Measurement and modeling of vapor–liquid equilibria at high salt concentrations

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Abstract

Isobaric vapor–liquid equilibrium data are reported for binary and ternary aqueous mixtures containing LiCl and $ZnCl_2$ at total salt concentrations between 10 and 50 wt.%. The measurements were carried out at 5.3, 9.3, 20, 40, and 101.3 kPa in a computer-controlled glass apparatus. Particular care was taken to ensure proper equilibration of the high-density, high-viscosity salt mixtures. The equilibrium data spanning temperatures between 303 and 423 K were successfully correlated using the electrolyte model by Wang and Anderko [Fluid Phase Equilibr. 203 (2002) 141–176].
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1. Introduction

Lithium is the first member in the IA series of alkaline metals and is very strongly hydrated in aqueous solutions due to the small radius and high charge density of the lithium ion. Each lithium ion binds about three water molecules and lithium halogenide salts exhibit high solubilities in water (ca. 20 mol/kg H_2O or 45–50 wt.%) [1]. The combination of these properties makes the lithium salts prime candidates for regenerable absorbents in desiccant cooling and drying systems. The use of such systems for temperature and humidity control in large residential and commercial buildings has been under study and development in recent years. Particularly attractive for this process is the possibility of utilizing various types of 'low grade' heat sources for the regeneration of the desiccant solutions, such as waste heat, solar energy or biomass fuels [2].

Lithium chloride appears to be the most stable liquid desiccant with a high dehydration capacity and a wide dehydration window (between ca. 30 and 45 wt.%). However, its drawback for the desiccation process is a relatively high cost. During the last decade several studies have been carried out on the use of mixed salts with the objective to find a stable, effective, and low-cost working fluid [2,3].

Extensive phase equilibrium data are available in the literature for the binary system $LiCl + H_2O$ [4–11]. On the other hand, vapor–liquid equilibrium (VLE) data are much scarcer for aqueous solutions of divalent metals, such as $ZnCl_2 + H_2O$ where they are mostly limited to water activity data at 298 K [12–16]. This paper reports VLE data of binary and ternary aqueous solutions of LiCl and $ZnCl_2$ at high total salt concentrations (10–50 wt.%) and temperatures between 303 and 423 K.

2. Experimental

VLE measurements were carried out at 5.3, 9.3, 20, 40, and 101.3 kPa in a computer-controlled glass ebulliometer with the capacity of 500 cm^3 (Fig. 1). The apparatus was equipped with a pressure sensor (Model 215A, Paroscientific
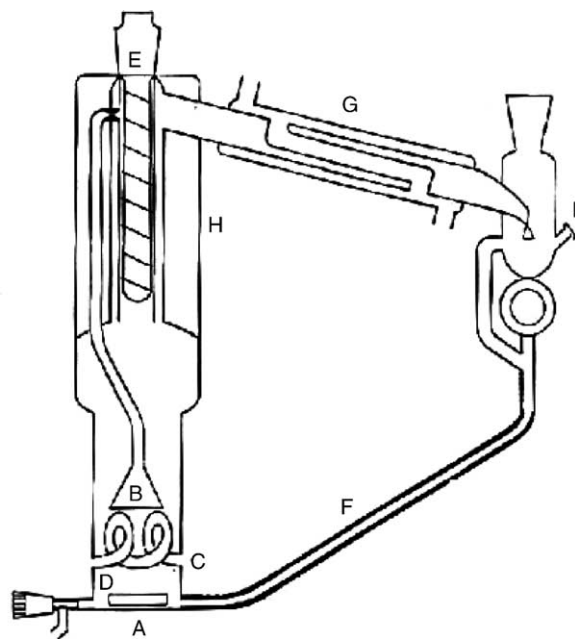

Fig. 1. Scheme of VLE apparatus used in this work: (A) boiler, (B) Cotrell pump, (C) electric heater, (D) magnetic stirrer, (E) thermometer well, (F) reflux line, (G) condenser, (H) jacket, and (I) sampling port.

Anhydrous LiCl (purity >99 wt.%) and $ZnCl_2$ (purity >98 wt.%) were purchased from Wako Chemicals Inc., Osaka, Japan, and used as received. Aqueous solutions of the salts were prepared by weighing (LIBROR AEL-200 and EB-3200H balances, Shimadzu Corp., Japan). Distilled and deioinized water (CPW-100, Advantech Toyo Ltd., Japan) was used for the preparation of the solutions. Considerable amount of heat was liberated on dissolving the anhydrous salts in water. Correspondingly, the dissolution process was carried out in a water bath maintained at 293 K.

The salt solutions had a high density and viscosity (ca. $1.5 \, g/cm^3$ and $40 \, mPa \, s$, respectively, for the most concentrated solutions), and intensive circulation in the cell was necessary to ensure the attainment of equilibrium in the apparatus. The reliability of the measurement at high salt concentrations was verified by comparing our experimental data for the binary system $LiCl + H_2O$ with those in the literature (Fig. 2).

Our *P–T* experimental data for the ternary system $LiCl + ZnCl_2 + H_2O$ at different mass ratios of $LiCl:ZnCl_2$ are listed in Table 1. Considering the condensate hold-up in the recirculation apparatus, the uncertainty in the reported liquid compositions is estimated to be 0.6%.

Inc., Redmont, WA, USA) and a Pt-resistance thermometer (Model 1502A, Hart Scientific Inc., American Fork, UT, USA). The estimated uncertainty in the pressure and temperature readings was ±0.01 kPa and ±0.05 K, respectively. The pressure was controlled to ±0.1 kPa using a Ruska Series 7000 controller (Ruska Instrument Corp., Houston, TX, USA).

3. Modeling

3.1. Binary system $LiCl + H_2O$

For modeling of the experimental data we used the mixed solvent electrolyte (MSE) model [17] as implemented in the ESP simulator (OLI Systems Inc., Morris Plains, NJ, USA).
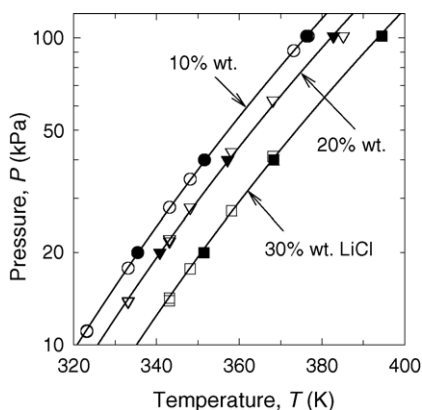
Table 1
Experimental VLE data

LiCl + H₂O binary system				ZnCl₂ + H₂O binary system				LiCl + ZnCl₂ + H₂O ternary system[a]				LiCl + ZnCl₂ + H₂O ternary system[b]			
LiCl (wt.%)	ZnCl₂ (wt.%)	P (kPa)	T (K)	LiCl (wt.%)	ZnCl₂ (wt.%)	P (kPa)	T (K)	LiCl (wt.%)	ZnCl₂ (wt.%)	P (kPa)	T (K)	LiCl (wt.%)	ZnCl₂ (wt.%)	P (kPa)	T (K)
10	0	101.3	376.30	0	30	101.3	376.27	4.3	5.7	101.3	374.62	16.7	3.3	20.0	339.42
10	0	40.0	351.60	0	30	40.0	351.79	8.6	11.4	5.3	309.68	16.7	3.3	40.0	355.68
10	0	20.0	335.45	0	30	20.0	335.69	8.6	11.4	20.0	335.62	16.7	3.3	101.3	380.47
20	0	101.3	382.77	0	40	101.3	379.86	8.6	11.4	40.0	351.38	25.0	5.0	20.0	347.50
20	0	40.0	357.17	0	40	40.0	355.10	8.6	11.4	101.3	376.64	25.0	5.0	40.0	364.32
20	0	20.0	340.81	0	40	20.0	338.74	12.9	17.1	5.3	312.39	25.0	5.0	101.3	390.00
30	0	101.3	394.47	0	50	101.3	385.14	12.9	17.1	20.0	338.19	33.4	6.6	20.0	359.04
30	0	40.0	368.38	0	50	40.0	359.70	12.9	17.1	40.0	354.98	33.4	6.6	40.0	377.50
30	0	20.0	351.47	0	50	20.0	343.26	12.9	17.1	101.3	380.08	33.4	6.6	101.3	404.20
				0	50	9.3	326.65	17.1	22.9	5.3	317.12	41.7	8.3	19.9	376.23
								17.1	22.9	20.0	344.18	41.7	8.3	40.0	394.33
								17.1	22.9	40.0	361.17	41.7	8.3	101.3	420.79
								17.1	22.9	101.3	386.65				
								21.4	28.6	5.3	325.96				
								21.4	28.6	20.0	354.56				
								21.4	28.6	40.0	371.86				
								21.4	28.6	101.3	398.45				

[a] LiCl:ZnCl₂ mass ratio = 0.75.
[b] LiCl:ZnCl₂ mass ratio = 5.

Fig. 2. Vapor–liquid equilibrium in the binary system LiCl + H$_2$O at salt concentrations 10, 20, and 30 wt.%. Empty symbols: literature data [4–11]; full symbols: experimental VLE data (this work); lines: MSE model.

The model for the excess Gibbs energy consists of three terms:

$$\frac{G^{\mathrm{E}}}{RT} = \frac{G^{\mathrm{E}}_{\mathrm{LR}}}{RT} + \frac{G^{\mathrm{E}}_{\mathrm{SR}}}{RT} + \frac{G^{\mathrm{E}}_{\mathrm{MR}}}{RT} \tag{1}$$

The long-range contribution, $G^{\mathrm{E}}_{\mathrm{LR}}$, is expressed by the Pitzer–Debye–Hückel term,

$$\frac{G^{\mathrm{E}}_{\mathrm{LR}}}{RT} = -\left(\sum n_i\right) \frac{4 A_x I_x}{\rho} \ln\left(\frac{I + \rho I_x^{1/2}}{\sum x_i [1 + \rho (I_x^0)^{1/2}]}\right) \tag{2}$$

where I_x is the ionic strength, $I_x = 1/2 \sum x_i z_i^2$. For aqueous solutions, the long-range term does not contain any adjustable parameters.

The short-range contribution, $G^{\mathrm{E}}_{\mathrm{SR}}$, is given by the standard UNIQUAC term [18]. The middle range term, $G^{\mathrm{E}}_{\mathrm{MR}}$, is represented by a symmetrical second virial coefficient-type
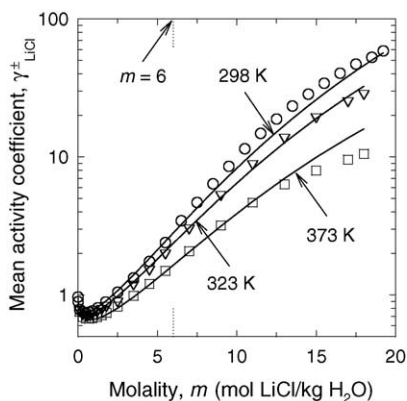

Fig. 3. Mean ionic activity coefficients in the binary system LiCl + H$_2$O as a function of the salt molal concentration. Symbols: literature data [20–23]; lines: MSE model. All lines at $m > 6$ are extrapolated. Only two middle-range parameters for Li$^+$/Cl$^-$, $b_{\mathrm{Li^+/Cl^-}}$ and $c_{\mathrm{Li^+/Cl^-}}$ in Eq. (3), are necessary at a single temperature. The results are obtained by fitting data at $m < 6$ and all three temperatures using four parameters $b_{ij}^{(0)}$, $b_{ij}^{(1)}$, $c_{ij}^{(0)}$, $c_{ij}^{(1)}$.

Table 2
Model parameters for the system LiCl + ZnCl$_2$ + H$_2$O

| | Binary parameters | | | | | | Parameters for aqueous complexes | | | Parameters for solids | | |
	$b_{ij}^{(0)}$	$b_{ij}^{(1)}$	$b_{ij}^{(2)}$	$c_{ij}^{(0)}$	$c_{ij}^{(1)}$	$c_{ij}^{(2)}$		ΔG_f° (cal mol^{-1})	S^0 (cal mol^{-1} K^{-1})		ΔG_f° (cal mol^{-1})	S^0 (cal mol^{-1} K^{-1})
Li$^+$/Cl$^-$	−74.444	0.123183	0	65.83046	−0.112711	0	ZnCl$^+$	−63486.5	63.723	ZnCl$_2$(s)	−89512.1	70.464
Zn^{2+}/Cl$^-$	−23.91367	0	−507.5484	33.86339	0	−221.3743	ZnCl$_2$(aq)	−90961.3	79.497	ZnCl$_2$·1.5H$_2$O	−177251.7	33.461
ZnCl$^+$/Cl$^-$	−0.5216043	0	−1923.864	−0.2712924	0	−126.9201				ZnCl$_2$·2.5H$_2$O	−235329.9	24.456
ZnCl$_2$(aq)/Cl$^-$	−0.7854023	0	−1367.001	−0.3174097	0	−212.5515				ZnCl$_2$·3H$_2$O	−264436.7	40.019
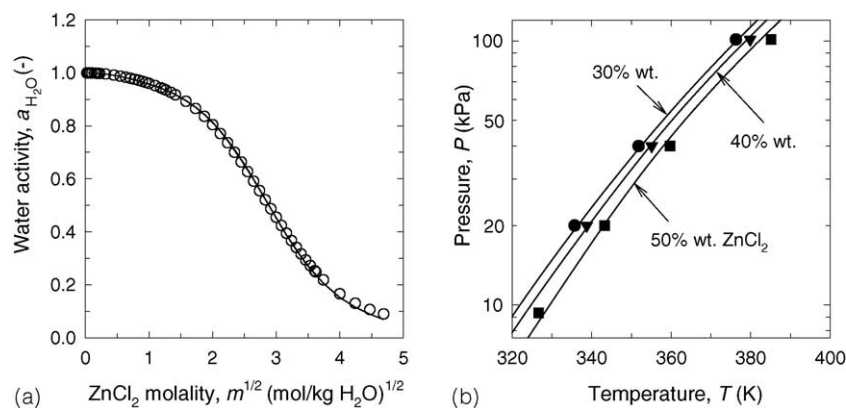
Fig. 4. Properties of the binary system $ZnCl_2 + H_2O$ as a function of the salt concentration. (a) Water activity at 298 K. Triangles: experimental data [16]; (b) isobaric VLE data. Symbols: experimental VLE data (this work). Lines: MSE model.
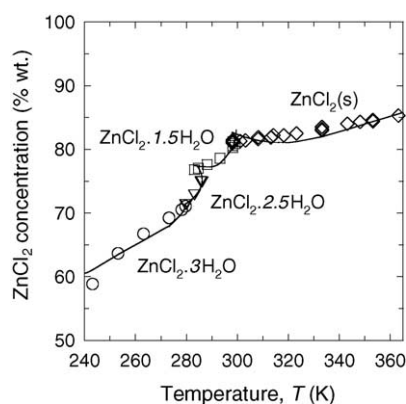

Fig. 5. Solid–liquid equilibria in the binary system $ZnCl_2 + H_2O$. Symbols: experimental data [24]; lines: MSE model.

expression

$$\frac{G_{MR}^{E}}{RT} = - \left(\sum n_i \right) \sum \sum x_i x_j B_{ij}(I_x) \qquad (3)$$

where

$$B_{ij} = b_{ij} + c_{ij} \exp \left(-\sqrt{I_x + 0.01} \right) \qquad (4)$$

The new MSE model has been applied to both aqueous and non-aqueous mixed solvent electrolyte systems, ranging from infinite dilution to molten salts or pure acids [19]. The model parameters are obtained by simultaneous regression of phase equilibrium, enthalpy, and heat capacity data. The parameters in the middle range expression are usually most effective for correlating of electrolyte systems.

In the case of the binary system $LiCl + H_2O$, two middle-range parameters b_{ij} and c_{ij} were sufficient for completely describing the system at isothermal conditions. For correlating data at different temperatures, the following temperature-dependence of the parameters b_{ij} and c_{ij} was used

$$b_{ij} = b_{ij}^{(0)} + b_{ij}^{(1)} T + \frac{b_{ij}^{(2)}}{T} \qquad (5)$$

$$c_{ij} = c_{ij}^{(0)} + c_{ij}^{(1)} T + \frac{c_{ij}^{(2)}}{T} \qquad (6)$$

In the final model, four parameters (i.e. $b_{ij}^{(0)}$, $c_{ij}^{(0)}$ and either $b_{ij}^{(1)}$, $c_{ij}^{(1)}$ or $b_{ij}^{(2)}$, $c_{ij}^{(2)}$) were fitted to the literature data [4–11,20–23] and our VLE data (Table 1). In Fig. 3, only the mean ionic activity coefficients at molal concentrations, $m < 6$, were correlated. The MSE model correctly predicted
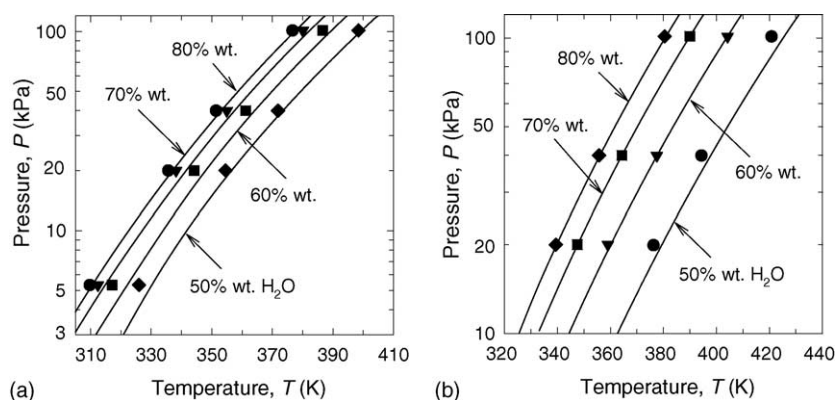

Fig. 6. Correlation of experimental VLE data for the ternary system $LiCl + ZnCl_2 + H_2O$ system at various salt concentrations and $LiCl:ZnCl_2$ mass ratios (P–T projection). (a) $LiCl:ZnCl_2 = 0.75$; (b) $LiCl:ZnCl_2 = 5.0$. Symbols: experimental VLE data (this work) and lines: MSE model.

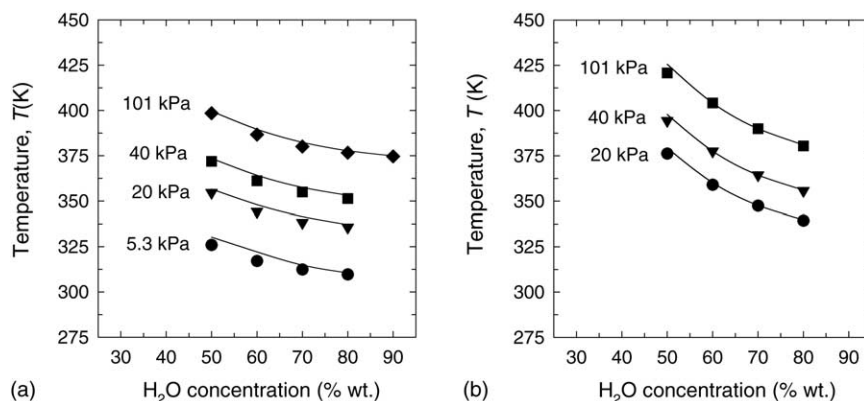Fig. 7. Correlation of experimental VLE data for the ternary system LiCl + ZnCl$_2$ + H$_2$O at various salt concentrations and LiCl:ZnCl$_2$ mass ratios ($T - x$ projection). (a) LiCl:ZnCl$_2$ = 0.75; (b) LiCl:ZnCl$_2$ = 5.0. Symbols: experimental VLE data (this work) and lines: MSE model.

the trend of the activity coefficients at the higher salt concentrations. The correlation of vapor pressures over the aqueous solutions of LiCl at different salt concentrations is shown in Fig. 2. The model parameters are listed in Table 2.

3.2. Binary system ZnCl$_2$ + H$_2$O

The system ZnCl$_2$ + H$_2$O exhibits a complex behavior; depending on the conditions ZnCl$_2$ may exist in aqueous solutions in three types of species: Zn^{2+}, $ZnCl^+$ and $ZnCl_2$(aq) [16]. Consequently, in the MSE model we introduced three types of ion pairs (Zn^{2+}/Cl^-, $ZnCl^+/Cl^-$ and $ZnCl_2$(aq)/Cl^-) and fitted their middle-range parameters b_{ij} and c_{ij} to the available water activity data [16], solid–liquid equilibria [24], and our VLE data (Table 1). Figs. 4 and 5 show the correlation results using the MSE model.

3.3. Ternary system: LiCl + ZnCl$_2$ + H$_2$O

Figs. 6 and 7 show the correlation results for the ternary system LiCl + ZnCl$_2$ + H$_2$O at different ratios of LiCl and ZnCl$_2$. In modeling of this system, no additional ion pair interactions were necessary and the data could be well described using only the binary pair parameters.

4. Conclusion

Modeling of lithium and zinc chloride solutions in a wide range of concentrations is a difficult task for electrolyte models, especially when the component speciation changes with temperature and concentration (e.g., the formation of Zn^{2+}, $ZnCl^+$ and $ZnCl_2$(aq) from ZnCl$_2$). The newly developed MSE model could successfully correlate binary and ternary VLE data of these salts using a small number of parameters.

References

[1] Gmelins Handbuch der anorganischen Chemie: Lithium, Verlag Chemie, Weinheim, 1960.
[2] A. Ertas, E.E. Anderson, I. Kiris, Sol. Energy 49 (1992) 205–212.
[3] R. Saravanan, M.P. Mayia, Appl. Therm. Eng. 18 (1998) 553–568.
[4] A. Lannung, Z. Phys. Chem. A 170 (1934) 134–144.
[5] E.F. Johnson, M.C. Molstad, J. Phys. Chem. 55 (1951) 257–281.
[6] M. Broul, K. Hlavatý, J. Linek, Collect. Czech. Chem. C. 34 (1969) 3428–3435.
[7] E. Sada, T. Morisue, H. Yamaji, Can. J. Chem. Eng. 53 (1975) 350–353.
[8] A.N. Campbell, O.N. Bhatnagar, Can. J. Chem. 57 (1979) 2542–2545.
[9] R. Patil, A.D. Tripathi, G. Pathak, S.S. Katti, J. Chem. Eng. Data 35 (1990) 166–168.
[10] R.K. Patil, F. Olive, A. Coronas, J. Chem. Eng. Jpn. 27 (1994) 680–681.
[11] L.-S. Lee, C.-C. Lee, J. Chem. Eng. Data 43 (1998) 469–472.
[12] R.H. Stokes, Trans. Faraday Soc. 44 (1948) 295–307.
[13] L.S. Lilich, V.I. Timofeev, Vestn. Leningr. Univ., Fiz. Khim. 10 (1956) 68–74.
[14] L.S. Lilich, M.D. Anikeeva, A.A. Loginov, Zh. Neorg. Khim. 6 (1961) 447–452.
[15] C.-F. Pan, W.J. Argersinger, J. Chem. Eng. Data 32 (1987) 205–210.
[16] J.A. Rard, D.G. Miller, J. Chem. Thermodyn. 21 (1989) 463–482.
[17] P. Wang, A. Anderko, Fluid Phase Equilibr. 203 (2002) 141–176.
[18] D.S. Abrams, J.M. Prausnitz, AIChE J. 21 (1975) 116–128.
[19] P. Wang, R.D. Springer, A. Anderko, R.D. Young, Fluid Phase Equilibr. 222–223 (2004) 11–17.
[20] W.J. Hamer, Y.-C. Wu, J. Phys. Chem. Ref. Data 1 (1972) 1047–1099.
[21] H.F. Gibbard Jr., G. Scatchard, J. Chem. Eng. Data 18 (1973) 293–298.
[22] A.N. Campbell, O.N. Bhatnagar, Can. J. Chem. 57 (1979) 2542–2545.
[23] H.F. Holmes, R.E. Mesmer, J. Phys. Chem. 87 (1983) 1242–1255.
[24] W.F. Linke, Solubilities of Inorganic and Metal-Organic Compounds, 4th ed., American Chemical Society, Washington, DC, 1965.