

Thermodynamic Properties of Aqueous Electrolyte Solutions.[†] 2. Vapor Pressure of Aqueous Solutions of NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CsBr, CsI, MgCl₂, CaCl₂, CaBr₂, CaI₂, SrCl₂, SrBr₂, SrI₂, BaCl₂, and BaBr₂

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A differential static method was used for the measurement of vapor pressures of aqueous solutions of NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CsBr, CsI, MgCl₂, CaCl₂, CaBr₂, CaI₂, SrCl₂, SrBr₂, SrI₂, BaCl₂, and BaBr₂ from 0.5 to 8.6 *m* and in the temperature range of 303.15–343.15 K. The experimental data for the binary solutions were fitted to the Antoine type of equation, $\log [P \text{ (kPa)}] = A(m) + B(m)/[T \text{ (K)}] + C(m)/[T \text{ (K)}]^2$, where *A*, *B*, and *C* are constants and are concentration dependent. Vapor pressure data were used to calculate activity and osmotic coefficients in the temperature range studied for understanding the nonideal behavior of these solutions.

Introduction

The thermodynamic properties of aqueous electrolyte solutions have been under investigation for many years. Extensive data exist for a wide variety of aqueous electrolytes at 298.15 K. A need for thermodynamic data at temperatures above 298.15 K has been felt in recent years, owing mainly to the interest in desalination processes and absorption heat pumps. Several electrolytes have been studied by different investigators at temperatures between 373.15 and 573.15 K. However, very few precise data are available for aqueous electrolytes in the range 303.15–373.15 K.

In continuation of the recent publication (1), exhaustive study has been undertaken in this laboratory on the measurements of vapor pressures of aqueous solutions of NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CsBr, CsI, MgCl₂, CaCl₂, CaBr₂, CaI₂, SrCl₂, SrBr₂, SrI₂, BaCl₂, and BaBr₂ with high precision in the temperature range 303.15–343.15 K for various concentrations. These results were fitted to an Antoine type of equation. The experimental data may be used to correlate the local composition theory on single-solute aqueous solutions up to very high concentration (up to 20 *m*), as well as over a range of temperatures (2, 3). The activity and osmotic coefficients have been also calculated from the present data.

Experimental Section

Apparatus and Procedure. The differential static method has been used for the measurements of vapor pressures, which involves the difference between the vapor pressures of solution and pure water. The experimental method used and the procedure followed were described in a previous publication (1). The necessity of removing the last traces of air in all vapor pressure measurements is well-known. For this purpose, the procedure adopted was to freeze the liquids in both the bulbs by dipping them in liquid nitrogen. The bulbs were then evac-

uated. The procedure was repeated until further evacuation gave no lowering of the vapor pressure. The temperature of water thermostat was controlled to within ± 0.002 °C and was measured with the help of a quartz thermometer (Hewlett Packard, Model 2804A). The differences in the manometer levels were measured with a cathetometer that could read down to 0.01 mm. The data on vapor pressures of water were obtained from the literature (4).

Materials. All the salts used were of analytical reagent grade and anhydrous with reported purities of +99%. NaBr (Aldrich), NaI and KI (E. Merck, Darmstadt), KCl and KBr (Guaranteed reagent grade from Sarabhai Chemicals Co.), CsCl (Lobachemie Industrial Co.), RbCl (Fluka), CsBr and CsI (SAS Chemicals), MgCl₂ and CaCl₂ (Fluka), CaBr₂, CaI₂, and BaBr₂ (Fisons, Philadelphia) SrCl₂, SrBr₂, SrI₂, and BaCl₂ (John Baker Inc., Colorado). All salts were dried in a vacuum oven at 120 °C for several days and used without further purification. Stock solutions were prepared by using double-distilled, but previously deionized, water throughout the experimental work. The concentrations were determined by density measurement using a vibrating reed densimeter from Anton Paar Co., Ltd. (DMA 60/602). The reproducibility of the concentration measurements was within 0.35%.

Results and Discussion

Measurements on vapor pressures were made in the temperature range 303.15–343.15 K and concentration range 1.0–8.6 *m* with the binary systems NaBr–H₂O, NaI–H₂O, KCl–H₂O, KBr–H₂O, KI–H₂O, RbCl–H₂O, CsCl–H₂O, CsBr–H₂O, CsI–H₂O, MgCl₂–H₂O, CaCl₂–H₂O, CaBr₂–H₂O, CaI₂–H₂O, SrCl₂–H₂O, SrBr₂–H₂O, SrI₂–H₂O, BaCl₂–H₂O, and BaBr₂–H₂O. The data are summarized in Table I. These data may be correlated to the Antoine type of equation

$$\log [P \text{ (kPa)}] = A(m) + B(m)/[T \text{ (K)}] + C(m)/[T \text{ (K)}]^2 \quad (1)$$

where the parameters *A*, *B*, and *C* are the cubic functions of concentration, *m*, of the electrolyte and are calculated from the relations

$$A(m) = A_0 + A_1m + A_2m^2 + A_3m^3 \quad (2)$$

$$B(m) = B_0 + B_1m + B_2m^2 + B_3m^3 \quad (3)$$

$$C(m) = C_0 + C_1m + C_2m^2 + C_3m^3 \quad (4)$$

where the parameters *A*₀–*A*₃, *B*₀–*B*₃, and *C*₀–*C*₃ were determined from the experimental vapor pressure data by the least-squares method. The calculated vapor pressures from eqs 1–4 were in good agreement with the experimental results for all the solutions, and the average deviation was within 1.0%. Table II summarizes the best-fit parameters in eqs 2–4.

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Table I. Vapor Pressures (*P*) of Aqueous Solutions

<i>m</i>	<i>P</i> at various <i>T</i> , kPa					<i>m</i>	<i>P</i> at various <i>T</i> , kPa				
	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K		303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
						NaBr					
2.003	3.94	6.85	11.45	18.49	28.92	4.989	3.38	5.87	9.78	15.75	24.62
2.994	3.73	6.50	10.89	17.61	27.56	5.801	3.20	5.55	9.27	14.95	23.34
4.012	3.55	6.18	10.32	16.67	26.06	7.981	2.60	4.59	7.78	12.69	20.15
						NaI					
1.004	4.10	7.13	11.92	19.25	30.10	3.958	3.50	6.08	10.16	16.43	25.72
1.673	3.99	6.93	11.58	18.71	29.25	5.073	3.24	5.63	9.40	15.19	23.79
2.158	3.89	6.77	11.31	18.25	28.65	6.693	2.84	4.95	8.26	13.35	20.91
3.303	3.65	6.34	10.59	17.12	26.83	8.398	2.46	4.28	7.16	11.57	18.06
						KCl					
1.275	4.10	7.13	11.89	19.21	30.13	2.917	3.88	6.71	11.23	18.12	28.41
2.010	3.99	6.92	11.58	18.69	29.33	3.687	3.80	6.56	10.93	17.60	27.57
2.555	3.93	6.80	11.36	18.32	28.71	4.286	3.68	6.37	10.63	17.18	26.97
						KBr					
1.255	4.04	7.05	11.81	19.08	29.92	3.021	3.82	6.62	11.08	17.90	28.10
1.608	4.01	6.98	11.67	18.86	29.56	3.810	3.71	6.42	10.75	17.36	27.29
2.220	3.93	6.82	11.43	18.45	28.94	4.349	3.53	6.13	10.32	16.78	26.47
						KI					
1.006	4.11	7.17	12.01	19.36	30.22	3.027	3.89	6.71	11.12	17.89	27.94
1.523	4.07	7.06	11.80	19.02	29.67	4.059	3.73	6.43	10.65	17.14	26.74
2.003	4.01	6.96	11.59	18.67	29.18	4.747	3.57	6.21	10.25	16.63	25.90
2.351	3.97	6.86	11.44	18.42	28.78	5.648	3.42	5.95	9.87	15.86	24.75
						RbCl					
1.493	4.04	7.03	11.76	19.00	29.73	4.463	3.62	6.32	10.59	17.09	26.67
2.968	3.83	6.67	11.17	18.02	28.19	5.966	3.37	5.92	9.96	16.08	25.11
3.550	3.74	6.54	10.94	17.66	27.63	6.949	3.15	5.58	9.41	15.25	23.82
						CsCl					
1.774	3.95	6.88	11.55	18.65	29.26	5.492	3.53	6.13	10.19	16.42	25.58
2.471	3.85	6.72	11.30	18.27	28.66	6.444	3.41	5.91	9.84	15.83	24.63
3.522	3.75	6.53	10.92	17.65	27.58	7.435	3.24	5.66	9.41	15.14	23.57
4.402	3.66	6.35	10.63	17.12	26.72	8.590	2.91	5.18	8.80	14.27	22.37
						CsBr					
1.570	4.02	7.00	11.75	19.01	29.62	3.485	3.83	6.62	11.03	17.84	27.85
2.244	3.95	6.86	11.47	18.54	28.98	4.320	3.75	6.48	10.77	17.35	27.09
2.768	3.91	6.77	11.30	18.23	28.52	5.888	3.59	6.22	10.32	16.57	25.88
						CsI					
1.345	4.08	7.07	11.82	19.12	29.86	2.014	3.99	6.91	11.56	18.67	29.25
1.546	4.05	7.01	11.73	18.98	29.68	2.595	3.87	6.80	11.35	18.33	28.62
1.799	4.02	6.95	11.62	18.79	29.39						
						MgCl ₂					
1.047	3.98	6.94	11.63	18.80	29.45	3.167	2.98	5.22	8.81	14.32	22.51
1.303	3.85	6.74	11.31	18.35	28.80	3.737	2.74	4.80	8.07	13.08	20.59
2.006	3.60	6.29	10.57	17.17	26.91	4.343	2.32	4.09	6.93	11.33	17.91
2.449	3.33	5.86	9.87	16.04	25.33	4.801	1.99	3.52	6.04	9.93	15.77
						CaCl ₂					
1.002	3.99	6.94	11.61	18.77	29.39	4.951	2.15	3.82	6.52	10.75	17.18
2.249	3.58	6.22	10.43	16.87	26.46	6.019	1.70	3.06	5.27	8.77	14.15
3.017	3.18	5.55	9.34	15.17	23.89	6.786	1.45	2.63	4.56	7.66	12.41
3.887	2.70	4.74	8.03	13.12	20.77	7.885	1.20	2.20	3.85	6.50	10.61
						CaBr ₂					
1.006	3.95	6.92	11.59	18.74	29.36	3.022	3.03	5.31	8.96	14.59	23.04
1.238	3.87	6.76	11.36	18.37	28.84	3.376	2.83	4.97	8.40	13.69	21.64
1.709	3.70	6.46	10.83	17.54	27.60	3.949	2.51	4.43	7.51	12.26	19.40
2.254	3.44	6.02	10.11	16.48	25.93	4.596	2.17	3.84	6.57	10.75	17.05
						CaI ₂					
1.138	3.94	6.91	11.59	18.72	29.34	2.273	3.58	6.24	10.45	16.88	26.41
1.464	3.84	6.72	11.25	18.20	28.47	2.915	3.22	5.63	9.45	15.32	24.06
1.875	3.69	6.46	10.83	17.50	27.46						
						SrCl ₂					
0.662	4.10	7.13	11.92	19.25	30.09	1.797	3.72	6.49	10.88	17.59	27.61
0.871	4.08	7.08	11.84	19.12	29.82	2.213	3.59	6.26	10.49	16.98	26.64
1.299	3.92	6.87	11.40	18.36	28.87	2.693	3.39	5.91	9.93	16.11	25.28
1.503	3.81	6.65	11.19	18.13	28.44	3.203	3.07	5.41	9.12	14.89	23.48
						SrBr ₂					
0.800	3.97	6.98	11.74	18.99	29.71	1.345	3.88	6.78	11.31	18.27	28.51
1.013	3.95	6.92	11.59	18.76	29.26	1.746	3.73	6.50	10.88	17.55	27.43

Table I (Continued)

P at various T, kPa						P at various T, kPa					
m	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K	m	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
1.996	3.59	6.29	10.50	17.05	26.66	2.656	3.27	5.70	9.59	15.52	24.31
2.395	3.44	6.00	10.04	16.25	25.40	3.340	2.91	5.11	8.58	13.93	21.89
						SrI ₂					
0.970	3.97	6.91	11.57	18.72	29.31	2.370	3.37	5.89	9.89	16.02	25.09
1.264	3.86	6.73	11.29	18.27	28.63	2.933	3.11	5.42	9.08	14.69	22.95
1.534	3.77	6.57	11.00	17.79	27.84	3.517	2.76	4.83	8.10	13.10	20.50
1.960	3.58	6.25	10.49	16.98	26.58	4.156	2.37	4.19	7.08	11.54	18.13
						BaCl ₂					
0.504	4.07	7.15	12.03	19.44	30.44	1.214	3.90	6.85	11.53	18.67	29.27
0.738	4.03	7.07	11.88	19.23	30.10	1.388	3.85	6.77	11.42	18.54	29.05
0.975	3.98	6.97	11.72	18.97	29.68						
						BaBr ₂					
1.001	3.98	6.96	11.69	18.88	29.54	1.888	3.70	6.48	10.85	17.54	27.43
1.265	3.91	6.84	11.47	18.55	28.95	2.245	3.59	6.29	10.54	17.01	26.61
1.445	3.85	6.73	11.31	18.27	28.53	2.503	3.50	6.14	10.26	16.53	25.90
1.706	3.76	6.59	11.05	17.89	27.95	3.398	3.11	5.58	9.23	14.98	25.56

Table II. Parameters in Equations 2-4

KCl + H ₂ O			KBr + H ₂ O			KI + H ₂ O		
A ₀	7.626 0110	6.086 2080	5.486 5980	B ₂	-166.5893	132.1589	127.8404	
A ₂	-0.426 4450	0.999 9371	1.252 8540	B ₃	18.8654	-12.5391	-1.2463	
A ₃	0.208 8903	-0.235 9758	-0.190 7485	C ₀	-27 305.940	-198 207.300	-275 912.900	
B ₀	-0.023 0629	0.024 0659	0.001 5253	C ₁	-68 353.780	90 661.930	141 167.700	
B ₁	-2022.4850	-995.1476	-565.9023	C ₂	32 669.500	-16 890.200	-21 502.850	
B ₂	339.4568	-616.6810	-845.7852	C ₃	-3771.469	1370.040	247.165	
CsCl + H ₂ O			CsBr + H ₂ O			CsI + H ₂ O		
A ₀	8.510 3620	4.023 5550	13.845 3600	B ₂	-206.4201	352.0935	-5659.5240	
A ₁	-1.205 5230	2.447 0970	-13.283 3600	B ₃	16.0836	-23.9989	1185.6090	
A ₂	0.292 7137	-0.547 3995	8.742 4280	C ₀	65 296.600	-425 155.800	610 472.900	
A ₃	-0.022 8582	0.037 5162	-1.830 0890	C ₁	-144 555.900	258 012.000	-1396 017.000	
B ₀	-2599.6630	369.7632	-5994.1790	C ₂	36 297.510	-56 506.730	919 810.900	
B ₁	830.9444	-1595.1460	8583.0890	C ₃	-2827.031	3832.014	-192 615.200	
NaBr + H ₂ O			NaI + H ₂ O			RbCl + H ₂ O		
A ₀	7.208 1640	6.641 8220	7.089 4480	B ₂	-19.9145	63.0511	16.9304	
A ₁	-0.067 5379	0.491 4986	0.020 2094	B ₃	0.8825	-3.2720	0.7410	
A ₂	-0.000 3880	-0.100 8282	-0.030 7190	C ₀	-61 252.4500	-146 462.900	-98 560.310	
A ₃	0.001 0449	0.005 1828	-0.000 6476	C ₁	-30 106.550	51 849.160	307.495	
B ₀	-1782.1310	-1340.4910	-1631.0570	C ₂	6662.861	-10 123.010	-2047.276	
B ₁	106.4015	-323.2146	-14.3337	C ₃	-418.569	525.534	-195.086	
CaCl ₂ + H ₂ O			CaBr ₂ + H ₂ O			CaI ₂ + H ₂ O		
A ₀	7.133 9460	5.061 9340	5.865 7030	B ₂	-10.1648	428.0288	183.7660	
A ₁	0.066 6601	2.306 5260	0.931 1616	B ₃	1.9557	-35.5699	-29.9868	
A ₂	0.017 1253	-0.684 1989	-0.345 4942	C ₀	-101 301.800	-309 687.000	-217 515.900	
A ₃	-0.003 0351	0.057 0572	0.056 9615	C ₁	16 194.170	234 931.300	69 980.930	
B ₀	-1647.3340	-328.2416	-848.7688	C ₂	-640.718	-68 599.570	-17 450.280	
B ₁	-65.8949	-1472.7120	-559.4583	C ₃	-176.317	5633.943	2568.411	
SrCl ₂ + H ₂ O			SrBr ₂ + H ₂ O			SrI ₂ + H ₂ O		
A ₀	7.352 3180	5.312 8390	7.479 4540	B ₂	-407.5421	380.6414	-152.2275	
A ₁	-0.815 0023	1.566 6820	-0.488 4127	B ₃	77.3810	-44.3367	22.7994	
A ₂	0.570 4963	-0.528 8308	0.148 9571	C ₀	-61 019.430	-310 093.800	-41 393.050	
A ₃	-0.109 2873	0.059 7050	-0.024 1059	C ₁	-106 639.700	200 127.700	-82 610.700	
B ₀	-1830.6650	-410.3850	-1938.9650	C ₂	73 013.390	-70 100.460	32 319.110	
B ₁	579.8124	-1121.6660	410.7994	C ₃	-13 895.060	8282.056	-4821.754	
BaCl ₂ + H ₂ O			BaBr ₂ + H ₂ O			MgCl ₂ + H ₂ O		
A ₀	4.980 3270	6.210 0830	6.852 9260	B ₂	1900.9680	212.0607	-7.8757	
A ₁	4.014 0250	0.676 4170	0.163 6174	B ₃	-392.1857	-36.6102	-0.1009	
A ₂	-3.060 8950	-0.411 6864	-0.065 6395	C ₀	-324 645.600	-180 287.900	-99 192.550	
A ₃	0.667 0547	0.070 8084	0.008 6453	C ₁	409 351.600	43 730.630	-23 502.530	
B ₀	-253.9579	-1093.9780	-1545.4780	C ₂	-297 548.100	-25 558.640	10 382.470	
B ₁	-2563.5440	-363.3954	0.7887	C ₃	58 009.080	4354.658	-1127.883	

The activity of water, $a_{\text{H}_2\text{O}}$, was calculated from the equation

$$\ln a_{\text{H}_2\text{O}} = \ln (P/P^\circ) \quad (5)$$

where P and P° are the vapor pressures of the solution and pure water, respectively.

The osmotic coefficients of the electrolyte solutions were calculated from the relation

$$\phi = -1000(\ln a_{\text{H}_2\text{O}})/\nu mM \quad (6)$$

where ν is the number of moles of ions formed from 1 mol of

Table III. Osmotic Coefficients of Aqueous Solutions and Activity Coefficients for Water

<i>m</i>	<i>T</i> = 303.15 K		313.15 K		323.15 K		333.15 K		343.15 K	
	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
NaBr										
2.003	1.02	0.963	1.03	0.962	1.04	0.961	1.03	0.962	1.04	0.961
2.994	1.19	0.927	1.18	0.928	1.16	0.930	1.14	0.932	1.14	0.932
4.012	1.23	0.898	1.23	0.898	1.24	0.897	1.23	0.897	1.24	0.897
4.989	1.26	0.869	1.27	0.867	1.29	0.864	1.31	0.862	1.31	0.861
5.801	1.35	0.834	1.36	0.831	1.37	0.830	1.37	0.829	1.38	0.827
7.981	1.70	0.701	1.65	0.711	1.60	0.721	1.57	0.729	1.52	0.739
NaI										
1.004	0.93	0.984	0.95	0.984	0.96	0.983	0.95	0.984	0.97	0.983
1.673	1.01	0.969	1.04	0.967	1.05	0.967	1.04	0.968	1.05	0.967
2.158	1.11	0.953	1.11	0.953	1.12	0.952	1.13	0.952	1.08	0.955
3.303	1.26	0.912	1.28	0.910	1.29	0.909	1.27	0.911	1.26	0.912
3.958	1.34	0.884	1.36	0.883	1.36	0.882	1.35	0.884	1.35	0.884
5.073	1.47	0.834	1.48	0.833	1.49	0.831	1.48	0.832	1.48	0.833
6.693	1.66	0.751	1.66	0.752	1.66	0.750	1.66	0.751	1.66	0.752
8.398	1.80	0.668	1.80	0.668	1.80	0.668	1.80	0.669	1.80	0.667
KCl										
1.275	0.73	0.989	0.75	0.988	0.81	0.986	0.79	0.987	0.74	0.989
2.010	0.84	0.975	0.89	0.972	0.88	0.972	0.88	0.972	0.84	0.975
2.555	0.82	0.970	0.89	0.964	0.90	0.963	0.91	0.962	0.89	0.963
2.917	0.84	0.963	0.91	0.957	0.90	0.958	0.90	0.957	0.88	0.959
3.687	0.82	0.956	0.89	0.948	0.91	0.945	0.93	0.942	0.92	0.943
4.286	0.92	0.935	0.95	0.930	0.97	0.928	0.96	0.929	0.94	0.932
KBr										
1.255	1.07	0.974	1.01	0.977	0.97	0.979	0.95	0.979	0.91	0.982
1.608	0.96	0.973	0.96	0.973	0.96	0.973	0.94	0.974	0.92	0.976
2.220	0.95	0.964	0.99	0.961	0.96	0.963	0.96	0.963	0.93	0.966
3.021	0.96	0.950	1.00	0.946	0.99	0.947	0.98	0.947	0.95	0.951
3.810	0.97	0.935	1.02	0.930	1.00	0.931	1.00	0.931	0.97	0.936
4.349	1.17	0.898	1.18	0.896	1.14	0.902	1.09	0.908	1.04	0.916
KI										
1.006	0.86	0.987	0.80	0.989	0.75	0.991	0.79	0.990	0.85	0.987
1.523	0.75	0.986	0.81	0.983	0.82	0.982	0.84	0.981	0.90	0.978
2.003	0.77	0.980	0.81	0.977	0.87	0.973	0.90	0.971	0.91	0.970
2.351	0.78	0.976	0.86	0.969	0.89	0.966	0.92	0.964	0.94	0.962
3.027	0.79	0.967	0.87	0.959	0.95	0.950	0.99	0.947	1.00	0.945
4.059	0.88	0.944	0.94	0.935	1.01	0.926	1.03	0.923	1.05	0.921
4.747	1.01	0.914	1.01	0.913	1.08	0.902	1.06	0.906	1.08	0.902
5.648	1.06	0.889	1.06	0.888	1.10	0.881	1.12	0.877	1.13	0.875
RbCl										
1.493	0.90	0.978	0.90	0.978	0.89	0.979	0.88	0.979	0.88	0.979
2.968	0.95	0.952	0.95	0.952	0.93	0.954	0.94	0.953	0.94	0.953
3.550	0.98	0.938	0.94	0.943	0.94	0.943	0.94	0.943	0.94	0.943
4.463	0.98	0.922	0.96	0.925	0.95	0.927	0.95	0.927	0.97	0.924
5.996	1.07	0.880	1.03	0.888	1.00	0.894	1.00	0.894	1.01	0.892
6.949	1.19	0.836	1.12	0.851	1.08	0.858	1.07	0.861	1.07	0.860
CsCl										
1.774	1.11	0.961	1.10	0.962	1.04	0.966	1.03	0.966	0.99	0.969
2.471	1.08	0.948	1.05	0.951	0.99	0.956	0.97	0.958	0.94	0.960
3.522	0.97	0.941	0.96	0.941	0.96	0.941	0.95	0.942	0.96	0.941
4.402	0.93	0.932	0.95	0.929	0.94	0.930	0.96	0.928	0.97	0.925
5.492	0.93	0.915	0.94	0.913	0.97	0.907	0.98	0.906	1.00	0.902
6.444	0.94	0.898	0.96	0.894	0.98	0.890	0.99	0.887	1.01	0.882
7.435	1.00	0.867	0.99	0.870	1.01	0.865	1.02	0.862	1.04	0.857
8.590	1.22	0.793	1.14	0.811	1.09	0.823	1.08	0.827	1.07	0.829
CsBr										
1.570	0.94	0.975	0.93	0.975	0.87	0.979	0.83	0.981	0.90	0.977
2.244	0.88	0.969	0.90	0.967	0.90	0.967	0.89	0.968	0.90	0.967
2.768	0.81	0.968	0.87	0.963	0.88	0.961	0.89	0.961	0.89	0.961
3.485	0.81	0.960	0.87	0.953	0.89	0.950	0.88	0.952	0.90	0.950
4.320	0.79	0.953	0.84	0.946	0.87	0.941	0.89	0.939	0.90	0.937
5.888	0.78	0.937	0.81	0.932	0.84	0.925	0.87	0.920	0.88	0.918
CsI										
1.345	0.79	0.986	0.89	0.981	0.89	0.981	0.85	0.983	0.89	0.981
1.546	0.82	0.982	0.92	0.976	0.91	0.977	0.87	0.979	0.88	0.979
1.799	0.82	0.979	0.93	0.972	0.93	0.972	0.90	0.974	0.91	0.973
2.014	0.84	0.975	0.91	0.970	0.90	0.971	0.89	0.971	0.88	0.972
2.595	0.98	0.955	0.88	0.964	0.89	0.963	0.89	0.963	0.91	0.961

Table III (Continued)

<i>m</i>	<i>T</i> = 303.15 K		313.15 K		323.15 K		333.15 K		343.15 K	
	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
MgCl₂										
1.047	1.12	0.956	1.09	0.958	1.05	0.960	1.02	0.962	1.00	0.963
1.303	1.37	0.929	1.29	0.935	1.24	0.938	1.17	0.943	1.12	0.946
2.006	1.51	0.880	1.47	0.883	1.43	0.888	1.37	0.893	1.35	0.895
2.449	1.83	0.820	1.74	0.829	1.69	0.835	1.64	0.841	1.57	0.848
3.167	2.06	0.743	2.02	0.748	1.97	0.755	1.93	0.760	1.89	0.765
3.737	2.16	0.690	2.13	0.694	2.10	0.698	2.08	0.702	2.05	0.705
4.343	2.57	0.590	2.51	0.598	2.46	0.606	2.41	0.613	2.36	0.620
4.801	2.91	0.510	2.85	0.518	2.75	0.532	2.68	0.542	2.63	0.550
CaCl₂										
1.002	1.12	0.958	1.13	0.957	1.13	0.958	1.10	0.959	1.09	0.960
2.249	1.39	0.879	1.41	0.877	1.39	0.879	1.37	0.881	1.35	0.883
3.017	1.77	0.791	1.75	0.793	1.71	0.798	1.67	0.803	1.63	0.808
3.887	2.15	0.681	2.11	0.687	2.05	0.696	1.99	0.705	1.93	0.713
4.951	2.54	0.552	2.46	0.564	2.39	0.575	2.31	0.588	2.23	0.600
6.019	2.81	0.444	2.71	0.460	2.61	0.473	2.52	0.488	2.43	0.503
6.786	2.93	0.384	2.81	0.400	2.71	0.415	2.61	0.432	2.51	0.447
7.885	2.96	0.323	2.84	0.340	2.73	0.356	2.63	0.373	2.53	0.389
CaBr₂										
1.006	1.30	0.948	1.19	0.955	1.15	0.956	1.12	0.958	1.10	0.959
1.238	1.37	0.933	1.31	0.936	1.24	0.941	1.21	0.943	1.16	0.946
1.709	1.47	0.900	1.44	0.902	1.41	0.905	1.38	0.908	1.32	0.913
2.254	1.71	0.844	1.67	0.849	1.63	0.853	1.55	0.861	1.51	0.866
3.022	2.06	0.754	2.01	0.759	1.96	0.766	1.91	0.772	1.85	0.779
3.376	2.21	0.708	2.17	0.714	2.11	0.722	2.05	0.729	2.00	0.736
3.949	2.45	0.634	2.39	0.643	2.33	0.652	2.27	0.659	2.22	0.667
4.596	2.70	0.554	2.63	0.563	2.54	0.576	2.48	0.584	2.43	0.592
CaI₂										
1.138	1.19	0.948	1.07	0.956	1.02	0.958	1.01	0.959	0.99	0.961
1.464	1.25	0.930	1.19	0.935	1.17	0.936	1.14	0.938	1.15	0.937
1.875	1.37	0.900	1.31	0.905	1.29	0.907	1.28	0.908	1.25	0.911
2.273	1.38	0.879	1.37	0.880	1.35	0.882	1.35	0.882	1.35	0.882
2.915	1.75	0.799	1.72	0.803	1.69	0.806	1.67	0.809	1.65	0.812
SrCl₂										
0.662	0.94	0.979	0.96	0.978	0.97	0.977	0.95	0.978	0.99	0.977
0.871	0.82	0.977	0.88	0.974	0.88	0.975	0.87	0.975	0.94	0.972
1.299	1.12	0.946	1.02	0.953	1.13	0.945	1.16	0.943	1.09	0.948
1.503	1.31	0.923	1.28	0.925	1.21	0.931	1.16	0.935	1.13	0.937
1.797	1.35	0.906	1.32	0.908	1.29	0.910	1.28	0.912	1.25	0.914
2.213	1.39	0.880	1.37	0.882	1.36	0.884	1.33	0.886	1.31	0.889
2.693	1.54	0.838	1.53	0.840	1.49	0.844	1.46	0.848	1.44	0.850
3.203	1.87	0.766	1.79	0.775	1.75	0.782	1.68	0.791	1.63	0.797
SrBr₂										
0.800	1.52	0.950	1.29	0.959	1.15	0.965	1.11	0.967	1.11	0.967
1.013	1.29	0.949	1.18	0.955	1.15	0.956	1.10	0.959	1.16	0.956
1.345	1.22	0.937	1.17	0.941	1.20	0.939	1.19	0.939	1.23	0.937
1.746	1.36	0.907	1.35	0.908	1.33	0.909	1.34	0.909	1.35	0.908
1.996	1.54	0.877	1.48	0.883	1.50	0.881	1.44	0.887	1.45	0.886
2.395	1.62	0.846	1.60	0.848	1.59	0.849	1.57	0.851	1.58	0.850
2.656	1.81	0.808	1.80	0.809	1.76	0.814	1.74	0.816	1.73	0.817
3.340	2.09	0.728	2.04	0.734	2.01	0.737	1.98	0.741	1.96	0.745
SrI₂										
0.970	1.26	0.953	1.26	0.953	1.23	0.954	1.19	0.956	1.17	0.957
1.264	1.37	0.931	1.35	0.933	1.30	0.936	1.27	0.938	1.24	0.939
1.534	1.42	0.914	1.40	0.915	1.39	0.916	1.36	0.918	1.36	0.918
1.960	1.60	0.874	1.57	0.877	1.53	0.880	1.51	0.883	1.50	0.883
2.370	1.79	0.829	1.76	0.832	1.73	0.836	1.70	0.839	1.69	0.839
2.933	1.96	0.772	1.95	0.773	1.94	0.775	1.92	0.776	1.93	0.775
3.517	2.26	0.692	2.23	0.696	2.21	0.698	2.20	0.699	2.20	0.699
4.156	2.59	0.601	2.52	0.611	2.47	0.617	2.43	0.623	2.41	0.625
BaCl₂										
0.504	1.50	0.969	1.16	0.978	0.93	0.984	0.90	0.985	0.87	0.985
0.738	1.27	0.963	1.08	0.971	0.95	0.976	0.88	0.978	0.88	0.979
0.975	1.20	0.955	1.08	0.961	0.98	0.966	0.93	0.969	0.93	0.969
1.214	1.27	0.940	1.14	0.948	1.03	0.955	0.99	0.958	0.96	0.960
1.388	1.29	0.931	1.15	0.940	1.03	0.949	0.96	0.954	0.94	0.955
BaBr₂										
1.001	1.17	0.958	1.08	0.960	1.00	0.964	0.99	0.965	0.99	0.965
1.265	1.19	0.943	1.11	0.948	1.07	0.951	1.04	0.952	1.08	0.950
1.445	1.24	0.932	1.18	0.936	1.12	0.940	1.11	0.941	1.13	0.939

Table III (Continued)

<i>m</i>	<i>T</i> = 303.15 K		313.15 K		323.15 K		333.15 K		343.15 K	
	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
1.706	1.30	0.914	1.23	0.920	1.20	0.923	1.17	0.926	1.18	0.924
1.888	1.34	0.902	1.27	0.908	1.26	0.909	1.25	0.910	1.25	0.910
2.245	1.37	0.881	1.32	0.887	1.30	0.889	1.30	0.888	1.30	0.888
2.503	1.42	0.868	1.36	0.869	1.36	0.869	1.38	0.867	1.37	0.868
3.398	1.60	0.778	1.62	0.788	1.58	0.794	1.55	0.798	1.52	0.802

electrolyte, *m* is the molality of the solution, and *M* is the molecular weight of water. The activity coefficients of water were obtained from

$$\gamma = a_{\text{H}_2\text{O}}/x \quad (7)$$

where *x* is the mole fraction of water. Osmotic coefficients of electrolyte solutions and the activity coefficients of water were calculated from experimental vapor pressure data and are tabulated in Table III. From Table III it may be observed that the activity coefficients of water are always less than unity. This means that these electrolyte solutions exhibit nonideal behavior.

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Glossary

A, *B*, *C* constants of the Antoine equation

*A*₀, *A*₁, parameters in eq 2

*A*₂,

*A*₃

*B*₀, *B*₁, parameters in eq 3

*B*₂,

*B*₃

*C*₀, *C*₁, parameters in eq 4

*C*₂,

*C*₃

m molality of electrolyte, mol/kg

M molecular weight

P vapor pressure, kPa

T temperature, K

ϕ osmotic coefficient

ν number of moles of ions formed from 1 mol of electrolyte

γ activity coefficient of water

Registry No. NaBr, 7647-15-6; NaI, 7681-82-5; KCl, 7447-40-7; KBr, 7758-02-3; KI, 7681-11-0; RbCl, 7791-11-9; CsCl, 7647-17-8; CsBr, 7787-89-1; CsI, 7789-17-5; MgCl₂, 7786-30-3; CaCl₂, 10043-52-4; CaBr₂, 7789-41-5; CaI₂, 10102-66-8; SrCl₂, 10476-85-4; SrBr₂, 10476-81-0; SrI₂, 10476-86-5; BaBr₂, 10553-31-8; BaCl₂, 10361-37-2.

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