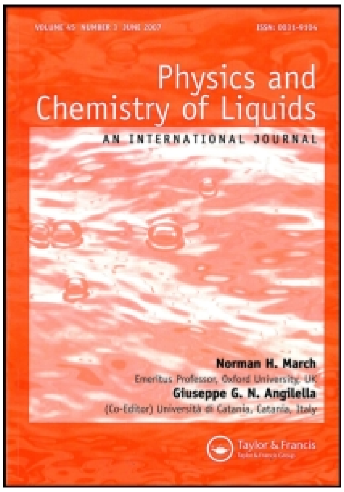

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THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE

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Vapor pressure of aqueous solutions of lithium chloride were measured by differential static method, in a concentration range of 12.9–44.2% weight and in the temperature range of 30–100°C. The experimental data were fitted to the Antoine type equation: $\log P = \mathrm{A}(m) + \mathrm{B}(m)/T + \mathrm{C}(m)/T^2$, where A, B, and C are constants which are concentration dependent. Enthalpies of solution were calculated by the Haltenberger method using experimental vapor pressure data and heat capacity data. The Duhring and enthalpy–concentration charts have been constructed. These charts may be useful in the performance studies of absorption heat pumps.

Keywords: Vapor pressure; Aqueous lithium chloride; Enthalpy

INTRODUCTION

The thermodynamic and physical properties of aqueous electrolyte solutions are useful in the chemical industry, desalination processes, geochemistry and in the performance studies of absorption heat pumps.

Aqueous solutions of lithium bromide have been employed for many years in air conditioning to produce refrigeration by means of an absorption cycle. The absorbing medium is a highly concentrated aqueous solution of LiBr and the refrigerant is water itself. The uses

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of aqueous LiI solutions in air conditioning and in solar space heating have been discussed [1,2]. Also some work been carried out on aqueous LiI solutions in absorption heat pump [3]. Lithium chloride can also be used as an absorbent in the heat pumps. The *P–T–X* and *H–T–X* data for a particular system are necessary for understanding the basic operating conditions such as pressure (*P*), temperature (*T*) and concentration (*X*) in the various components of an absorption heat pump. Enthalpy–concentration charts are available for only a few systems [4–8]. For the aqueous solutions of LiCl some thermodynamic data are available in the literature [9–12].

The experimental data required for the construction of enthalpy–concentration chart are (i) vapor pressure of solutions over the concentration and temperature range to be covered and (ii) heat capacity of solution at any one concentration and temperature. The method is applicable to all systems containing a single volatile constituent.

In continuation of our earlier work [8,10,13], the measurements of vapor pressures of aqueous LiCl solution with high precision in the temperature range of 30–100°C for various concentrations have been undertaken by the differential static method. The heat capacity of 30% of aqueous LiCl solution was measured using a microcalorimeter. The Duhring chart has been constructed from vapor pressure data which is useful in calculating enthalpies and also to visualize the operating temperature levels in an absorption heat pump.

EXPERIMENTAL

A differential static method has been used for the determination of vapor pressure, which involves the measurement of the difference between the vapor pressures of solution and pure water. Experimental method used and the procedure followed are described in our previous publication [10]. In this method, the samples (solutions and pure water) are held in two bulbs attached to two ends of a manometer. The apparatus was kept in a silicone oil bath whose temperature was controlled to 0.005°C, at a desired temperature between 30 and 100°C at 10° intervals. The bath temperatures were measured using a quartz thermometer (Hewlett Packard, model 2804 A) The important precaution to be taken in these experiments were to degas the samples thoroughly before each run and to avoid any condensation in the manometer arm. The difference in the levels of the mercury in the manometer was measured using a cathetometer which could read to 0.01 mm.

The stock solutions were prepared from anhydrous, analytical reagent LiCl of + 99% purity (Hans Heinrich-Hutte GmbH, Germany). The salt was dried in vacuum oven at 120°C, for several hours before it was dissolved in distilled but previously deionised water. The solution concentrations were determined from density measurements with a high precision densitymeter (Anton Paar, model DMA 60/602).

The relationship between the percent concentration by weight of salt, X and the density, d is found to be as follows:

$$X = -205.2893 + 162.897\,d + 105.8709\,d^2 - 63.04517\,d^3 \tag{1}$$

The average error was 0.04%.

Heat capacity of 30% aqueous solution of LiCl was measured at 30°C using a microcalorimeter (C-80, SETARAM, France). The value obtained is 2.98 kJ/kg°C.

RESULTS AND DISCUSSION

(i) Vapor Pressure Data

Vapor pressures of LiCl–H_2O system measured between 30 and 100°C, at various concentrations are given in Table I. The vapor pressures of water were taken from the literature [14]. Figure 1 represents the relationship between (log P) versus ($1/T$) for aqueous LiCl solutions, which show a very nearly linear curve. The experimental vapor pressure data were filled to Antoine type equation:

$$\log P = \mathrm{A}(m) + \mathrm{B}(m)/T + \mathrm{C}(m)/T^2 \tag{2}$$

$$\mathrm{A}(m) = a_0 + a_1 m + a_2 m^2 + a_3 m^3 \tag{3}$$

$$\mathrm{B}(m) = b_0 + b_1 m + b_2 m^2 + b_3 m^3 \tag{4}$$

$$\mathrm{C}(m) = c_0 + c_1 m + c_2 m^2 + c_3 m^3 \tag{5}$$

TABLE I Experimental vapor pressure data of aqueous LiCl solutions

LiCl conc.		*t* (°C)							
wt%	*m*	*30.0*	*40.0*	*50.0*	*60.0*	*70.0*	*80.0*	*90.0*	*100.0*
Vapor pressure (mm Hg)									
12.907	3.496	26.82	46.79	78.49	127.11	199.38	303.87	451.16	654.05
19.265	5.629	22.53	39.37	66.16	107.33	168.68	257.61	383.27	556.81
22.768	6.954	19.56	34.31	57.87	94.24	148.67	227.87	340.25	496.06
26.456	8.486	16.22	28.64	48.62	79.67	126.45	194.98	292.83	429.36
29.788	10.008	13.23	23.55	40.30	66.55	106.42	165.30	250.02	369.10
33.692	11.986	10.01	18.03	31.22	52.16	84.34	132.40	202.34	301.70
36.976	13.840	7.70	14.04	24.59	41.54	67.90	107.70	166.21	250.20
40.756	16.228	5.61	10.38	18.44	31.58	52.27	83.92	131.02	199.40
44.186	18.675	4.28	8.01	14.40	24.92	41.65	67.48	106.26	163.03

Equations

$$\log P = \mathrm{A} + \mathrm{B}/T + \mathrm{C}/T^2$$

where, $\mathrm{A} = 8.202988 - 0.1353801\,\mathrm{m} + 0.0179222\,\mathrm{m}^2 - 0.0005292\,\mathrm{m}^3$;

$\mathrm{B} = -1727.8 + 58.3845\,\mathrm{m} - 10.208\,\mathrm{m}^2 + 0.3125\,\mathrm{m}^3$;

$\mathrm{C} = -95014.0 - 4701.526\,\mathrm{m} + 929.081\,\mathrm{m}^2 - 31.766\,\mathrm{m}^3$;

$T = (t + 273.15)\,\mathrm{K}$.

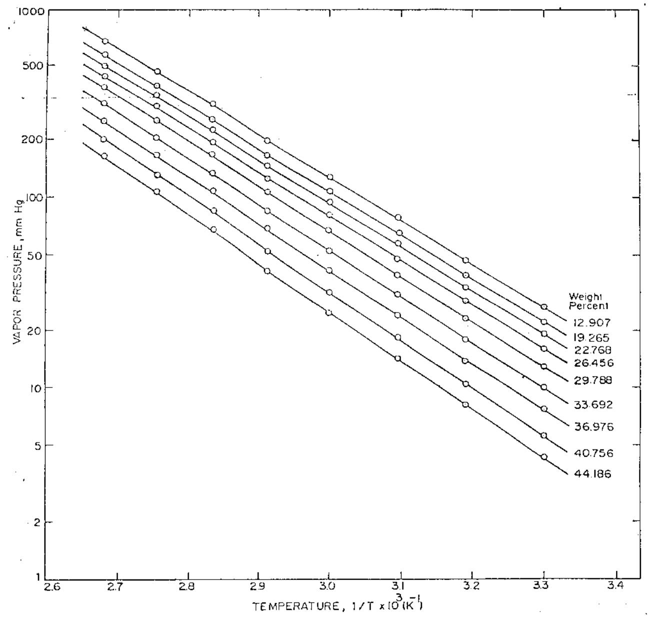

FIGURE 1 Log P–$1/T$ plot for aqueous LiCl solutions o – experimental point, — from Eq. (2).

where, m is the molality of the electrolyte. The parameters a_0–a_3, b_0–b_3 and c_0–c_3 are determined by the least squares method. The calculated vapor pressures from Eqs. (2)–(5) were in good agreement with the experimental data. The average deviation is less than 1.0%. The fitting parameters of Eqs. (3)–(5) are given in Table I.

(ii) Duhring Chart

Duhring equation can be derived from Claperon equation [4]. The vapor pressure data of Table I were used to fix the Duhring lines. The dew points were calculated by the use of Eqs. (2–5) and steam table values [8]. Table II summarizes the dew points for a limited extrapolated concentration range of 0–50 weight percent of LiCl and temperature range of 0–120°C and also the Duhring constants A and B. Straight line interpolation was used to determine these constants. The maximum deviation in dew point was 0.2°C at higher concentrations. Figure 2 shows Duhring lines at all concentrations.

TABLE II Dew point and solution temperatures of aqueous LiCl

wt%	*constants*		*Solution temperatures* °C *(t)*												
LiCl	*A*	*B*	*0*	*10*	*20*	*30*	*40*	*50*	*60*	*70*	*80*	*90*	*100*	*110*	*120*
Dew point temperatures (°C (t'))															
0	1.00000	0.00000	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100.0	110.0	120.0
5	0.99006	1.62456	– 1.4	8.5	18.6	28.6	38.7	48.8	58.8	68.9	79.1	89.2	99.4	109.5	119.7
10	1.00674	1.94195	– 1.9	8.0	17.9	27.9	37.8	47.7	57.6	67.6	77.5	87.5	97.4	107.4	117.3
15	1.02351	3.14420	– 3.1	6.7	16.5	26.2	36.0	45.8	55.6	65.3	75.1	84.9	94.6	104.4	114.2
20	1.03983	5.41434	– 5.2	4.4	14.0	23.6	33.3	42.9	52.5	62.1	71.7	81.3	91.0	100.6	110.2
25	1.05560	8.88062	– 8.4	1.1	10.5	20.0	29.5	38.9	48.4	57.9	67.3	76.8	86.3	95.8	105.3
30	1.07066	13.58124	– 12.5	– 3.3	6.0	15.3	24.6	33.9	43.3	52.6	62.0	71.3	80.7	90.1	99.5
35	1.08547	19.37353	– 17.6	– 8.5	0.6	9.7	18.9	28.0	37.2	46.5	55.7	65.0	74.3	83.6	93.0
40	1.10120	25.79075	–	– 14.1	– 5.2	3.7	12.7	21.7	30.8	39.9	49.0	58.2	67.4	76.7	86.0
45	1.12037	31.76921	–	– 19.2	– 10.5	– 1.7	7.2	16.0	24.9	33.9	42.8	51.9	60.9	70.0	79.2
50	1.14887	34.92365	–	–	– 13.0	– 4.3	4.4	13.1	21.8	30.5	39.2	47.9	56.6	65.4	74.1

Equations and constants

$$t = (\mathrm{a}_0 + \mathrm{a}_1 X + \mathrm{a}_2 X^2 + \mathrm{a}_3 X^3)t' + (\mathrm{b}_0\, \mathrm{b}_1 X + \mathrm{b}_2 X^2 + \mathrm{b}_3 X^3)$$

where,
$a_0 = 0.96616$ $b_0 = 5.17733$ Range: $-20 < t' < 120$
$a_1 = 0.00493$ $b_1 = -0.85879$ $0 < t < 120$
$a_2 = -0.00009$ $b_2 = 0.05273$ $b_3 = -0.0047$ $5\% < x < 50$

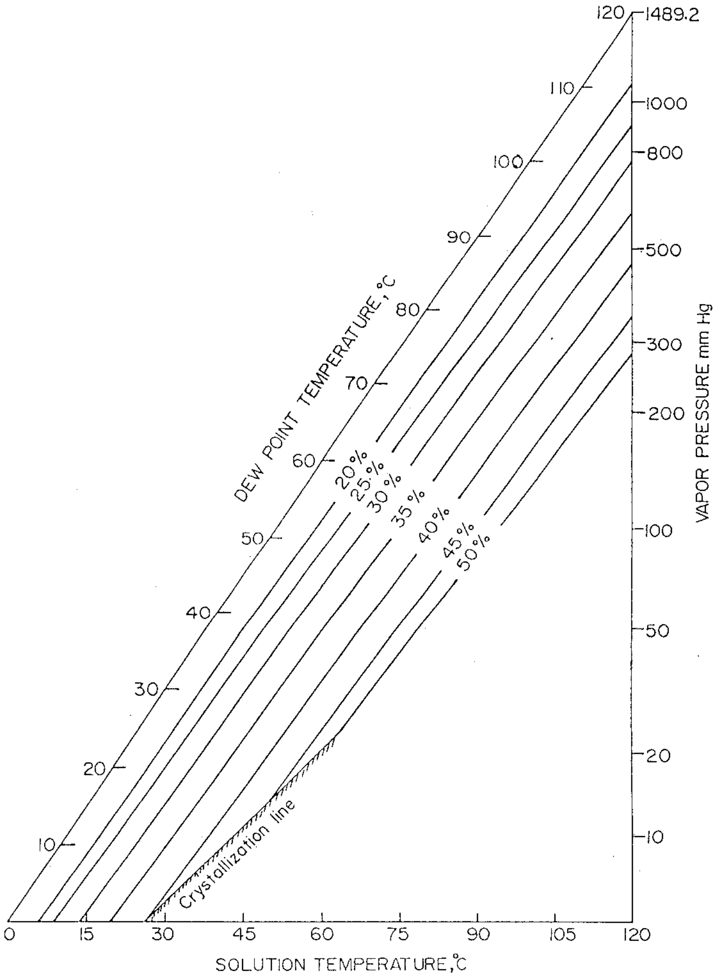

FIGURE 2 Duhring Chart (t *vs.* t' plot) for aqueous LiCl solutions.

(iii) Enthalpy–Concentration Diagram

There are several methods of calculating the isotherms on an enthalpy–concentration diagram. W. Haltenberger, Jr [6], has described a method for calculating the enthalpy of solution at concentration, X and temperature, t, by using the Duhring chart data and heat capacity for a single concentration, over the range of temperatures. McNeely [4]

TABLE III Enthalpy of aqueous lithium chloride solutions

%LiCl	*t* (°C)												
	0	*10*	*20*	*30*	*40*	*50*	*60*	*70*	*80*	*90*	*100*	*110*	*120*
Enthalpy (kJ/kg)													
0	0.0	41.9	83.8	125.7	167.6	209.5	251.4	293.3	335.2	377.1	419.0	460.9	502.8
5	–27.0	12.5	52.4	92.2	132.1	171.9	211.7	251.4	291.2	330.9	370.7	410.5	450.5
10	–13.4	22.7	58.8	95.1	131.4	167.7	204.1	240.6	277.1	313.6	350.2	387.0	423.9
15	–12.9	20.9	54.8	88.8	122.9	157.0	191.2	225.5	259.7	294.1	328.5	363.1	397.8
20	–14.4	17.8	50.1	82.5	115.0	147.5	180.1	212.6	245.3	277.9	310.7	343.5	376.4
25	–11.6	19.4	50.5	81.5	112.6	143.8	174.9	206.1	237.3	268.5	299.7	331.0	362.4
30	0.0	29.8	59.6	89.4	119.2	149.0	178.8	208.6	238.4	268.2	298.0	327.8	357.6
35	–	–	80.1	108.5	136.8	165.2	193.5	221.9	250.2	278.6	306.9	335.1	363.3
40	–	–	–	–	166.3	193.0	219.8	246.5	273.3	300.0	326.7	353.4	379.9
45	–	–	–	–	–	230.9	256.0	281.0	306.1	331.2	356.2	381.2	406.0
50	–	–	–	–	–	–	–	319.8	343.3	366.8	390.3	413.7	436.9

Equations

$\mathrm{H} = \mathrm{A} + \mathrm{B}t + \mathrm{C}t^2$, kJ/kg solution, where, t in °C;

$\mathrm{A} = -66.2324 + 11.2711X - 0.79853X^2 + (2.1534\text{E-}02)X^3 - (1.66352\text{E-}04)X^4$

$\mathrm{B} = 4.5751 - 0.146924X + (6.307226\text{E-}03)X^2 - (1.38054\text{E-}04)X^3 + (1.06690\text{E-}06)X^4$

$\mathrm{C} = (-8.09689\text{E-}04) + (2.18145\text{E-}04)X - (1.36194\text{E-}05)X^2 + (3.20998\text{E-}07)X^3 - (2.64266\text{E-}09)X^4$

has used this method for LiBr–H_2O pair. The details of calculations are given in our previous publication [8]. The enthalpies of solution, *H* at different isotherms are given in Table III. These enthalpy data were fitted to a polynomial equation by least squares method within the limited range of temperature 0–120°C (for interpolations and limited extrapolations). The constants of equations are included in Table III. The enthalpy–concentration isotherms for lithium chloride solutions are plotted in Fig. 3 which also shows the limitations imposed by the crystallization points of the solutions.

CONCLUSION

The Duhring chart shows a good correlation with the vapor pressure data. An enthalpy–concentration diagram that is thermodynamically consistent with the Duhring chart has been constructed. By using the Duhring chart and an enthalpy–concentration diagram (or the equations), one can evaluate the performance of an absorption refrigeration cycle and the absorption heat pumps using the LiCl–H_2O system.

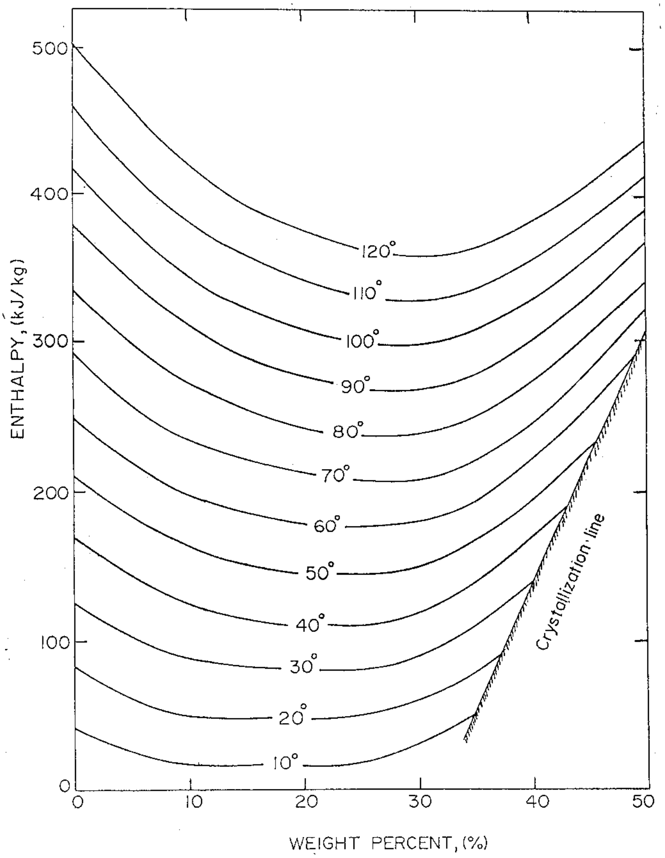

FIGURE 3 Enthalpy–concentration diagram for aqueous LiCl solutions.

NOMENCLATURE

A, B, C	constants of the equation
C_p	heat capacity, kJ/kg°C
H	enthalpy, kJ/kg
m	molality of electrolyte, mol/kg
P	vapor pressure, mm Hg
T	temperature, K
t, t'	solution and dew point temperature, °C
X	salt concentration, %weight LiCl

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