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Thermodynamic Properties of Aqueous Electrolyte Solutions.[†] 1. Vapor Pressure of Aqueous Solutions of LiCl, LiBr, and LiI

Kashinath R. Patil, Atri D. Tripathi, Gopal Pathak, and Sushilendra S. Katti*

National Chemical Laboratory, Pune 411008, India

The vapor pressures of aqueous solutions of lithium halides (viz., LiCl, LiBr, LiI) were measured at different concentrations and temperatures from 303.15 to 343.15 K with use of a differential static method. The experimental data were fitted to an Antoine type of equation, log P (kPa) = $A(m) + [B(m)]/T + [C(m)]/T^2$, where A, B, and C are constants and are concentration-dependent. Osmotic and activity coefficients were calculated and compared.

Introduction

Precise vapor pressure data of aqueous electrolyte solutions are required in the chemical industry, in, for example, desalination processes, process design, and performance range of absorption heat pumps.

A literature survey (*1*, *2*) revealed that systematic studies on vapor pressures of alkali and alkaline-earth aqueous salt solutions have not been carried out. Also, data on the thermodynamic activity of water and osmotic coefficients for salt solutions at temperatures other than 25 °C is not available (*3*).

Therefore, a systematic study has been undertaken on the measurements of vapor pressures of aqueous lithium halide solutions with high precision in the temperature range 303.15-343.15 K for various concentrations. These data may be used to optimize the operating conditions of absorption heat pumps and to evaluate new absorbents. The activity coefficients of aqueous solutions were calculated for understanding the nonideal behavior of these aqueous solutions.

Experimental Section

Apparatus. A number of methods for measuring the vapor pressures of aqueous electrolyte solutions were considered for reliability, simplicity, and quickness of measurements. A simple differential static apparatus was designed and constructed to measure the pressure differences between a reference water and aqueous solution of electrolyte each contained in separate vessels (50-mL capacity) at the same temperature. The differential manometer is shown in Figure 1. The sides of mercury manometer B were of 20 mm internal diameter Veridia precision glass tubing. A Teflon stopcock (E) that would withstand an internal pressure was fitted between the two sides of the manometer. The difference in the manometer levels was measured with a cathetometer that could be read to 0.01 mm. The mercury menisci were illuminated behind the manometer by horizontal light beams. The use of a metal screen ensured sharp images of the menisci. The mercury levels were thus read with a precision of ±0.01 mm. The vapor pressures were measured by a mercury manometer at different temperatures. Cathetometer readings were corrected by taking into account the thermal expansion coefficient of mercury. The water thermostat in which the manometer was immersed was controlled down to ±0.002 °C. Temperatures were read with the help of a quartz thermometer (Hewlett-Packard, Model 2804A).

Table I. Vapor Pressures (P, kPa) of Aqueous Solutions

m	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
			LiCl		
3.010	3.68	6.42	10.78	17.47	27.41
4.999	3.19	5.56	9.34	15.13	23.75
5.998	2.89	5.06	8.51	13.82	21.75
7.856	2.34	4.12	6.98	11.40	18.05
10.168	1.72	3.07	5.27	8.70	13.93
12.693	1.20	2.18	3.80	6.37	10.36
15.661	0.80	1.48	2.63	4.48	7.40
18.456	0.58	1.09	1.96	3.37	5.66
			LiBr		
2.000	3.82	6.67	11.21	18.27	28.84
3.494	3.49	6.09	10.22	16.58	26.14
5.092	2.98	5.23	8.82	14.40	22.72
7.026	2.43	4.28	7.20	11.75	18.55
9.192	1.74	3.09	5.27	8.66	13.75
11.318	1.18	2.12	3.64	6.02	9.66
13.777	0.70	1.29	2.26	3.82	6.25
15.971	0.39	0.74	1.33	2.31	3.88
			LiI		
0.800	4.11	7.16	11.98	19.34	30.26
2.508	3.69	6.44	10.82	17.54	27.53
3.798	3.38	5.90	9.90	15.99	25.12
4.987	3.03	5.29	8.88	14.38	22.57
7.493	2.27	3.95	6.61	10.67	16.69
10.126	1.36	2.41	4.06	6.64	10.49

The measurements were carried out with analytical reagent grade compounds of +99.0% purity. LiCl (Mayer and Rothlaender Co.), LiBr (Aldrich), and LiI (Aldrich) were used without further purification. Anhydrous salts were kept in the oven at 120 °C until constant weight was obtained. Then, these salts were evacuated for several hours. All solutions were prepared with double distilled, but previously deionized, water throughout the experimental work. A sample of the same water was used in the reference side of the apparatus. In order to determine the molality of the electrolyte solutions, the density of the sample was measured at 303.15 K with a vibrating-reed densimeter from Anton Paar Co. Ltd. (Model DMA 602/60). The reproducibility of the measurements was within 0.35%.

Experimental Procedure. The data reported were obtained by measuring the differential pressure developed between the solution and pure water. Before each run, mercury was distilled; the apparatus was cleaned with freshly prepared chromic acid and rinsed with deionized water several times and then with distilled acetone. The apparatus was kept under vacuum for several hours. The greatest source of error lies in the presence of air or other gases that were dissolved by the liquid or trapped by the mercury. The evacuation was repeated by freezing with liquid nitrogen and melting under vacuum until further evacuation gave no lowering of the vapor pressure. Measurements were made at a given concentration over the entire temperature range 303.15-343.15 K with an interval of at least 2 h for each temperature. The data on the vapor pressure of water was obtained from literature (*4*).

Results and Discussion

Data on vapor pressures of aqueous solutions of LiCl, LiBr, and LiI at different temperatures are given in Table I. Figure

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[*] To whom all correspondence should be addressed.

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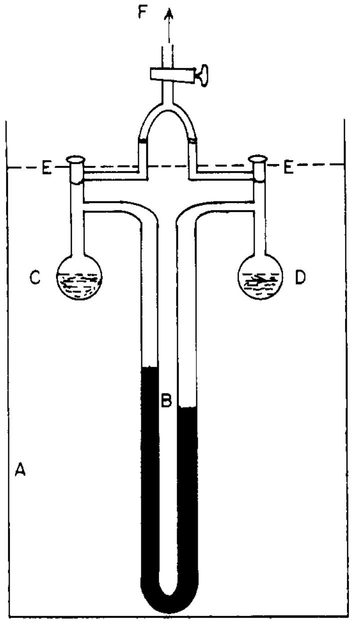

Figure 1. Vapor pressure apparatus: (A) water bath, (B) mercury manometer, (C) solution cell, (D) water cell, (E) Teflon stopcock, (F) lead to vacuum pump.

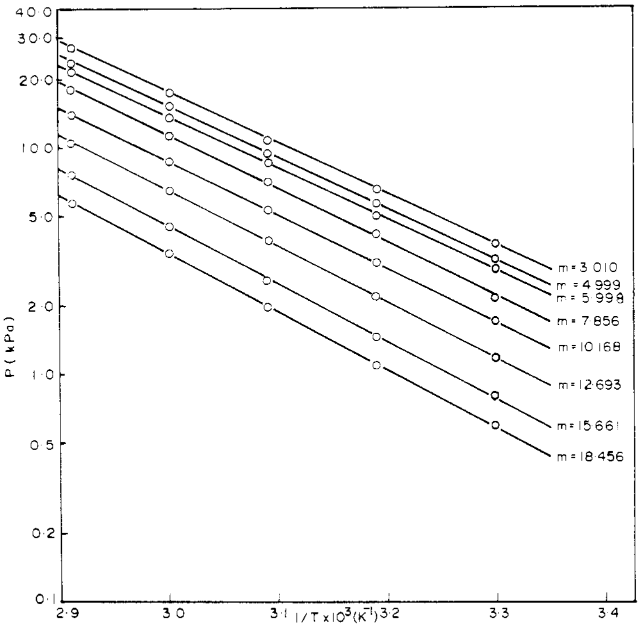

Figure 2. Relation between log P and $1/T$ for LiCl aqueous solution: (O) from experiment; (—) from eq 1.

2 represents the typical plot between log P vs $1/T$ for LiCl solution, which showed a very nearly linear curve. This can be attributed to the fact that experimental data may be correlated to the Antoine type of equation (*5*).

$$\log P\,(\text{kPa}) = A(m) + \frac{B(m)}{T\,(\text{K})} + \frac{C(m)}{T^2\,(\text{K})} \tag{1}$$

where the parameters A, B, and C are the cubic functions of molality, m, of the electrolyte. These parameters were calculated from the relations

$$A(m) = A_0 + A_1 m + A_2 m^2 + A_3 m^3 \tag{2}$$

$$B(m) = B_0 + B_1 m + B_2 m^2 + B_3 m^3 \tag{3}$$

$$C(m) = C_0 + C_1 m + C_2 m^2 + C_3 m^3 \tag{4}$$

Table II. Parameters in Equations 2–4

	LiCl + H_2O	LiBr + H_2O	LiI + H_2O
A_0	7.323 3550	8.064 8240	6.897 9820
A_1	−0.062 3661	−0.103 6791	0.153 5761
A_2	0.006 1613	−0.012 3511	−0.038 0009
A_3	−0.000 1042	0.000 9890	0.001 9389
B_0	−1718.1570	−2235.3810	−1516.9730
B_1	8.2255	62.4534	−84.7567
B_2	−2.2131	5.2484	17.1456
B_3	0.0246	−0.5253	−0.8985
C_0	−97 575.680	−6478.216	−115 482.300
C_1	3839.979	−10 555.860	8837.845
C_2	−421.429	−724.251	−1563.090
C_3	16.731	66.490	62.356

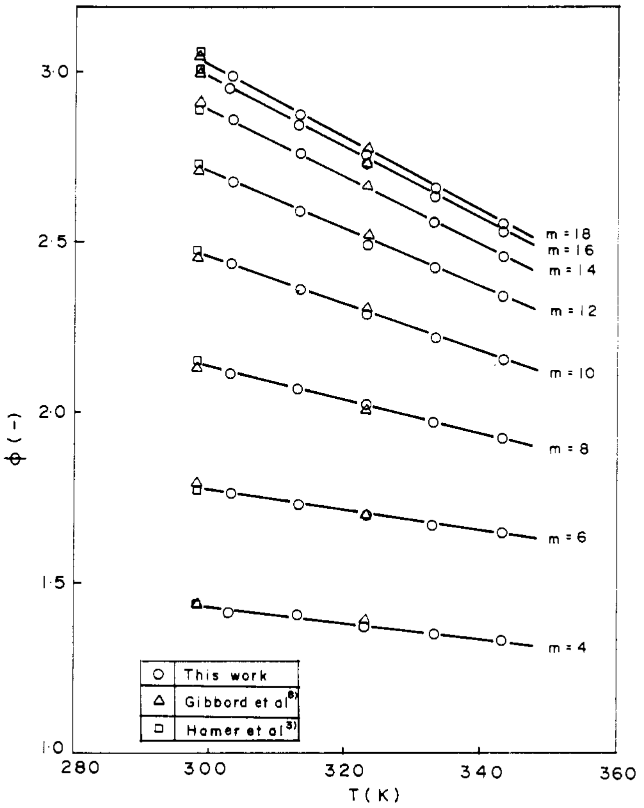

Figure 3. Osmotic coefficient as a function of temperature for LiCl aqueous solution.

where 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. Table II summarizes the best fit parameters in eqs 2–4. The calculated vapor pressures were in good agreement with the experimental results for all the solutions, and the average deviation was within 1.0%.

The osmotic coefficients of the solutions were calculated from the relation

$$\phi = -1000 \ln (a_{H_2O}/\nu\,(mM)) \tag{5}$$

where a_{H_2O} is the activity of water, ν is the number of moles of ions formed from 1 mol of electrolyte, m is the molality of solution, M is the molecular weight of water. The activity of water, a_{H_2O} was calculated from the equation (*6*)

$$\ln a_{H_2O} = \ln \left(\frac{P}{P^\circ}\right) + B_T\left(\frac{P - P^\circ}{RT}\right) \tag{6}$$

where P and P° are the vapor pressures of the solution and pure water, respectively; B_T is the second virial coefficient for water vapor, is a function of temperature, and was evaluated from literature (*7*); R is the gas constant, and T is the absolute temperature.

Table III. Osmotic Coefficients (ϕ) of Aqueous Solutions and Activity Coefficients (γ) for Water

	T = 303.15 K		T = 313.15 K		T = 323.15 K		T = 333.15 K		T = 343.15 K	
m	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
					LiCl					
3.010	1.3039	0.9152	1.2818	0.9174	1.2419	0.9214	1.2043	0.9252	1.1774	0.9279
4.999	1.5773	0.8205	1.5686	0.8218	1.5414	0.8258	1.5201	0.8290	1.5002	0.8320
5.998	1.7710	0.7557	1.7425	0.7604	1.7142	0.7650	1.6844	0.7700	1.6552	0.7748
7.856	2.0971	0.6305	2.0553	0.6380	2.0073	0.6467	1.9639	0.6547	1.9195	0.6630
10.168	2.4598	0.4805	2.3899	0.4929	2.3166	0.5064	2.2532	0.5183	2.1877	0.5309
12.693	2.7572	0.3482	2.6624	0.3636	2.5699	0.3793	2.4853	0.3943	2.3982	0.4103
15.661	2.9529	0.2423	2.8437	0.2577	2.7344	0.2741	2.6372	0.2895	2.5388	0.3060
18.456	2.9892	0.1826	2.8728	0.1972	2.7622	0.2123	2.6655	0.2264	2.5568	0.2434
					LiBr					
2.000	1.4451	0.9336	1.4002	0.9366	1.3280	0.9415	1.1939	0.9506	1.0708	0.9591
3.494	1.5437	0.8752	1.5225	0.8775	1.4923	0.8809	1.4510	0.8855	1.3889	0.8924
5.092	1.9191	0.7677	1.8728	0.7743	1.8247	0.7811	1.7609	0.7903	1.7130	0.7973
7.026	2.1959	0.6462	2.1478	0.6541	2.1221	0.6583	2.0768	0.6659	2.0388	0.6724
9.192	2.6861	0.4789	2.6241	0.4888	2.5625	0.4988	2.5064	0.5082	2.4592	0.5162
11.318	3.1333	0.3355	3.0542	0.3465	2.9874	0.3561	2.9256	0.3651	2.8607	0.3749
13.777	3.6256	0.2064	3.5093	0.2187	3.4315	0.2273	3.3186	0.2404	3.2257	0.2717
15.971	4.1438	0.1186	3.9926	0.1294	3.8655	0.1393	3.7361	0.1500	3.6101	0.1613
					LiI					
0.800	1.0784	0.9834	1.0472	0.9842	1.0234	0.9849	1.0199	0.9850	1.0207	0.9850
2.508	1.5349	0.9098	1.5040	0.9124	1.4496	0.9169	1.4013	0.9209	1.3650	0.9239
3.798	1.6538	0.8520	1.6318	0.8546	1.6046	0.8578	1.5985	0.8585	1.5669	0.8622
4.987	1.8671	0.7792	1.8489	0.7818	1.8255	0.7851	1.8057	0.7879	1.7858	0.7907
7.493	2.3111	0.6082	2.3107	0.6082	2.3059	0.6090	2.3035	0.6094	2.3015	0.6097
10.126	3.1132	0.3797	3.0626	0.3868	3.0401	0.3900	3.0018	0.3955	2.9720	0.3998

The activity coefficient of water was calculated by the following relation

$$\gamma = a_{H_2O}/x \qquad (7)$$

where a_{H_2O} is the activity of water and x is the mole fraction of water.

Osmotic coefficients of electrolyte solutions and activity coefficients of water calculated from the vapor pressure data are presented in Table III. Figure 3 shows values of ϕ obtained from the curve ϕ vs $1/T$ agreed well with the literature values (*3*, *8*).

It may be observed from Table III that activity coefficients of the solvent deviate from unity by a small amount whereas the osmotic coefficients of the salt solution deviate by several percent. These deviations indicate the nonideal behavior of these electrolyte solutions. The higher the deviations the more ionic the interactions. The activity coefficient of water decreased from LiCl to LiI; therefore, aqueous solutions of LiI have higher negative deviations from Raoult's law than LiBr and LiCl. Therefore, the ion power to hydrate water increases as Cl^-, Br^-, and I^-.

Glossary

A, B, C	constants of the Antoine equation
A_0, A_1, A_2, A_3	parameters in eq 2
B_0, B_1, B_2, B_3	parameters in eq 3
C_0, C_1, C_2, C_3	parameters in eq 4
B_T	second virial coefficient for water vapor, cm^3/mol
m	molality of electrolyte, mol/kg
M	molecular weight
P	vapor pressure, kPa
R	gas constant, cm^3·Pa/(mol·K)
T	temperature, K
ϕ	osmotic coefficient
ν	number of moles of ions formed from 1 mol of electrolyte
γ	activity coefficient of water

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