EXPERIMENTAL MEASUREMENTS OF VAPOR PRESSURES OF ELECTROLYTE SOLUTIONS BY DIFFERENTIAL STATIC METHOD

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Introduction

Absorption refrigerating machines and heat pumps have been considered as possible devices for utilizing low-temperature waste heat. The performance of these machines depends on the circulating fluids or mixtures used in the systems. Therefore, thermodynamic properties of these mixtures (electrolyte solutions) are of wide interest to designers of all refrigeration system components. Very few precise vapor pressure data are available for aqueous electrolyte solutions in the range of 348. 15-373. 15 K. Also, the activity of water and osmotic coefficients for salt solutions at tempteratures other than 298.15 K are not available.

Therefore, a systematic study has been undertaken at this University on the measurement of vapor pressures of aqueous electrolyte solutions of LiCl, LiBr, NaBr, NaI, KCl, KBr, KI, RbCl, CsCl, CsBr and CsI with high precision in the temperature range of 384.15-368.15 K for various concentrations. In our earlier studies, we have presented data in the temperatures range 303.15-343.15 K for various aqueous electrolyte solution at different concentrations.

Experimental Section

Apparatus and Procedure The vapor pressures of the aqueous electrolyte solutions were measured by the differential static method. The experimental methods and procedure followed were described in previous publications[2-5]. The temperture of the oil themostat was controlled to ±0.005 °C at any given temperature between 348.15-368.15 K. Temperatures were measured using a platinum resistance thermometer MKT 100 (Anton Paar).

The difference in heights of the mercury meniscuses in the manometer limbs was measured by means of a cathetometer, capable of reading to 0.01 mm. These readings were corrected by taking into account the thermal expansion coefficient of mercury. By considering the accuracy of the cathetometer, the temperature measurement and the concentration of the salt solution, the uncertainty in vapor pressure was estimated to be 0.01 kPa. The vapor pressure of pure water was taken from the literature[1].

Materials All the salts used were of analytical reagent grade and anhydrous with reported purities of > 99 %. LiCl, LiBr, NaBr, CsCl, CsBr, CsI and RbCl were supplied by Fluka, NaI, and KBr by Aldrich, and NaI and KI by E. Merck Darmstadt. All salts were dried in a vacuum oven at 120°C for several days. These salts were dissolved in distilled water firstly from alkaline potassium permanganate and secondly from itself using previously deionized water. A solution was carefully prepared by weighing to obtain the desired initial concentration by using a Mettler balance accurate to 1.0×10^{-5} g. The concentration of the solution was changed by addition of water. The densities were determined at 303.15 K for different concentrations by the use of a densimeter from Anton Paar Co., Ltd. (DMA 60/602 H). The densities were reproducible to $\pm 2 \times 10^{-5}$ g cm^{-3}. The concentrations of the salt solutions were calculated from density measurements. The reproducibility of the measurements was within 0.35 %.

Results and Discussion

Vapor pressure measurements were made in the temperature range 348.15-368.15 K and concentration range 1.296-18.575 mol/kg with the aqueous solutions of the salts. The experimental data are summarized in **Table 1.**

The experimental data can be correlated to the Antoine type of equation

$$log\, P = \sum_{i=0}^{3} A_i\, m^i + T^{-1} \sum_{i=0}^{3} B_i\, m^i + T^{-2} \sum_{i=0}^{2} C_i\, m^i \qquad (1)$$

and the parameters A_i, B_i and C_i were determined from the experimental vapor pressure data by the least-squares method. The experimental data in the temperature range 303.15 to 343.15 K were used from earlier publications[1, 2]. **Table 2** summarizes the best fit parameters. The calculated vapor pressures were in good agreement with the experimental results for all solutions and the average deviation was within 1.0 %.

Nomenclature

A_i, B_i, C_i = parameters in Eg. (1)

Table 1. Vapor pressure (P) of Aqueous Solutions

m	P at various T, [kPa] 348.15K	353.15K	358.15K	363.15K	368.15
LiCl					
3.496	32.84	40.72	49.87	60.90	73.47
5.629	27.95	34.68	42.40	51.99	62.52
6.954	24.61	30.61	37.62	46.13	55.76
8.486	21.04	26.15	32.23	39.60	47.93
10.008	17.69	22.10	27.30	33.66	41.01
11.986	14.19	17.81	22.14	27.36	33.52
13.840	11.51	14.54	18.13	22.55	27.71
16.222	8.93	11.38	14.18	17.87	22.06
18.575	7.13	9.10	11.40	14.37	17.68
LiBr					
2.564	34.75	42.94	52.74	64.40	77.71
4.780	30.11	37.04	45.28	54.93	66.17
7.612	22.07	27.08	32.96	39.81	47.81
9.484	16.71	20.61	25.25	30.70	37.02
11.506	11.92	14.90	18.36	22.43	27.32
13.128	8.77	11.01	13.59	16.73	20.41
14.694	6.54	8.22	10.26	12.72	15.83
16.359	4.88	6.21	7.92	9.76	12.28
NaBr					
1.901	35.99	44.22	53.99	65.50	78.55
2.896	35.33	42.19	51.51	62.50	75.23
3.780	32.72	40.21	49.09	59.57	71.40
4.564	31.35	38.38	46.84	56.81	67.62
5.368	29.70	36.50	44.55	54.01	65.10
6.823	27.04	33.20	40.51	49.12	59.03
7.752	25.43	31.28	38.21	46.24	55.63
NaI					
1.660	36.31	44.64	54.55	66.25	79.87
2.594	34.69	42.70	52.13	63.20	75.94
3.653	32.46	40.09	49.04	59.63	71.58
4.980	29.69	36.53	44.67	54.28	65.56
5.992	27.45	33.75	41.23	50.06	60.10
6.824	25.63	31.50	38.47	46.66	56.18
7.767	23.64	29.04	35.46	43.00	51.81
8.848	21.51	26.41	32.22	39.06	47.12
CsCl					
2.124	36.00	44.34	54.05	65.96	79.17
2.962	35.02	43.34	53.01	64.71	77.99
3.846	33.93	41.76	51.23	62.28	75.24
5.012	32.39	40.21	49.24	60.20	72.70
6.142	30.93	38.22	46.81	56.96	68.63
7.694	28.87	35.68	43.69	53.27	64.20
8.126	28.08	34.70	42.30	51.57	62.00
CsBr					
1.748	36.41	44.72	55.34	67.35	81.01
2.592	35.45	43.68	53.40	65.21	78.27
3.326	34.67	42.83	52.33	63.92	76.97
4.108	33.66	41.72	51.05	62.39	74.97
5.263	32.62	40.34	49.35	60.31	72.56
6.008	31.74	39.23	47.99	58.72	71.24
CaI					
1.484	37.05	45.82	56.15	68.21	82.27
1.603	36.84	45.57	55.92	67.99	81.94
1.953	36.54	45.11	55.25	67.46	81.22
2.264	36.09	44.70	54.79	66.78	80.51
2.643	35.44	43.88	53.74	65.49	79.11
KCl					
1.725	36.83	45.74	55.89	67.95	81.88
2.134	36.15	44.90	54.84	67.03	81.16
3.224	35.02	43.43	53.25	65.37	79.21
3.951	34.07	42.23	51.75	63.24	76.75
4.408	33.39	41.33	50.62	62.00	74.77
KBr					
2.103	35.96	44.03	53.73	65.38	78.45
2.612	35.27	43.32	52.85	64.21	77.20
3.112	34.67	42.34	51.78	62.89	75.28
3.654	33.83	41.43	50.50	61.38	73.19
4.028	33.27	40.70	49.62	60.38	72.02
4.525	32.57	39.93	48.56	59.14	70.54
KI					
1.746	36.53	44.73	54.59	66.37	79.08
2.528	35.39	43.51	53.07	64.59	76.86
3.240	34.37	42.28	51.30	62.64	74.43
3.908	33.49	41.04	49.92	60.40	72.17
4.629	32.20	39.61	48.21	58.60	70.04
5.382	31.08	38.12	46.46	56.37	67.56
RbCl					
1.296	37.09	45.58	55.66	67.50	81.21
2.303	35.74	43.90	53.58	64.95	78.01
3.254	34.58	42.44	51.70	62.56	75.07
4.368	33.12	40.58	49.43	59.86	71.79
5.192	32.03	39.24	47.72	57.67	68.83
6.117	30.72	37.60	45.70	55.07	66.16
7.094	29.28	35.78	43.46	52.38	62.44

m	= molality of the salt solution	[mol/kg]
P	= vapor pressure	[kPa]
T	= temperature	[K]

Table 2. Parameters in Equation (1)

	LiCl	LiBr	NaBr
A_0	6.88364	8.16619	7.24219
A_1	0.13615	-0.15878	-0.08989
A_2	-0.00679	-0.00956	-0.00127
A_3	0.00011	0.00115	-
B_0	-1521.726	-2402.954	-1748.398
B_1	-85.836	153.648	55.784
B_2	2.513	-3.728	-
B_3	-	-0.366	-
C_0	-113248.8	36187.4	-76938.6
C_1	12754.6	-33775.3	-10203.4
C_2	-517.2	1822.7	-

	NaI	CsCl	CsBr
A_0	7.36822	7.72288	7.11059
A_1	-0.05696	-0.07964	0.13134
A_2	-0.00142	-0.00105	-
B_0	-1802.385	-2045.424	-1627.889
B_1	25.962	48.128	-100.051
C_0	-72579.8	-33338.7	-102778.9
C_1	-4187.9	-7881.0	17242.9

	CsI	KCl	KBr
A_0	8.01261	7.52992	7.40989
A_1	-0.18170	0.14896	-0.19013
B_0	-2228.961	-1902.742	-1830.380
B_1	113.340	-108.645	114.097
C_0	-2423.3	-57064.7	-67879.1
C_1	-19189.9	17881.7	-18826.6

	KI	RbCl
A_0	7.37361	7.44884
A_1	-0.03597	-0.25437
B_1	-1805.011	-1864.052
B_2	7.527	157.930
C_0	-71874.2	-60644.9
C_1	-571.3	-26289.8

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