

Glossary

A_j	coefficients in eq 1
C_p	molar isobaric heat capacity, $\text{J mol}^{-1} \text{K}^{-1}$
G	molar Gibbs energy, J mol^{-1}
H	molar enthalpy, J mol^{-1}
n_D	refractive index
p	pressure, Pa
T	temperature, K
V	molar volume, $\text{cm}^3 \text{mol}^{-1}$
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
Z	any quantity Z (V , H , C_p , or G) divided by corresponding unit

Greek Letters

δ	maximum deviation in units of fitted data, eq 3
ρ	density, g cm^{-3}
σ	standard deviation in units of fitted data, eq 2

Subscript

calc	calculated value
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Superscript

E	excess quantity
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Registry No. Chlorobenzene, 108-90-7; 2-chloro-2-methylpropane, 507-20-0; 2,2,4-trimethylpentane, 540-84-1.

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Thermodynamic Properties of Aqueous Electrolyte Solutions. 3. Vapor Pressure of Aqueous Solutions of LiNO_3 , $\text{LiCl} + \text{LiNO}_3$, and $\text{LiBr} + \text{LiNO}_3$ [†]

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Vapor pressures were determined for binary and ternary mixtures of $\text{H}_2\text{O}-\text{LiNO}_3$, $\text{H}_2\text{O}-\text{LiCl} + \text{LiNO}_3$ (salt mole ratio 0.88:0.12), and $\text{H}_2\text{O}-\text{LiBr} + \text{LiNO}_3$ (salt mole ratio 0.70:0.30) at 303.15–373.15 K and in the range of concentration from 9.874 to 60.687 wt %. The vapor pressure measurements were made by the differential static method. Experimental data were fitted to the Antoine type of equation $\log(P/\text{kPa}) = A(X) + B(X)/(T/\text{K}^{-1}) + C(X)/(T^2/\text{K}^{-2})$, where A , B , and C are concentration-dependent parameters. The calculated values from these equations were in good agreement with the experimental data.

Introduction

In continuation with our earlier work (1–3), precise measurements of vapor pressures of aqueous electrolyte solutions of LiNO_3 , $\text{LiCl} + \text{LiNO}_3$, and $\text{LiBr} + \text{LiNO}_3$, over the concentration range 9.874–60.687 wt % and at temperatures between 303.15 and 373.15 K have been undertaken. The experimental vapor pressure data for the aqueous electrolyte solutions were fitted to the Antoine type of equation. These data may be useful for calculating the theoretical coefficient of performance and hence the design of absorption refrigerating machines,

absorption heat pumps, and absorption heat transformers. Iyoki and co-workers (4, 5) studied the vapor pressures of aqueous solutions of $\text{LiBr} + \text{ZnCl}_2 + \text{CaBr}_2$ and $\text{LiBr} + \text{LiI}$ at 280.85–383.05 K and in the range of concentrations 10–64.5 wt %. Also they discussed the use of the above mixtures in the absorption heat pumps. A literature survey revealed that vapor pressure data are not available for these systems except a few data for aqueous LiNO_3 (6, 7).

Experimental Section

Materials. Stock solutions were prepared from the following anhydrous analytical reagents (purity): LiCl (+99%) (Hans Heinrich-Hutte, GmbH, Germany), LiBr (+99%) (Aldrich Chemical Co.), and LiNO_3 (>98%) (Fluka, Switzerland).

All salts were dried in a vacuum oven at 120 °C for several days. These salts were dissolved in distilled but previously deionized water, and if necessary the solutions were filtered. The concentration of solution was changed by addition of water. The densities (ρ) were determined at 303.15 K for different concentrations (w) by the use of a densimeter from Anton Paar Co., Ltd. (DMA 60/602). The densities were reproducible to $\pm 2 \times 10^{-5} \text{ g cm}^{-3}$. The $\rho-w$ data of each system were fitted to a polynomial:

$$w/(\text{wt } \%) = A + B(\rho/(\text{g cm}^{-3})) + C(\rho^2/(\text{g}^2 \text{cm}^{-6})) + D(\rho^3/(\text{g}^3 \text{cm}^{-9})) \quad (1)$$

The fitting constants A , B , C , and D along with the average percent deviations are given in Table I for all the systems at

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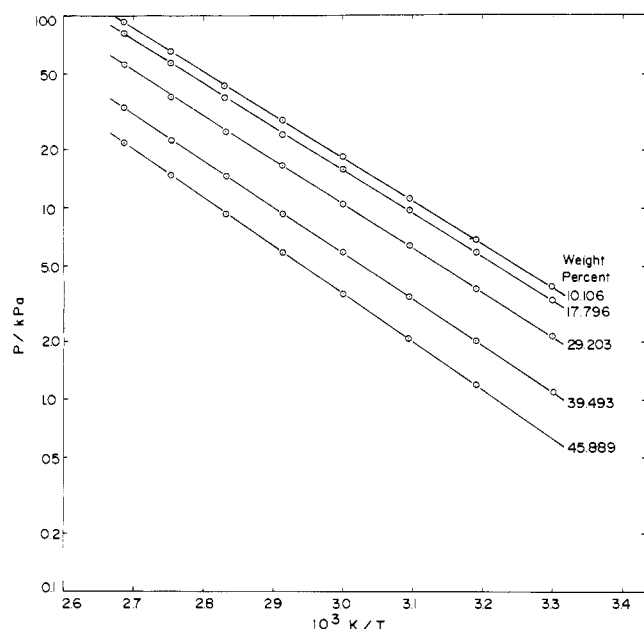
Table I. Constants in Equation 1 at 303.15 K

$$W = A + B\rho + C\rho^2 + D\rho^3$$

compd	A	B	C	D	av dev/%
LiNO ₃	-197.899 20	180.101 60	68.937 60	-50.103 43	0.10
LiCl + LiNO ₃	-307.997 20	436.147 00	-132.476 80	4.780 50	0.06
LiBr + LiNO ₃	-244.737 00	367.088 70	-136.566 70	16.991 02	0.07

Table II. Vapor Pressures P of Aqueous Electrolyte Solutions for Various Concentration w /(wt %) of Salt

w /(wt %)	p /kPa at T /K							
	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
H ₂ O-LiNO ₃								
9.874	4.06	7.05	11.70	18.88	29.57	45.08	66.77	97.27
14.840	3.85	6.70	11.14	18.01	28.18	42.88	63.75	93.47
20.275	3.71	6.40	10.64	17.09	26.60	40.57	60.42	87.10
27.647	3.29	5.67	9.50	15.30	24.03	36.64	54.40	78.70
30.225	3.12	5.40	9.03	14.55	22.82	34.81	51.86	75.06
39.980	2.54	4.43	7.39	11.94	18.76	28.65	42.75	62.34
49.500	1.81	3.15	5.36	8.63	13.68	20.89	31.61	46.77
54.840		2.55	4.33	7.15	11.38	17.71	26.72	39.99
H ₂ O-LiCl + LiNO ₃								
10.106	3.89	6.73	11.23	18.00	28.18	42.93	63.88	92.89
17.796	3.32	5.77	9.67	15.65	24.57	37.48	55.74	80.98
20.013	3.08	5.39	9.08	14.71	22.90	35.31	52.48	76.56
29.203	2.11	3.72	6.29	10.30	16.35	25.24	37.99	55.86
39.493	1.10	1.98	3.42	5.70	9.23	14.52	22.27	33.35
45.889		1.19	2.09	3.61	5.86	9.29	14.45	22.08
H ₂ O-LiBr + LiNO ₃								
24.060	3.44	6.02	10.10	16.49	25.98	39.83	59.72	87.40
31.123	3.16	5.47	9.20	15.07	23.48	35.87	53.52	77.90
37.990	2.66	4.71	7.93	12.94	20.47	31.43	47.30	69.42
45.257	2.24	3.96	6.69	10.95	17.38	26.78	40.42	59.60
53.177	1.63	2.86	4.88	8.09	12.98	19.95	30.50	45.08
60.687		1.65	2.88	4.81	7.69	12.33	18.71	28.31

Figure 1. Relation between $\log P$ and $1/T$ for the system H₂O-LiCl + LiNO₃: O, experimental; —, calculated from eqs 2-5.

303.15 K. Thus, by measuring the density of the salt solution and using eq 1, the concentration can be calculated.

Apparatus and Procedure. The differential static method was used for the measurement of vapor pressures of these aqueous electrolyte solutions. The details of the method have been described elsewhere (1, 3). In this method, samples in the two bulbs connected to the ends of a manometer are held in a silicone oil thermostat which was controlled to ± 0.005 °C at any desired temperature between 303.15 and 373.15 K. The

equilibrium temperatures were measured using a quartz thermometer (Hewlett Packard, model 2804A). The most important precaution in this work was to degas the samples properly before each run and to avoid any condensate drops in any portion of the apparatus. The difference in heights of the mercury menisci in the manometer limbs was measured by means of a cathetometer fitted with a vernier scale, capable of readings to 0.01 mm.

Results and Discussion

The vapor pressures of the H₂O-LiNO₃, H₂O-LiCl + LiNO₃, and H₂O-LiBr + LiNO₃ systems were measured from 303.15 to 373.15 K and in the range of concentrations from 9.874 to 60.687 wt %. The vapor pressure for pure water was taken from the literature (6). The experimental results of these systems at various temperatures and concentrations are given in Table II. Figure 1 shows the relationship between $\log P$ and $1/T$ at various concentrations for a typical system, H₂O-LiCl + LiNO₃. In Figure 1, the $\log P$ vs $1/T$ relationship for various concentrations over the temperatures and pressures measured is linear. The vapor pressure data of the above systems were fitted to Antoine type of equation with parameters A , B , and C which are concentration dependent

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

$$A(w) = A_0 + A_1w + A_2w^2 + A_3w^3 \quad (3)$$

$$B(w) = B_0 + B_1w + B_2w^2 + B_3w^3 \quad (4)$$

$$C(w) = C_0 + C_1w + C_2w^2 + C_3w^3 \quad (5)$$

where the parameters A_i , B_i , and C_i were determined from the experimental vapor pressure data by the least-squares method. Parameters in eqs 3-5 are given in Table III. The calculated vapor pressures were in good agreement with the experimental

Table III. Parameters in Equations 3-5^a

	LiNO ₃ -H ₂ O (9.874-54.840 wt %)	LiCl + LiNO ₃ -H ₂ O (10.106-45.889 wt %)	LiBr + LiNO ₃ -H ₂ O (24.060-60.687 wt %)
A ₀	7.4226540	9.0528890	12.2518200
A ₁	0.0162903	-0.2322710	-0.3737608
A ₂	-0.0012804	0.0090442	0.0089077
A ₃	0.0000204	-0.0001037	-0.0000659
B ₀	-1860.6460	-2970.0880	-4683.4370
B ₁	-10.1972	156.9612	218.2461
B ₂	0.7100	-6.2421	-5.1838
B ₃	-0.0124	0.0705	0.0371
C ₀	-59063.180	125122.100	394143.500
C ₁	1284.726	-26161.280	-35862.060
C ₂	-95.858	1031.518	861.298
C ₃	1.689	-11.987	-6.337

^aThe weight percent range of the salt concentration is a guess.

results for all solutions, and the average deviation was within 1.0%. Our data agree well with the literature data (6, 7). The osmotic and activity coefficients of water can be calculated by the method given in our earlier papers (1, 2).

Glossary

A, B,	constants in eq 1
C, D	
A, B, C	parameters in eq 2
A ₀ , A ₁ ,	parameters in eq 3
A ₂ ,	
A ₃	

B₀, B₁,

B₂,

B₃

C₀, C₁,

C₂,

C₃

ρ

P

T

w

density

vapor pressure

temperature

concentration of salt

Registry No. LiNO₃, 7790-69-4; LiCl, 7447-41-8; LiBr, 7550-35-8.

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