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Table 3. Densities d, Molar Volumes V, and Molar Concentrations c of Ethanol (1) + Water (2) + Potassium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Potassium 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}
0.698 45	0.300 30	0.001 250	0.699 32	827.45	45.579	0.0274	12 ± 4
0.449 35	0.548 21	0.002 446	0.450 45	873.39	35.294	0.0693	35.1 ± 1.2
0.494 96	0.502 60	0.002 442	0.496 17	864.18	37.151	0.0657	33.0 ± 1.3
0.544 26	0.453 28	0.002 463	0.545 60	854.99	39.169	0.0629	29.9 ± 1.4
0.599 65	0.397 83	0.002 521	0.601 17	844.96	41.479	0.0608	34.9 ± 1.5
0.024 82	0.970 14	0.005 040	0.024 95	1002.68	19.080	0.2642	39.8 ± 0.4
0.049 67	0.945 36	0.004 974	0.049 92	993.18	19.959	0.2492	40.1 ± 0.4
0.074 37	0.920 61	0.005 016	0.074 75	985.47	20.822	0.2409	39.0 ± 0.4
0.099 55	0.895 39	0.005 054	0.100 06	977.75	21.712	0.2328	38.8 ± 0.4
0.124 35	0.870 66	0.004 993	0.124 97	970.04	22.596	0.2210	38.0 ± 0.4
0.149 78	0.845 24	0.004 986	0.150 53	961.15	23.547	0.2118	42.4 ± 0.4
0.174 23	0.820 82	0.004 958	0.175 09	953.23	24.460	0.2027	43.0 ± 0.4
0.198 31	0.796 75	0.004 939	0.199 30	945.34	25.377	0.1946	44.1 ± 0.4
0.223 56	0.771 41	0.005 030	0.224 69	937.61	26.350	0.1909	43.9 ± 0.4
0.248 84	0.746 09	0.005 060	0.250 11	930.51	27.316	0.1853	39.9 ± 0.4
0.273 23	0.721 75	0.005 024	0.274 61	923.26	28.268	0.1777	38.4 ± 0.5
0.298 23	0.696 75	0.005 029	0.299 73	915.81	29.264	0.1718	39.0 ± 0.5
0.323 43	0.671 45	0.005 114	0.325 10	908.94	30.271	0.1689	38.5 ± 0.5
0.347 66	0.647 36	0.004 988	0.349 40	902.39	31.232	0.1597	36.8 ± 0.5
0.372 58	0.622 44	0.004 979	0.374 44	895.69	32.246	0.1544	38.7 ± 0.5
0.397 98	0.597 03	0.004 985	0.399 98	889.50	33.272	0.1498	38.5 ± 0.6
0.423 41	0.571 68	0.004 914	0.425 50	883.77	34.288	0.1433	35.9 ± 0.6
0.447 49	0.547 57	0.004 940	0.449 72	878.25	35.275	0.1400	37.4 ± 0.6
0.472 88	0.522 09	0.005 027	0.475 27	873.10	36.308	0.1385	36.6 ± 0.6
0.024 86	0.965 14	0.010 002	0.025 11	1018.19	19.195	0.5211	40.41 ± 0.18
0.049 48	0.940 59	0.009 933	0.049 97	1008.01	20.069	0.4949	40.84 ± 0.19
0.073 79	0.916 23	0.009 979	0.074 53	999.66	20.922	0.4770	40.72 ± 0.19
0.099 19	0.890 66	0.010 142	0.100 21	991.54	21.826	0.4647	40.90 ± 0.19
0.123 70	0.866 11	0.010 189	0.124 97	983.24	22.714	0.4486	41.61 ± 0.19
0.148 72	0.841 19	0.010 097	0.150 23	974.95	23.619	0.4275	40.97 ± 0.20
0.173 86	0.816 19	0.009 956	0.175 61	965.72	24.563	0.4053	42.08 ± 0.21
0.198 14	0.791 87	0.009 992	0.200 14	958.48	25.462	0.3924	39.92 ± 0.21
0.223 05	0.767 10	0.009 857	0.225 27	949.91	26.415	0.3732	39.71 ± 0.22
0.247 33	0.742 58	0.010 085	0.249 85	942.15	27.376	0.3684	40.59 ± 0.22
0.272 14	0.717 88	0.009 982	0.274 89	933.98	28.352	0.3521	40.65 ± 0.23
0.296 92	0.693 19	0.009 888	0.299 89	926.43	29.325	0.3372	39.75 ± 0.24
0.321 48	0.668 47	0.010 054	0.324 74	919.86	30.298	0.3318	38.58 ± 0.25
0.024 79	0.960 27	0.014 939	0.025 17	1033.58	19.305	0.7739	40.51 ± 0.12
0.049 28	0.935 69	0.015 029	0.050 04	1023.36	20.176	0.7449	40.73 ± 0.12
0.073 54	0.911 58	0.014 874	0.074 65	1013.36	21.034	0.7071	41.37 ± 0.13
0.098 63	0.886 40	0.014 979	0.100 13	1004.64	21.926	0.6832	41.53 ± 0.13
0.123 22	0.861 84	0.014 933	0.125 09	995.83	22.809	0.6547	41.63 ± 0.13
0.148 16	0.836 80	0.015 042	0.150 42	987.22	23.725	0.6340	41.84 ± 0.13
0.172 21	0.812 87	0.014 925	0.174 82	978.07	24.627	0.6060	42.48 ± 0.14
0.174 17	0.810 76	0.015 068	0.176 84	978.36	24.689	0.6103	41.41 ± 0.14
0.196 38	0.788 72	0.014 891	0.199 35	969.86	25.532	0.5832	41.81 ± 0.14
0.221 67	0.763 19	0.015 142	0.225 08	960.01	26.555	0.5702	44.69 ± 0.14
0.024 52	0.955 36	0.020 120	0.025 03	1049.13	19.421	1.0360	41.02 ± 0.09
0.048 96	0.931 03	0.020 008	0.049 96	1037.56	20.290	0.9861	41.36 ± 0.09
0.073 64	0.906 40	0.019 963	0.075 14	1027.37	21.161	0.9434	41.65 ± 0.09
0.097 84	0.882 15	0.020 011	0.099 84	1018.06	22.026	0.9085	42.03 ± 0.09
0.122 31	0.857 76	0.019 928	0.124 80	1007.95	22.921	0.8694	43.00 ± 0.10
0.147 50	0.832 36	0.020 146	0.150 53	999.08	23.850	0.8447	43.16 ± 0.10
0.171 58	0.808 40	0.020 013	0.175 09	989.35	24.756	0.8084	43.81 ± 0.10
0.024 66	0.950 47	0.024 871	0.025 29	1063.22	19.539	1.2729	41.17 ± 0.07
0.048 55	0.926 31	0.025 137	0.049 80	1052.13	20.403	1.2320	41.69 ± 0.07
0.073 11	0.901 87	0.025 019	0.074 99	1040.81	21.278	1.1758	42.28 ± 0.07
0.097 77	0.877 37	0.024 861	0.100 26	1030.02	22.159	1.1219	42.82 ± 0.08
0.121 62	0.853 25	0.025 130	0.124 75	1020.78	23.037	1.0908	43.44 ± 0.08
0.024 18	0.945 80	0.030 028	0.024 92	1078.76	19.642	1.5287	41.21 ± 0.06
0.049 10	0.921 01	0.029 882	0.050 62	1064.65	20.548	1.4542	42.15 ± 0.06
0.072 48	0.897 49	0.030 027	0.074 73	1054.59	21.377	1.4046	42.30 ± 0.06
0.024 51	0.940 47	0.035 020	0.025 40	1092.57	19.782	1.7703	41.57 ± 0.05
0.048 42	0.916 60	0.034 978	0.050 17	1079.00	20.649	1.6939	42.23 ± 0.05
0.072 12	0.892 94	0.034 942	0.074 73	1067.26	21.496	1.6255	42.68 ± 0.05
0.073 63	0.891 41	0.034 957	0.076 30	1066.59	21.551	1.6221	42.70 ± 0.05
0.023 97	0.935 98	0.040 057	0.024 97	1106.60	19.896	2.0134	41.94 ± 0.04
0.048 01	0.912 00	0.039 991	0.050 00	1092.77	20.760	1.9264	42.33 ± 0.04
0.011 72	0.943 25	0.045 033	0.012 27	1128.16	19.577	2.3003	42.02 ± 0.04
0.024 48	0.930 52	0.045 002	0.025 63	1119.57	20.045	2.2450	42.23 ± 0.04
0.011 66	0.938 17	0.050 170	0.012 27	1142.27	19.708	2.5457	42.21 ± 0.03
0.023 70	0.926 39	0.049 913	0.024 94	1133.46	20.140	2.4783	42.32 ± 0.03
0.011 73	0.933 15	0.055 125	0.012 41	1155.70	19.836	2.7789	42.33 ± 0.03
0.011 63	0.928 39	0.059 980	0.012 38	1168.52	19.962	3.0047	42.52 ± 0.03

Table 4. Densities *d*, Molar Volumes *V*, and Molar Concentrations *c* of Ethanol (1) + Water (2) + Sodium Nitrate (3) Mixtures and Apparent Molar Volumes V_ϕ of Sodium 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}
0.049 46	0.940 50	0.010 047	0.049 96	1005.33	19.970	0.5031	30.85 ± 0.19
0.098 93	0.891 06	0.010 004	0.099 93	987.99	21.722	0.4605	31.78 ± 0.19
0.148 91	0.841 16	0.009 921	0.150 41	970.81	23.545	0.4214	33.25 ± 0.20
0.197 47	0.792 45	0.010 084	0.199 48	954.57	25.384	0.3973	34.55 ± 0.21
0.247 60	0.742 38	0.010 018	0.250 10	938.26	27.320	0.3667	34.08 ± 0.22
0.296 99	0.693 09	0.009 922	0.299 96	923.02	29.265	0.3390	33.37 ± 0.24
0.344 12	0.645 61	0.010 274	0.347 69	910.42	31.148	0.3298	32.37 ± 0.25
0.395 81	0.593 99	0.010 206	0.399 89	897.82	33.195	0.3075	28.7 ± 0.3
0.445 51	0.544 64	0.009 850	0.449 95	885.11	35.221	0.2797	29.9 ± 0.3
0.496 55	0.493 52	0.009 930	0.501 53	874.12	37.308	0.2662	30.1 ± 0.3
0.543 71	0.446 18	0.010 106	0.549 26	865.20	39.235	0.2576	28.6 ± 0.3
0.592 61	0.397 06	0.010 326	0.598 80	856.33	41.261	0.2503	28.2 ± 0.4
0.643 00	0.346 96	0.010 038	0.649 52	847.03	43.360	0.2315	27.7 ± 0.4
0.691 94	0.297 87	0.010 186	0.699 06	838.61	45.444	0.2241	29.4 ± 0.4
0.048 94	0.931 04	0.020 019	0.049 94	1031.99	20.087	0.9966	31.26 ± 0.09
0.098 07	0.881 96	0.019 965	0.100 07	1011.92	21.844	0.9140	32.58 ± 0.10
0.147 41	0.832 66	0.019 932	0.150 40	992.93	23.654	0.8427	33.75 ± 0.10
0.195 33	0.784 67	0.019 993	0.199 32	975.14	25.468	0.7850	34.45 ± 0.10
0.245 03	0.735 03	0.019 936	0.250 02	956.89	27.407	0.7274	35.22 ± 0.11
0.294 15	0.685 71	0.020 140	0.300 20	941.21	29.342	0.6864	34.64 ± 0.12
0.343 17	0.636 77	0.020 059	0.350 19	926.63	31.282	0.6412	33.52 ± 0.13
0.392 22	0.587 78	0.019 993	0.400 23	912.76	33.260	0.6011	33.48 ± 0.14
0.440 09	0.539 92	0.019 989	0.449 07	900.81	35.192	0.5680	32.92 ± 0.15
0.490 10	0.489 86	0.020 040	0.500 13	888.94	37.244	0.5381	33.41 ± 0.16
0.539 23	0.440 67	0.020 095	0.550 29	878.52	39.259	0.5119	33.07 ± 0.17
0.048 55	0.921 31	0.030 141	0.050 06	1058.05	20.223	1.4904	31.80 ± 0.06
0.097 11	0.872 89	0.029 998	0.100 12	1035.53	21.969	1.3654	33.02 ± 0.06
0.146 02	0.824 00	0.029 983	0.150 53	1014.56	23.775	1.2611	34.18 ± 0.07
0.193 77	0.776 22	0.030 006	0.199 76	995.04	25.589	1.1726	34.87 ± 0.07
0.242 44	0.727 50	0.030 068	0.249 95	976.06	27.489	1.0938	35.35 ± 0.07
0.291 16	0.678 74	0.030 097	0.300 20	958.81	29.412	1.0233	35.16 ± 0.08
0.338 93	0.631 16	0.029 912	0.349 38	942.55	31.327	0.9548	35.35 ± 0.08
0.387 50	0.582 51	0.029 990	0.399 48	928.26	33.283	0.9010	35.16 ± 0.09
0.436 43	0.533 30	0.030 263	0.450 05	915.49	35.267	0.8581	34.91 ± 0.10
0.048 06	0.911 92	0.040 021	0.050 06	1082.99	20.355	1.9661	32.16 ± 0.04
0.097 34	0.862 63	0.040 032	0.101 40	1058.64	22.130	1.8089	33.10 ± 0.05
0.145 08	0.814 89	0.040 031	0.151 13	1035.93	23.908	1.6743	34.30 ± 0.05
0.191 86	0.768 24	0.039 903	0.199 83	1015.57	25.671	1.5544	34.50 ± 0.05
0.239 85	0.720 14	0.040 017	0.249 84	995.93	27.537	1.4532	34.63 ± 0.05
0.287 73	0.672 16	0.040 112	0.299 76	977.38	29.441	1.3625	34.83 ± 0.06
0.335 67	0.624 49	0.039 846	0.349 60	960.10	31.353	1.2709	34.74 ± 0.06
0.383 95	0.575 89	0.040 161	0.400 02	944.72	33.319	1.2053	35.03 ± 0.07
0.047 60	0.902 43	0.049 967	0.050 10	1107.54	20.494	2.4381	32.46 ± 0.04
0.094 98	0.855 00	0.050 022	0.099 98	1082.60	22.197	2.2535	33.12 ± 0.04
0.142 65	0.807 39	0.049 957	0.150 15	1057.03	23.996	2.0819	34.58 ± 0.04
0.189 52	0.760 40	0.050 075	0.199 51	1034.34	25.801	1.9408	35.45 ± 0.04
0.237 51	0.712 31	0.050 176	0.250 06	1013.29	27.672	1.8132	35.67 ± 0.04
0.285 26	0.664 70	0.050 033	0.300 29	994.02	29.547	1.6934	35.43 ± 0.04
0.046 95	0.893 00	0.060 043	0.049 95	1132.32	20.626	2.9111	32.62 ± 0.03
0.094 29	0.845 90	0.059 809	0.100 28	1102.48	22.374	2.6731	34.02 ± 0.03
0.141 11	0.798 88	0.060 013	0.150 12	1079.70	24.075	2.4927	34.07 ± 0.03
0.187 32	0.752 78	0.059 892	0.199 26	1056.33	25.828	2.3189	34.39 ± 0.03
0.235 30	0.704 67	0.060 033	0.250 32	1033.68	27.705	2.1669	34.67 ± 0.03
0.046 60	0.883 22	0.070 186	0.050 12	1154.69	20.806	3.3734	33.27 ± 0.02
0.093 34	0.836 74	0.069 926	0.100 36	1124.06	22.524	3.1045	34.33 ± 0.03
0.139 55	0.790 52	0.069 930	0.150 04	1096.78	24.266	2.8818	35.32 ± 0.03
0.185 41	0.744 75	0.069 843	0.199 33	1071.36	26.037	2.6824	36.05 ± 0.03
0.232 37	0.697 61	0.070 027	0.249 86	1048.00	27.887	2.5111	36.44 ± 0.03
0.046 30	0.873 71	0.079 989	0.050 33	1176.98	20.963	3.8158	33.50 ± 0.02
0.091 65	0.828 56	0.079 788	0.099 60	1146.31	22.621	3.5271	34.30 ± 0.02
0.091 99	0.828 08	0.079 935	0.099 98	1146.25	22.640	3.5308	34.35 ± 0.02
0.138 39	0.781 67	0.079 941	0.150 41	1119.65	24.340	3.2843	34.60 ± 0.02
0.183 58	0.736 42	0.079 996	0.199 55	1092.85	26.101	3.0649	35.39 ± 0.02
0.045 50	0.864 42	0.090 079	0.050 00	1200.64	21.094	4.2704	33.54 ± 0.02
0.091 11	0.818 75	0.090 141	0.100 14	1167.71	22.788	3.9557	34.49 ± 0.02
0.136 43	0.773 60	0.089 971	0.149 92	1137.34	24.504	3.6717	35.37 ± 0.02
0.022 43	0.877 45	0.100 120	0.024 93	1240.23	20.441	4.8981	33.62 ± 0.02
0.044 95	0.854 98	0.100 071	0.049 95	1221.61	21.267	4.7055	33.92 ± 0.02
0.067 36	0.832 64	0.099 997	0.074 85	1204.36	22.089	4.5270	34.29 ± 0.02
0.090 01	0.810 03	0.099 957	0.100 01	1187.72	22.931	4.3589	34.71 ± 0.02
0.112 33	0.787 70	0.099 968	0.124 80	1172.34	23.767	4.2062	35.06 ± 0.02
0.112 30	0.787 51	0.100 184	0.124 81	1171.44	23.797	4.2099	35.33 ± 0.02
0.135 07	0.764 87	0.100 053	0.150 09	1157.00	24.638	4.0608	35.45 ± 0.02
0.022 17	0.868 09	0.109 742	0.024 90	1261.72	20.598	5.3279	33.77 ± 0.01
0.044 34	0.845 63	0.110 033	0.049 82	1243.82	21.410	5.1394	33.99 ± 0.01

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}
0.066 63	0.823 35	0.110 021	0.074 86	1225.66	22.236	4.9478	34.39 ± 0.02
0.088 98	0.801 03	0.109 985	0.099 98	1209.77	23.045	4.7727	34.56 ± 0.02
0.111 17	0.778 87	0.109 957	0.124 90	1195.16	23.846	4.6112	34.60 ± 0.02
0.022 10	0.858 02	0.119 887	0.025 11	1282.79	20.787	5.7673	34.05 ± 0.01
0.043 94	0.836 07	0.119 985	0.049 93	1263.13	21.601	5.5545	34.38 ± 0.01
0.065 55	0.814 37	0.120 073	0.074 50	1245.20	22.404	5.3595	34.73 ± 0.01
0.088 12	0.791 99	0.119 894	0.100 12	1226.90	23.244	5.1580	35.11 ± 0.01
0.021 75	0.848 40	0.129 851	0.025 00	1304.00	20.954	6.1971	34.20 ± 0.01
0.043 39	0.826 51	0.130 098	0.049 88	1284.81	21.752	5.9810	34.42 ± 0.01
0.065 09	0.805 05	0.129 865	0.074 80	1269.22	22.486	5.7753	34.24 ± 0.01
0.021 88	0.838 19	0.139 926	0.025 44	1323.52	21.157	6.6137	34.46 ± 0.01
0.043 17	0.816 95	0.139 883	0.050 19	1302.90	21.948	6.3734	34.74 ± 0.01
0.021 21	0.828 78	0.150 018	0.024 95	1343.71	21.328	7.0338	34.66 ± 0.01

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 04, and the accuracy of salt mole fractions was better than 0.000 01. No ethanol + electrolyte mixtures were prepared because the two salts studied in this work are both not soluble in ethanol.

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 ±0.05 kg·m^{-3}.

Results and Discussion

In Table 1 the densities, d, of the water (2) + potassium nitrate (3) mixtures are reported; in Table 2, we show the densities of the water (2) + sodium nitrate (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) + potassium 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) + sodium nitrate (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

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

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 potassium nitrate calculated at 298.15 K are also shown in Tables 1 and 3, and those of sodium nitrate, 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 equation (1929)

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

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_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:

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

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

From the V_ϕ values of potassium nitrate in water (given in Table 1) and of sodium nitrate in water (given in Table 2), we have calculated the V_ϕ^∞ values. These values can be compared with the experimental values reported in the literature, shown in Tables 5 and 6.

We have found for potassium nitrate that V_ϕ^∞ = 38.28 cm^3·mol^{-1}. This value is very similar to the values reported by Gibson and Kincaid (1937), Zen (1957), Millero and Drost-Hansen (1968), Olofsson (1979), Isono (1984), and Krumgalz et al. (1996). For sodium nitrate, we have found that V_ϕ^∞ = 28.22 cm^3·mol^{-1}. This value is in good agreement with those obtained by Robinson (1937) and Krumgalz et al. (1996).

From the V_ϕ values of potassium 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 0.012 ≤ x'_1 ≤ 0.70. These parameters are given in Table 7. The mean absolute deviation of the apparent molar volume for the potassium nitrate is 0.64 cm^3·mol^{-1}, and the standard deviation is 0.98 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

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

reference	V_ϕ^∞/cm^3·mol^{-1}
this work	38.28
Beattie (1928)	38.1[a]
Palitzsch (1928) and Geffcken (1929)	38.1[a,b]
Jones and Talley (1933)	37.6
Longsworth (1935)	37.98
Gibson and Kincaid (1937)	38.18
Robinson (1937)	38.0
Halasey (1941)	37.77
Owen and Brinkley (1941)	38.0
Fajans and Johnson (1942)	37.8
Zen (1957)	38.2
Dunn (1966)	38.05
Ellis (1968)	38.0
Millero and Drost-Hansen (1968)	38.34
Millero et al. (1977)	38.1[a]
Olofsson (1979)	38.2[a]
Doan and Sangster (1981)	37.7[a]
Isono (1984)	38.3[a]
Woldan (1985)	38.0
Krumgalz et al. (1996)	38.324

[a] Value obtained from density data reported. [b] Referenced in Pietsch (1936).

Table 6. Apparent Molar Volume of Sodium Nitrate in Water at Infinite Dilution, at 298.15 K

reference	V_ϕ^∞/cm^3·mol^{-1}
this work	28.22
Beattie (1928)	27.9[a,c]
Manchot (1924)	27.9[a,b]
Gucker (1934)	27.48[d]
Pearce and Hopson (1937)	27.5[a,c]
Robinson (1937)	28.0
Drucker (1941)	27.6[a]
Fajans and Johnson (1942)	27.7
Gellings (1956)	27.4[a]
Zen (1957)	27.8
Volova and Egorov (1960)	27.6[a]
Janz et al. (1970)	27.71
Millero et al. (1977)	27.9[a]
Doan and Sangster (1981)	28.6[a]
Isono (1984)	27.2[a]
Krumgalz et al. (1996)	28.007

[a] Value obtained from density data reported. [b] Referenced in Meyer (1928). [c] Referenced in Meyer (1966). [d] Referenced in Millero (1972).

Table 7. Parameters of Eqs 3 and 4

	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
	Ethanol + Water + Potassium Nitrate System				
b_ν	40.359	−77.254	610.51	−1208.9	218.1
c_ν	1.362	24.991	432.28	−3977.3	6961.9
	Ethanol + Water + Sodium Nitrate System				
b_ν	25.113	88.051	−276.28	194.8	−70.1
c_ν	3.554	−30.296	113.14	−133.2	278.3

ethanol + water + potassium nitrate solutions. The mean absolute deviation of molar volume is 0.006 cm^3·mol^{-1}, and the corresponding standard deviation is 0.009 cm^3·mol^{-1}. The mean absolute deviation of the density is 0.23 kg·m^{-3}, and the standard deviation is 0.33 kg·m^{-3}.

From the V_ϕ values of sodium nitrate in ethanol + water system, we have found the values of b_ν and c_ν in the range $0.025 \leq x'_1 \leq 0.70$. These parameters are given also in Table 7. The mean absolute deviation of the apparent molar volume for the sodium nitrate is 0.31 cm^3·mol^{-1}, and the standard deviation is 0.47 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 + sodium nitrate solutions. The mean absolute deviation of molar volume is 0.014 cm^3·mol^{-1}, and the corresponding standard deviation is 0.020 cm^3·mol^{-1}. The mean absolute deviation of the density is 0.61 kg·m^{-3}, and the standard deviation is 0.89 kg·m^{-3}.

Therefore, the apparent molar volumes of potassium nitrate and sodium nitrate 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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