

Solid–liquid phase equilibrium in the systems of LiBr–H₂O and LiCl–H₂O

J. Pátek*, J. Klomfar

Institute of Thermomechanics, Academy of Sciences of the Czech Republic, Dolejškova 5, CZ 182 00 Prague 8, Czech Republic

Received 24 April 2006; received in revised form 7 September 2006; accepted 8 September 2006

Available online 16 September 2006

Abstract

A set of empirical temperature–molar fraction expressions for solid–liquid equilibrium curves of LiBr–H₂O and LiCl–H₂O systems is presented. The expressions are based upon a body of experimental data that have been compiled and critically evaluated. The equations cover the full composition range for LiCl–H₂O system and compositions up to the salt mole fraction of $x = 0.46$ (i.e. mass fraction of $w = 0.805$) for LiBr–H₂O, corresponding to transition from monohydrate to anhydrate. Temperatures and solution compositions at the eutectic point and at transition points between hydrates have been determined from intersections of the curves corresponding to the adjacent hydrate ranges of the phase diagram. Equations of a special structure were used, involving the coordinates of the transition points as parameters, which makes possible their direct non-linear optimization. To obtain more reliable results, a procedure was employed optimizing both the temperature–composition and composition–temperature equations simultaneously. The uncertainty in the obtained values of the transition point coordinates are estimated to be of the order of 1 K for temperature and 0.001 for the composition expressed in salt mole fraction. Gaps in the database are shown to give experimenters orientation for future research.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Aqueous solutions; Salt–water system; Lithium bromide; Lithium chloride; Solubility; Solid–liquid equilibrium

1. Introduction

The properties of phase diagrams of condensed aqueous systems of alkali halides are required not only in process design in the chemical industry, in desalination and dehydration processes, but they are of interest to a wider variety of fields such as geochemistry, oceanology, limnology, and atmospheric chemistry. It is also necessary in performance studies of absorption refrigeration machines, absorption heat pumps and heat transformers. The solid–liquid boundary forms the lower temperature limit of the liquid region of the system, determining thus the concentration range within which the system actually could be used in absorption machinery. Crystallization, which might occur in the liquid phase, can cause serious problems during operation. The temperature–saturated liquid composition (T – x) relation describing the boundary (most often called solubility curve) represents an indispensable information to compute the thermodynamic properties of the system. As for the pressure dependence of the solid–liquid equilibrium

of the salt–water system, it is generally considered insignificant.

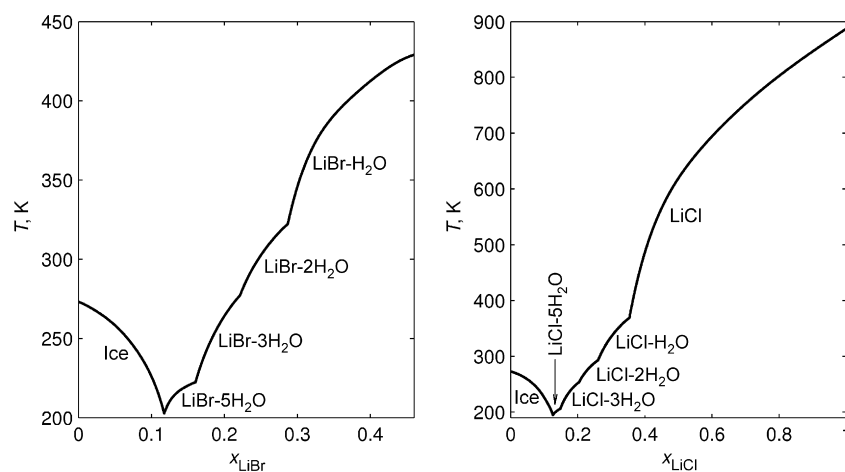
Among the methods used for determining the solid–liquid equilibrium are measurements of the melting point (last crystal disappearing temperature) or of the freezing point (initial crystallization temperature), classical solubility measurement at constant temperature, and thermal analysis, as a rule conducted at ambient pressure. None of these methods seems to provide substantially more reliable results than the others.

The aim of the present study was to provide a reliable description of the solid–liquid coexistence curve based on critically evaluated experimental data compiled from the literature. A description of the solid–liquid equilibrium boundary of LiCl–H₂O system has been given by Conde [1] and by Monnin et al. [2] in the form of functional dependence of, respectively, temperature on mass fraction and molality on temperature. As far as we are aware, no similar study concerning LiBr–H₂O system has been published.

2. Two-solids saturation points

In equilibrium with saturated solution, the solid phase of alkali halide–water systems such as LiBr–H₂O and LiCl–H₂O

* Corresponding author. Tel.: +420 266053153; fax: +420 28584695.
E-mail address: patek@it.cas.cz (J. Pátek).

Fig. 1. Schematic phase diagrams for the LiBr–H₂O and LiCl–H₂O system.

is formed by ice on the low concentration side, by hydrates with 5, 3, 2, and 1 water molecule as the salt concentration in the solution increases, and by anhydrous salt at the highest concentrations. The solid–liquid phase diagram of the system thus consists of branches corresponding to the particular hydrates separated either by eutectic or by peritectic points, where two solids are precipitating simultaneously (Fig. 1).

To determine the transition temperatures between hydrates and the corresponding saturated solution composition, thermal analysis is used or the transition points are fixed by intersection of extrapolated curves for hydrates. An overview of the results of studies on the two-solids points is given in Tables 1 and 2 for the LiBr–H₂O and LiCl–H₂O system, respectively. In the tables, the temperatures are given in degrees Celsius in order not to confuse by the conversion to Kelvin the number of significant figures as it was stated by particular authors. The coordinates of the two-solids points obtained by various authors are scattered over the interval with the width of the order of several K for temperature and of the order of 0.001 for composition expressed in salt mole fraction.

Data found in the literature are conflicting especially for LiCl. Determinations of the transition temperatures show greater discrepancies than would be expected from the estimated accuracy of individual determinations. The results for the eutectic temperature are the most scattered. The thermal analysis seems not to provide much more reliable results than the data obtained from extrapolation. The scatter of the experimental data, most probably, should be ascribed especially to impurities as even small quantities of impurities change the melting point.

3. Data selection

Within the present study, 21 experimental studies have been collected containing a total of 288 data points on the solid–liquid equilibrium relation between temperature and composition for the LiBr–H₂O system and 73 published studies containing 463 data points concerning the LiCl–H₂O system. A body of 125 and 379 of them, respectively, were selected as the primary data used for fitting of the representative empirical equations. Though the temperature scale corrections are of the order of the data

Table 1

Literature data on the temperature and the saturated solution composition at two-solids saturation points of the LiBr–H₂O system

Solid phases	Bogorodski [3]	Hüttig and Studemann ^{TA} [4]	ICT ^{EX} [5]	Heiks and Garrett ^{EX} [6]	Biancifiore ^{EX} [7]	Carrett and Woodruff ^{EX} [8]	Kessis ^{TA} [9]	Ennan and Lapshin [10]	Broul et al. ^{EX} [11]	This work ^{EX}
Eutectic point (°C)		–72		–67.5	–67.5	–73	–67.5	–72		–70.3
Ice + LiBr–5H ₂ O (wt.%)		39.1		39.3	39.3	39.4	39.07	39.4		39.09
Peritectic point (°C)		–53		–49	–47		–51.2			–50.7
LiBr–5H ₂ O + LiBr–3H ₂ O (wt.%)		47.3		48.9	49.1		47.5			47.94
Peritectic point (°C)	4	4	4	5	4		2.9		5.7	4.0
LiBr–3H ₂ O + LiBr–2H ₂ O (wt.%)	56.74	59.2	61.2	59.0	59.0		58.2		59.2	57.81
Peritectic point (°C)	44	32	44		32		42.8		34.6	49.1
LiBr–2H ₂ O + LiBr–H ₂ O (wt.%)	65.07	65.2	67.6		66		64.7		67.6	65.98
Peritectic point (°C)	159	159					156			156.0
LiBr–H ₂ O + LiBr (wt.%)							80.5			80.50

Method: EX, extrapolation; TA, thermal analysis.

Table 2
Literature data on the temperature and the saturated solution composition at two-solids saturation points of the LiCl–H₂O system

Solid phases	Bogorodski [3]	Hüttig and Reuscher [12]	Hüttig and Steudemann ^{TA} [4]	ICT ^{EX} [5]	Benrath [13]	Applebey et al. [14]	Voskresenskaya and Yanateva ^{TA} [15]	Applebey and Cook [16]	Garrett and Woodruff [8]	Campbell and Griffiths [17]
Eutectic point (°C)			−80				−66		−73	
Ice + LiCl–5H ₂ O (wt. %)			25.3				24.4		24.85	
Peritectic point (°C)			−68				−57			
LiCl–5H ₂ O + LiCl–3H ₂ O (wt. %)			28.7				30.4			
Peritectic point (°C)		−16.5	−20	−16.5			−15.6			
LiCl–3H ₂ O + LiCl–2H ₂ O (wt. %)			36.9				37.2			
Peritectic point (°C)	21.5	12.5	12.5	12.5	20	19.1	20.5	19.07		12.5
LiCl–2H ₂ O + LiCl–H ₂ O (wt. %)	47.98		40.5	42.7	45.28		45.6			
Peritectic point (°C)		100.5	100.5	100.5		93.5		93.51		
LiCl–H ₂ O + LiCl (wt. %)		56.5	56.5	56.5						
Solid phases	Moran ^{TA} [18]	Schimmel ^{EX,TA} [19]	Vuillard and Kessiss ^{TA} [20]	Kessiss ^{TA} [21]	Akopov [22]	Ennan and Lapshin [10]	Broul et al. ^{EX} [11]	Monnin et al. ^{EX} [2]	Conde ^{EX} [1]	This work ^{EX}
Eutectic point (°C)	−75.9	−84.0	−74.75		−75.0	−67.0		−75.9	−75.5	−78.2
Ice + LiCl–5H ₂ O (wt. %)		25.2	25		24.8	23.9		25.02	25.3	25.33
Peritectic point (°C)	−65.6	−67.2	−65.4	−65.4	−64.5			−65.4	−68.2	−67.2
LiCl–5H ₂ O + LiCl–3H ₂ O (wt. %)		29.3		29.15	31.2			29.39	28.7	29.05
Peritectic point (°C)	−20.5	−19.0	−20.5	−20.5	−18.0			−17.26	−19.9	−19.5
LiCl–3H ₂ O + LiCl–2H ₂ O (wt. %)		38.0		37.80	38.5			38.23	36.9	37.59
Peritectic point (°C)	19.0	19.0		19.4	18.5		18.5	20.79	19.1	19.9
LiCl–2H ₂ O + LiCl–H ₂ O (wt. %)		45.2		45.15	45.0		45.0	45.34	45.2	45.32
Peritectic point (°C)	94.0				98		96.0	96.59	93.8	95.85
LiCl–H ₂ O + LiCl (wt. %)					56.7		55.8	56.19	55.8	56.30

Method: EX, extrapolation, TA, thermal analysis.

Table 3

Sources of data on the T - x relation of the LiBr–H₂O system at solid–liquid equilibrium

Author(s)	Year	Range of values		Number of data total/used
		Temperature (K)	Mass fraction (wt.%)	
Bogorodski [3]	1893	277–317	57–65	2/1
Biltz [26]	1902	269–273	0.07–0.8	4/4
Jones and Getman [27]	1904	229–273	1–30	7/5
Jones [28]	1907	263–273	1–50	8/5
Hüttig and Reuscher [12]	1924	277–368	59–72	20/0
Hüttig and Steudemann [4]	1927	201–305	39–65	4/1
Steudemann [29]	1927	205–266	14–55	12/11
Scott and Durham [30]	1930	298	60.4	1/1
Scatchard and Prentiss [31]	1933	268–273	0.005–9.2	29/29
Simmons et al. [32]	1936	298	65.3	1/0
Birnthaler and Lange-Erlangen [33]	1938	298	60.9	1/1
Blidin [34]	1947	298	64.7	1/0
Heiks and Garrett ^a [6]	1954	206–287	11–60	38/0
Biancifiore [7]	1963	208–305	39–66	4/1
Kessis [9]	1964	206–429	39–80	28/26
Boryta [35]	1970	220–374	45–70	30/28
Ennan and Lapshin [10]	1973	201	39.4	1/0
Raatschen [36]	1985	284–334	58–66	5/5
Peters et al. [37]	1993	242–309	50–64	7/7
Murakami ^a [38]	2002	250–300	58–64	78/0
Murakami and Kondo ^a [39]	2003	312–366	65–69	7/0

^a Data stated only in graphic forms.

experimental uncertainties, all the temperatures given in ITS-48 and IPTS-68 have been converted to ITS-90. To convert solution compositions expressed in mass fraction w of the salt in the solution and in molality m to molar fraction x :

$$x = \frac{w/M_{\text{salt}}}{w/M_{\text{salt}} + (1-w)/M_{\text{H}_2\text{O}}}, \quad (1)$$

$$x = \frac{m}{m + 1/M_{\text{H}_2\text{O}}}, \quad (2)$$

the following values of molar masses were used: 0.08685 kg mol^{−1} for LiBr [23], 0.04239 kg mol^{−1} for LiCl [23], and 0.018015268 kg mol^{−1} for water [24].

Not all the original works provide sufficient comparable evidence on which to base a judgement of the relative merits of the various sets of results. To assess the quality of the particular sets of experimental data, the data on each branch of the solid–liquid equilibrium curve were preliminarily fitted with weights equal to the reciprocal of the number of points in each set. In this way, the effect of different number of data points contained in particular data sets was cancelled. Mean relative (i.e., systematic) deviation of each particular data set provides an idea of how the set is shifted as a whole with respect to the common average values represented by the preliminary correlation. Data points with excessive deviation exceeding three times the obtained root mean square deviation (3σ) were rejected. In this way the experimental data were divided into two categories: primary data employed in the development of the correlation and secondary data used only for comparison purposes. The sources of the assessed sets of experimental data are listed in Tables 3 and 4. The number of points used for fitting is given in the tables for the primary data sets while for the secondary data

it is equalled to zero. Only original unsmoothed experimental data were included in the data used for fitting of the empirical equations.

A stepwise least-square regression technique by de Reuck [25] has been applied in the present work to determine the optimal set of polynomial terms to be incorporated into the fitting function. The procedure ensures statistical significance of the polynomial terms included and randomness of the deviations of the experimental data from values calculated from the resultant equation.

Conde [1] and Monnin et al. [2] have rejected from their fits the data by Schimmel [19] in the pentahydrate region of the LiCl–H₂O system, while the points of Hüttig and Steudemann [4] they have accepted here. As a matter of fact there is no well-grounded reason to reject these data of Schimmel. In comparison with the data of Hüttig and Steudemann [4], they show less or comparable scatter and less systematic deviation on all branches of the equilibrium curve belonging to other hydrates. When included into extrapolation, the data of Schimmel [19] result in lower eutectic temperature.

4. Methodology

It is the usual way to determine the coordinates of the two-solids saturation point from the intersection of the fits of the adjoining solubility curves (Conde [1], Monin et al. [2]). This procedure, though simple and plausible, brings some difficulties. With limited number of data points, the resultant intersection of the fitting curves can in some cases substantially depend on the choice of independent variable, i.e. whether the T - x data are fitted as a $T(x)$ or an $x(T)$ function. This can be demonstrated by comparison of the results obtained by Conde [1] and by Monin

Table 4

Sources of data on the T - x relation of the LiCl–H₂O system at solid–liquid equilibrium

Author(s)	Year	Range of values		Number of data total/used
		Temperature (K)	Mass fraction (wt.%)	
Kremers [40]	1856	273–433	38–59	6/5
Kremers [41]	1858	313–373	48–58	5/5
Arrhenius [42]	1888	271–273	0.4–1.9	4/0
Engel [43]	1888	273	40.5	1/1
Bogorodski [3]	1893	294	48	1/0
Loomis [44]	1897	271–273	0.04–2	6/5
Biltz [26]	1902	270–273	0.2–3.3	4/4
Jahn [45]	1905	272–273	0.1–1.2	9/9
Cheneveau [46]	1907	292	43.4	1/0
Jahn [47]	1907	272–273	0.03–0.44	8/8
Washburn and MacInnes [48]	1911	269–272	1.4–4	5/5
Piña de Rubies [49]	1913	298	44.9	1/0
Rivett [50]	1913	268–273	0.5–4.8	7/7
Rodebush [51]	1918	249–268	5–19	4/0
Schreinemakers and Kayser [52]	1918	303	46.1	1/1
Schreinemakers and Noorduyn [53]	1918	303	46.3	1/1
Klein and Svandberg [54]	1920	271–273	0.4–2	3/0
Demassieux [55]	1923	323	49.6	1/1
Hüttig and Reuscher [12]	1924	273–433	39–59	12/11
Smits et al. [56]	1924	298	45.8	1/1
Deacon [57]	1927	298	45.4	1/1
Hüttig and Steudemann [4]	1927	193–374	25–56	5/3
Steudemann [29]	1927	199–268	19–39	14/8
Palitzsch [58]	1928	298	45.77	2/2
Friend and Colley [59]	1931	273–361	41–55	21/21
Bassett and Sanderson [60]	1932	273–353	41–53	4/4
Benrath [13]	1932	273–373	41–56	12/12
Collins and Cameron [61]	1932	297	45.4	1/1
Pearce and Nelson [62]	1932	298	44.9	1/1
Scatchard and Prentiss [31]	1933	268–273	0.003–5	33/0
Applebey et al. [14]	1934	275–429	41–58	15/15
Lannung [63]	1934	291	45.48	1/0
Benrath [64]	1934	273–372	40–56	5/5
Simmons et al. [32]	1936	298	45.9	1/1
Friend et al. [65]	1937	345–427	52–59	18/18
Voskresenskaya and Yanateva [15]	1937	207–375	4–57	33/16
Benrath [66]	1938	273–373	41–56	4/4
Birnthaler and Lange-Erlangen [33]	1938	298	45.8	1/1
Robinson [67]	1945	298	45.83	1/1
Garrett and Woodruff [8]	1951	200	25	1/1
Johnson and Molstad [68]	1951	303–343	46–51	3/3
Novoselova and Sosnovskaja [69]	1951	273	41.3	1/1
Blidin [70]	1952	298	46	2/2
Blidin [71]	1953	303–313	45–48	2/1
Blidin [72]	1954	298–313	46–49	5/4
Blidin and Gordienko [73]	1954	298	45.95	1/1
Campbell and Griffiths [17]	1956	276–298	41–45	4/4
Campbell and Kartzmark [74]	1956	298	45.4	1/1
Moran [18]	1956	197	25	1/0
Plyushchev et al. [75]	1959	273–348	41–52	4/4
Schimmel [19]	1960	195–285	13–43	35/30
Vuillard and Kessiss [20]	1960	198	25	1/1
Kessiss [21]	1961	207–333	29–50	24/23
Akopov [22]	1962	198–371	25–48	9/4
Ravitch and Yastrebova [76]	1963	523–829	62–93	11/11
Hasaba et al. [77]	1964	253–433	36–59	19/14
Belyaev and Tyuk [78]	1966	298	45.6	1/1
Sheveleva [79]	1966	293–323	45.5–45.9	2/1
Shevtchuk and Vaisfeld [80]	1967	298	46.6	1/1
Momicchioli et al. [81]	1970	267–270	0.06–14.2	22/22
Vilcu and Irenei [82]	1971	258–267	6–11	6/6
Ennan and Lapshin [10]	1973	206	24.1	1/1

Table 4 (Continued)

Author(s)	Year	Range of values		Number of data total/used
		Temperature (K)	Mass fraction (wt.%)	
Gibbard and Fawaz [83]	1974	267–273	0.2–5.7	16/13
Skvortsov [84]	1975	293–303	45.4–46.2	2/2
Filipov and Mikelson [85]	1977	298–308	45–47	2/2
Kartzmark [86]	1977	298	45.4	1/1
Vaisfeld et al. [87]	1977	298	44.9	1/0
Lazorenko et al. [88]	1982	298–373	46–56	4/3
Sharina et al. [89]	1983	273	40.9	1/1
Claudy et al. [90]	1984	203–258	13–34	12/2
Khripun et al. [91]	1986	298	45.9	1/1
Apelblat [92]	1993	283–313	45–47	7/6
Gomis et al. [93]	1996	298	46	1/1

et al. [2]. Three data points from the data set of Kessiss [21] and three data points of Schimmel [19] fall into the composition interval corresponding to pentahydrate as found by Conde, while according to results by Monnin et al. the some data points belong to the trihydrate region. To avoid such ambiguities, a procedure was used, optimizing simultaneously the $T(x)$ and $x(T)$ equations as independent in such a way that within the data uncertainty both resultant equations generate the same T – x relation.

Polynomials of the following form have been used to fit the data:

$$T(x) = T_L + \frac{T_R - T_L}{x_R - x_L}(x - x_L) + T_t \sum_{i=1}^N a_i (x - x_L)^{m_i} (x_R - x)^{n_i}, \quad (3)$$

$$x(T) = x_L + \frac{x_R - x_L}{T_R - T_L}(T - T_L) + \sum_{i=1}^N b_i \left(\frac{T - T_L}{T_t} \right)^{m_i} \times \left(\frac{T_R - T}{T_t} \right)^{n_i}, \quad (4)$$

containing explicitly the temperatures T_L and T_R and compositions x_L and x_R of the transition points between hydrates. The subscripts L and R denote here the left and right endpoints of the interval, respectively. To introduce a dimensionless temperature variable and to make the coefficients a_i and b_i dimensionless, the water triple point temperature $T_t = 273.16$ K was arbitrarily selected as the reference temperature value. The optimal coordinates of the transition points were found using a simultaneous minimizing of the mean square deviation of the least square

Table 5
Coefficients and exponents of Eq. (3) for the LiBr–H₂O system

<i>i</i>	LiBr–5H ₂ O ^a			LiBr–3H ₂ O ^b		
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>
1	2.61161×10^1	1	1	2.47039×10^1	1	1
2	2.38994×10^4	1	3	4.65459×10^3	1	3
<i>i</i>	LiBr–2H ₂ O ^c			LiBr–H ₂ O ^d		
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>
1	1.62375×10^1	1	1	1.00743×10^1	1	1
2	2.47098×10^3	1	3	3.94593×10^3	1	4
<i>i</i>	Ice ^e					
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>			
1	1.33842×10^1	1	1			
2	-4.39293×10^1	2	1			
3	4.02577×10^3	3	1			
4	-5.52364×10^4	4	1			
5	3.28383×10^5	5	1			

^a $T_L = 202.8$ K, $T_R = 222.4$ K, $x_L = 0.1175$, $x_R = 0.1604$.

^b $T_L = 222.4$ K, $T_R = 277.1$ K, $x_L = 0.1604$, $x_R = 0.2213$.

^c $T_L = 277.1$ K, $T_R = 322.2$ K, $x_L = 0.2213$, $x_R = 0.2869$.

^d $T_L = 322.2$ K, $T_R = 429.15$ K, $x_L = 0.2869$, $x_R = 0.4613$.

^e $T_L = 273.16$ K, $T_R = 202.8$ K, $x_L = 0.0000$, $x_R = 0.1175$.

Table 6

Coefficients and exponents of Eq. (4) for the LiBr–H₂O system

<i>i</i>	LiBr–5H ₂ O ^a			LiBr–3H ₂ O ^b		
	<i>b_i</i>	<i>m_i</i>	<i>n_i</i>	<i>b_i</i>	<i>m_i</i>	<i>n_i</i>
1	-6.17446×10^0	1	1	-7.17618×10^{-1}	1	1
2	-1.46770×10^3	3	1	$-1.02551 \times 10^{+1}$	3	1
<i>i</i>	LiBr–2H ₂ O ^c			LiBr–H ₂ O ^d		
	<i>b_i</i>	<i>m_i</i>	<i>n_i</i>	<i>b_i</i>	<i>m_i</i>	<i>n_i</i>
1	-1.06305×10^0	1	1	-9.25082×10^{-1}	1	1
2	-1.90921×10^1	3	1	-7.22341×10^0	3	1
<i>I</i>	Ice ^e					
	<i>b_i</i>	<i>m_i</i>	<i>n_i</i>			
1	1.22335×10^0	1	1			
2	-1.67781×10^0	1	2			
3	-2.65346×10^2	1	4			
4	-1.93594×10^3	1	5			
5	-5.16209×10^3	1	6			

^a $T_L = 202.8$ K, $T_R = 222.4$ K, $x_L = 0.1175$, $x_R = 0.1604$.^b $T_L = 222.4$ K, $T_R = 277.1$ K, $x_L = 0.1604$, $x_R = 0.2213$.^c $T_L = 277.1$ K, $T_R = 322.2$ K, $x_L = 0.2213$, $x_R = 0.2869$.^d $T_L = 322.2$ K, $T_R = 429.15$ K, $x_L = 0.2869$, $x_R = 0.4613$.^e $T_L = 273.16$ K, $T_R = 202.8$ K, $x_L = 0.0000$, $x_R = 0.1175$.

fit of the Eqs. (3) and (4) to the experimental data. For each given set of values of the transition point coordinates T_L , x_L , T_R , and x_R the coefficients a_i and b_i of the optimal fitting polynomial and the corresponding mean square deviation of the least square fit were computed. Those values of the parameters T_L , x_L , T_R and x_R that minimize the mean square deviation were

accepted as the best estimate of the coordinates of the transition points. In this way, the method guarantees that the resultant transition points will not depend on the choice of the independent variable.

To start the optimizing procedure, the two-solids points found by Conde [1] were employed. Of course, the obtained final

Table 7

Coefficients and exponents of Eq. (3) for the LiCl–H₂O system

<i>i</i>	LiCl–5H ₂ O ^a			LiCl–3H ₂ O ^b		
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>
1	4.84382×10^1	1	1	2.82060×10^1	1	1
2	-6.09630×10^2	2	1	7.38829×10^3	1	3
<i>i</i>	LiCl–2H ₂ O ^c			LiCl–H ₂ O ^d		
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>
1	1.85930×10^1	1	1	1.42944×10^1	1	1
2	3.41697×10^3	1	3	1.10409×10^3	1	3
<i>i</i>	LiCl ^e			Ice ^f		
	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>	<i>a_i</i>	<i>m_i</i>	<i>n_i</i>
1	5.51421×10^0	3	1	1.21511×10^1	1	1
2	1.00361×10^1	1	2	3.84172×10^6	2	6
3	9.78161×10^1	1	7	1.78237×10^3	3	1
4				-6.26807×10^7	6	2
5				1.16751×10^{11}	8	3

^a $T_L = 195.0$ K, $T_R = 206.0$ K, $x_L = 0.1260$, $x_R = 0.1482$.^b $T_L = 206.0$ K, $T_R = 253.7$ K, $x_L = 0.1482$, $x_R = 0.2038$.^c $T_L = 253.7$ K, $T_R = 293.1$ K, $x_L = 0.2038$, $x_R = 0.2605$.^d $T_L = 293.1$ K, $T_R = 369.0$ K, $x_L = 0.2605$, $x_R = 0.3538$.^e $T_L = 369.0$ K, $T_R = 887.15$ K, $x_L = 0.3538$, $x_R = 1.0000$.^f $T_L = 273.16$ K, $T_R = 195.0$ K, $x_L = 0.0000$, $x_R = 0.1260$.

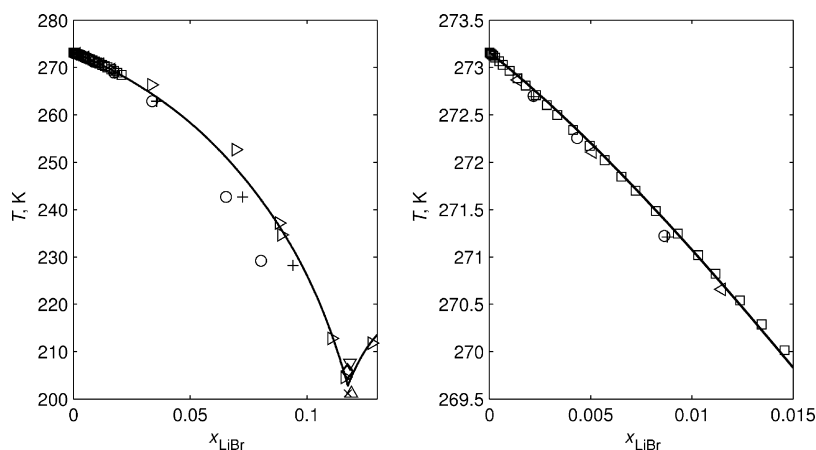


Fig. 2. Water-ice equilibrium curve for the LiBr–H₂O system. (▽) Biancifiiori [7], (<) Biltz [26], (Δ) Ennan and Lapshin [10], (×) Hüttig and Steudemann [4], (○) Jones and Getman [27], (+) Jones [28], (◇) Kessis [9], (□) Scatchard and Prentiss [31], (▷) Steudemann [29].

results are selfconsistent, i.e. when used as the starting values in the optimization of the two-solids point coordinates, the same values are reproduced by the procedure.

5. Results

Tables 5–8 give the coefficients a_i and b_i and the exponents n_i and m_i of Eqs. (3) and (4) for the LiBr–H₂O and LiCl–H₂O systems, respectively. The differences between Eqs. (3) and (4) are of the order of 0.1 K in temperature and of the order of 0.0001 in composition. The only exceptions are formed by the monohydrate region of the LiBr–H₂O system and by the anhy-

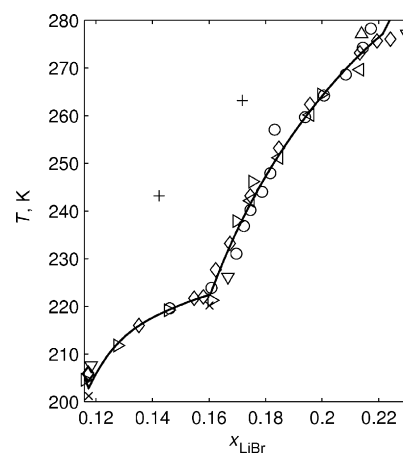


Fig. 3. The pentahydrate and trihydrate branches of the solid-liquid phase diagram of the LiBr–H₂O system. (▽) Biancifiiori [7], (Δ) Bogorodski [3], (○) Boryta [35], (×) Hüttig and Steudemann [4], (+) Jones [28], (▷) Steudemann [29], (◇) Kessis [9], (<) Peters et al. [37].

Table 8

Coefficients and exponents of Eq. (4) for the LiCl–H₂O system

i	LiCl–5H ₂ O ^a			LiCl–3H ₂ O ^b		
	b_i	m_i	n_i	b_i	m_i	n_i
1	-2.34477×10^2	2	1	-9.46096×10^{-1}	1	1
2	-4.40739×10^3	1	3	$-2.03875 \times 10^{+1}$	3	1
i	LiCl–2H ₂ O ^c			LiCl–H ₂ O ^d		
	b_i	m_i	n_i	b_i	m_i	n_i
1	-1.15613×10^0	1	1	-5.57535×10^{-1}	1	1
2	-2.78454×10^1	3	1	-4.01877×10^0	3	1
i	LiCl ^e			Ice ^f		
	b_i	m_i	n_i	b_i	m_i	n_i
1	-1.52782×10^{-1}	1	1	1.28989×10^1	3	1
2	8.24563×10^{-3}	9	4	-1.22492×10^1	1	2
3	-6.23202×10^{-2}	3	2	1.21810×10^5	6	3
4	8.28259×10^{-3}	2	5	-1.03126×10^3	2	4
5	1.79910×10^{-2}	6	5			

^a $T_L = 195.0$ K, $T_R = 206.0$ K, $x_L = 0.1260$, $x_R = 0.1482$.

^b $T_L = 206.0$ K, $T_R = 253.7$ K, $x_L = 0.1482$, $x_R = 0.2038$.

^c $T_L = 253.7$ K, $T_R = 293.1$ K, $x_L = 0.2038$, $x_R = 0.2605$.

^d $T_L = 293.1$ K, $T_R = 369.0$ K, $x_L = 0.2605$, $x_R = 0.3538$.

^e $T_L = 369.0$ K, $T_R = 887.15$ K, $x_L = 0.3538$, $x_R = 1.0000$.

^f $T_L = 273.16$ K, $T_R = 195.0$ K, $x_L = 0.0000$, $x_R = 0.1260$.

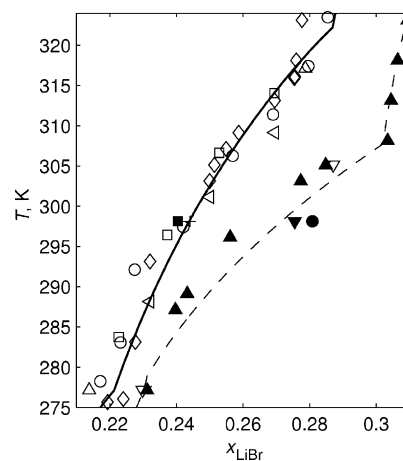


Fig. 4. The dihydrate branch of the solid-liquid phase diagram of the LiBr–H₂O system. (▽) Biancifiiori [7], (+) Birnthal and Lange-Erlangen [33], (▼) Blidin [34], (Δ) Bogorodski [3], (○) Boryta [35], (▲) Hüttig and Reuscher [12], (×) Hüttig and Steudemann [4], (◇) Kessis [9], (<) Peters et al. [37], (□) Raatschen [36], (■) Scott and Durham [30], (●) Simmons et al. [32], (---) Broul et al. [11].

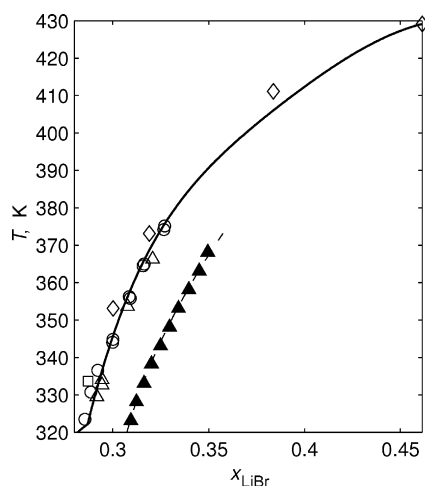


Fig. 5. The monohydrate branch of the solid-liquid phase diagram of the LiBr-H₂O system. (○) Boryta [35], (▲) Hüttig and Reuscher [12], (◇) Kessiss [9], (△) Murakami and Kondo [39], (□) Raatschen [36], (---) Broul et al. [11].

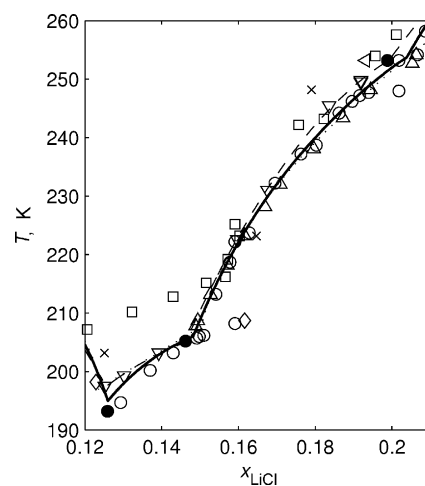


Fig. 7. The pentahydrate and trihydrate branches of the solid-liquid phase diagram of the LiCl-H₂O system. (◇) Akopov [22], (×) Claudy et al. [90], (◁) Hasaba et al. [77], (●) Hüttig and Steudemann [4], (△) Kessiss [21], (○) Schimmel [19], (▽) Steudemann [29], (□) Voskresenskaya and Yanateva [15], (---) Conde [1], (····) Monnin et al. [2].

hydrate region for the LiCl-H₂O system, where the differences are by one order of magnitude greater. The obtained coordinates of the two-solids points are given in Tables 1 and 2. In Figs. 2–5, T - x experimental data points are depicted together with solid-liquid equilibrium curves computed from the resultant representative equations (3) for the LiBr-H₂O system. Analogous information is shown in Figs. 6–10 for the LiCl-H₂O system.

The absolute and relative root mean square deviations of the experimental data from the Eqs. (3) and (4) are given for the LiBr-H₂O and the LiCl-H₂O system in the Tables 9 and 10, respectively. The deviations give an idea of the scatter in the data around the fitted curves and through it an idea of the uncertainty of the temperature and molar fraction when calculated from the model.

Table 9
LiBr-H₂O system

Solid phases	$T(x)$, Eq. (3)		$x(T)$, Eq. (4)	
	RMSD (K)	RMSD% (%)	RMSD	RMSD% (%)
Ice	1.0	0.45	0.0017	5.3
LiBr-5H ₂ O	0.2	0.10	0.0008	0.5
LiBr-3H ₂ O	1.9	0.76	0.0022	1.1
LiBr-2H ₂ O	2.5	0.83	0.0040	1.5
LiBr-H ₂ O	3.9	1.10	0.0037	1.1

Absolute (RMSD) and relative (RMSD%) root mean square deviations of the experimental T - x data from Eqs. (3) and (4).

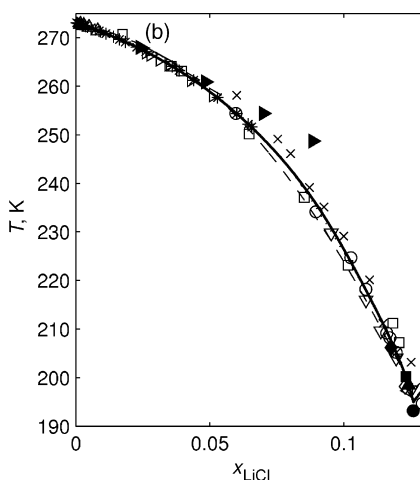
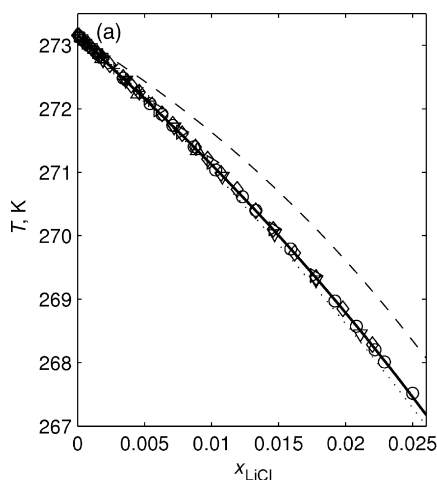


Fig. 6. Water-ice equilibrium curve for the LiCl-H₂O system. (a) (○) Gibbard and Fawaz [83], (*) Jahn [45], (□) Jahn [28], (△) Klein and Svandberg [54], (+) Loomis [44], (▽) Rivett [50], (◇) Scatchard and Prentiss [31], (▷) Washburn and MacInnes [48]. (b) (◇) Akopov [22], (△) Arrhenius [42], (+) Biltz [26], (×) Claudy et al. [90], (◆) Ennan and Lapshin [10], (■) Garrett and Woodruff [8], (●) Hüttig and Steudemann [4], (*) Momicchioli et al. [81], (◁) Moran [18], (○) Schimmel [19], (▽) Steudemann [29], (▷) Vilcu and Irenei [82], (□) Voskresenskaya and Yanateva [15], (▲) Vuillard and Kessiss [20], (▶) Rodebush [51], (---) Conde [1], (····) Monnin et al. [2].

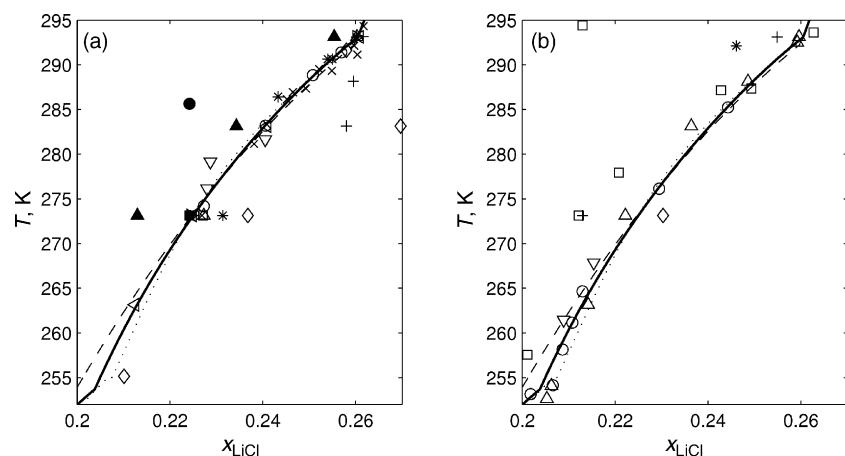


Fig. 8. The dihydrate branch of the solid–liquid phase diagram of the LiCl–H₂O system. (a) (◇) Akopov [22], (+) Apelblat [92], (○) Applebey et al. [14], (□) Bassett and Sanderson [60], (*) Benrath [13], (▷) Benrath [64], (Δ) Benrath [66], (▽) Campbell and Kartzmark [74], (■) Engel [43], (×) Friend and Colley [59], (◁) Hasaba et al. [77], (▲) Hüttig and Reuscher [12], (●) Hüttig and Steudemann [4]. (b) (*) Cheneveau [46], (Δ) Kessis [21], (+) Kremers [40], (◇) Novoselova and Sosnovskaya [69], (▷) Plyushchev et al. [75], (○) Schimmel [19], (▽) Steudemann [29], (□) Voskresenskaya and Yanateva [15], (---) Conde [1], (····) Monnin et al. [2].

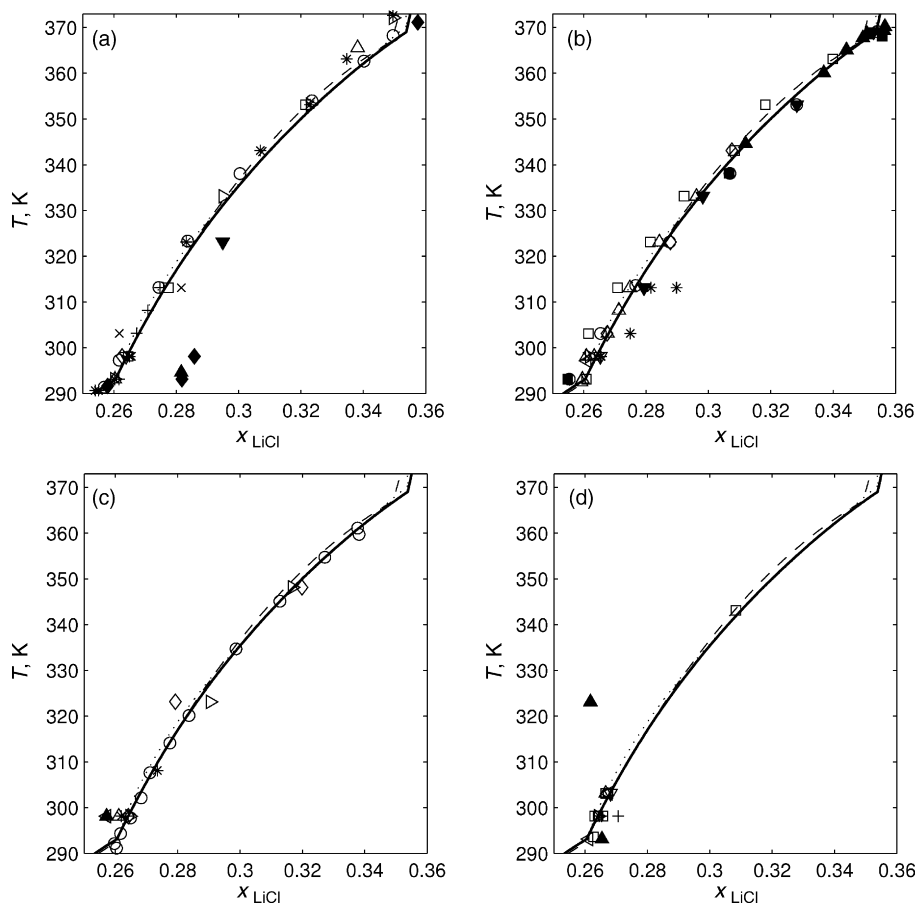


Fig. 9. The monohydrate branch of the solid–liquid phase diagram of the LiCl–H₂O system. (a) (◆) Akopov [22], (+) Apelblat [92], (○) Applebey et al. [14], (□) Bassett and Sanderson [60], (◇) Belyaev and Tyuk [78], (*) Benrath [13], (▷) Benrath [64], (Δ) Benrath [66], (▽) Birnthal and Lange-Erlangen [33], (×) Blidin [70], (◁) Blidin [71], (▲) Bogorodski [3], (▼) Demassieux [55]. (b) (+) Blidin [72], (*) Blidin and Gordienko [73], (×) Campbell and Griffiths [17], (▷) Campbell and Kartzmark [74], (◁) Collins and Cameron [61], (Δ) Deacon [57], (▲) Friend et al. [65], (□) Hasaba et al. [77], (○) Hüttig and Reuscher [12], (◇) Johnson and Molstad [68], (Δ) Kessis [21], (▽) Khripun et al. [91], (■) Kremers [40], (▼) Kremers [41], (○) Filipov and Mikelson [85], (○) Friend and Colley [59], (+) Gomis et al. [93], (Δ) Kartzmark [86], (◇) Lazorenko et al. [88], (▲) Pearce and Nelson [62], (▷) Plyushchev et al. [75], (◁) Vaisfeld et al. [87], (d) (*) Robinson [67], (▲) Sheveleva [79], (+) Shevtchuk and Vaisfeld [80], (Δ) Schreinemakers and Kayser [52], (×) Simmons et al. [32], (◁) Skvortsov [84], (▷) Smits et al. [56], (▽) Schreinemakers and Noorduyn [53], (□) Voskresenskaya and Yanateva [15], (---) Conde [1], (····) Monnin et al. [2].

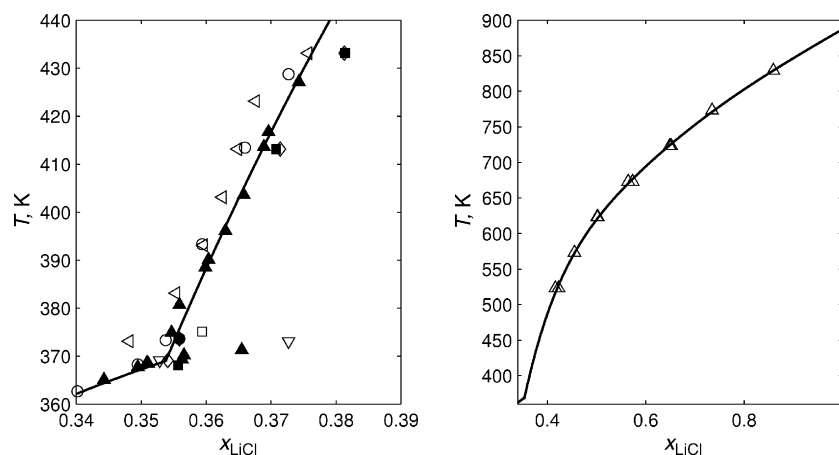


Fig. 10. The pure solid LiCl branch of the solid–liquid phase diagram of the LiCl–H₂O system. (○) Applebey et al. [14], (▲) Friend et al. [65], (◁) Hasaba et al. [77], (◇) Hüttig and Reuscher [12], (●) Hüttig and Steudemann [4], (■) Kremers [40], (▼) Kremers [41], (△) Ravitch and Yastrebova [76], (□) Voskresenskaya and Yanateva [15], (---) Conde [1], (···) Monnin et al. [2].

Table 10
LiCl–H₂O system

Solid phases	$T(x)$, Eq. (3)		$x(T)$, Eq. (4)	
	RMSD (K)	RMSD% (%)	RMSD	RMSD% (%)
Ice	0.06	0.03	0.0001	2.4
LiCl–5H ₂ O	1.1	0.58	0.0022	1.6
LiCl–3H ₂ O	1.4	0.60	0.0019	1.0
LiCl–2H ₂ O	1.7	0.62	0.0028	1.2
LiCl–H ₂ O	2.7	0.85	0.0039	1.2
LiCl	5.7	1.40	0.0030	0.7

Absolute (RMSD) and relative (RMSD%) root mean square deviations of the experimental T – x data from Eqs. (3) and (4).

6. Conclusion

Two sets of empirical equations describing solid–liquid boundary for LiBr–H₂O and LiCl–H₂O systems has been developed based upon a body of critically assessed experimental data. Temperature and composition of the liquid phase corresponding to the two-solids saturation points were derived from the data. To obtain unambiguous coordinates of the transition points a method based on combined linear and non-linear optimization procedure was used. The experimental solid–liquid equilibrium data are available in the full composition range for LiCl–H₂O system and up to the molar fraction $x=0.46$ for LiBr–H₂O corresponding to transition from monohydrate to anhydrate. The description of the solid–liquid boundary is based on data obtained by many different authors using at least four different methods. Therefore common systematic error in the data can be considered as negligible. The relative uncertainties associated with correlation can be estimated exclusively on the regression statistic (Tables 9 and 10) to be near $\pm 1\%$ both for temperature and composition.

Comparisons of the available measurements on the solid–liquid equilibrium of the LiBr–H₂O and LiCl–H₂O systems have shown that the amount of available experimental data is far less valuable to establish a description of that property of the systems than it might appear at a first glance. Some of

the available sets of the solid–liquid equilibrium data are only of limited value, because they show large scatter or systematic deviations when compared to other data. The largest gap in the data on the LiCl–H₂O system is clearly found at the region of compositions corresponding to saturated solution in equilibrium with pentahydrate. The LiBr–H₂O system is generally much less studied compared to the LiCl–H₂O system. No data are available for solutions in phase equilibrium with anhydrous LiBr.

List of symbols

a_i	coefficients of the fitting polynomial
b_i	coefficients of the fitting polynomial
m	molality (mol kg ^{−1})
m_i	exponents of the fitting polynomial
M	molar mass (kg mol ^{−1})
n	degree of a polynomial term
n_i	exponents of the fitting polynomial
N	number of the fitting polynomial terms
RMSD	absolute root mean square deviation $\text{RMSD} = [(1/N) \sum (z_{\text{exp}} - z_{\text{cal}})^2]^{1/2}$
RMSD%	relative root mean square deviation (%) $\text{RMSD}\% = 100[(1/N) \sum (z_{\text{exp}}/z_{\text{cal}} - 1)^2]^{1/2}$
t	temperature (°C)
T	temperature (K)
w	mass fraction of salt in the solution
x	molar fraction of salt in the solution

Subscripts

L	left endpoint of the hydrate interval
R	right endpoint of the hydrate interval
t	at triple point

Physical constants

$M_{\text{H}_2\text{O}}$	0.018015268 kg mol ^{−1}
M_{LiBr}	0.08685 kg mol ^{−1}
M_{LiCl}	0.04239 kg mol ^{−1}
T_t	273.16 K

Acknowledgement

The work described in this paper has been performed under the research intention No. AV0Z20760514 awarded by the Academy of Sciences of the Czech Republic.

References

- [1] M.R. Conde, *Int. J. Therm. Sci.* 43 (2004) 367–382.
- [2] Ch. Monnin, M. Dubois, N. Papaiconomou, J.P. Simonin, *J. Chem. Eng. Data* 47 (2002) 1331–1336.
- [3] A.Ya. Bogorodski, *J. Russ. PhysChem. Soc.* 25 (1893) 318–342.
- [4] G.F. Hüttig, W. Steudemann, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 126 (1927) 105–117.
- [5] International Critical Tables of Numerical Data, Physics, Chemistry and Technology, 1st ed., vol. III, McGraw-Hill Book Company, New York, 1928.
- [6] J.R. Heiks, A.B. Garrett, *J. Am. Chem. Soc.* 76 (1954) 2587–2590.
- [7] M.A. Biancifiore, *Termotechnica* 17 (1963) 437–444.
- [8] A.B. Garrett, S.A. Woodruff, *J. Phys. Colloid Chem.* 55 (1951) 477–490.
- [9] J.J. Kessiss, *Bull. Soc. Chim. Fr.* (1964) 48–52.
- [10] A.A. Ennan, V.A. Lapshin, *Zh. Struk. Khim.* 14 (1973) 21–29.
- [11] M. Broul, J. Nývlt, O. Söhnel, *Solubility in Organic Compounds, Physical Science Data* 6, Elsevier, Amsterdam, 1981.
- [12] G.F. Hüttig, F. Reuscher, *Z. Anorg. Allg. Chem.* 137 (1924) 155–180.
- [13] H. Benrath, *Z. Anorg. Allg. Chem.* 205 (1932) 417–424.
- [14] M.P. Applebey, F.H. Crawford, K. Gordon, *J. Chem. Soc.* 136 (1934) 1665–1671.
- [15] N.K. Voskresenskaya, O.K. Yanateva, *Izv. Akad. Nauk. SSSR, Otd. Mat. Estestv. Nauk., Ser. Khim.* 1 (1937) 97–121.
- [16] M.P. Applebey, R.P. Cook, *J. Chem. Soc.* 140 (1938) 547.
- [17] A.N. Campbell, J.E. Griffiths, *Can. J. Chem.* 34 (1956) 1647–1661.
- [18] H.E. Moran, *J. Phys. Chem.* 60 (1956) 1666–1667.
- [19] F.A. Schimmel, *J. Chem. Eng. Data* 5 (1960) 519–520.
- [20] G. Vuillard, J.J. Kessiss, *Bull. Soc. Chim. Fr.* 28 (1960) 2063–2067.
- [21] J.J. Kessiss, *Bull. Soc. Chim. Fr.* 29 (1961) 1503–1504.
- [22] E.K. Akopov, *Zh. Neorg. Khim.* 7 (1962) 385–388.
- [23] T.B. Coplen, *J. Phys. Chem. Ref. Data* 30 (2001) 701–712.
- [24] W. Wagner, A. Pruß, *J. Phys. Chem. Data* 31 (2002) 387–535.
- [25] K.M. de Reuck, *Cryogenics* 19 (1979) 505–512.
- [26] W. Biltz, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 49 (1902) 185–221.
- [27] H.C. Jones, F.H. Getman, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 49 (1904) 385–455.
- [28] H.C. Jones, *Carnegie Publication No. 60*, Washington, DC, 1907.
- [29] W. Steudemann, *Die thermische Analyse der Systeme des Wassers mit den Lithiumhalogeniden*, Jena, 1927.
- [30] A.F. Scott, E.J. Durham, *J. Phys. Chem.* 34 (1930) 531–537.
- [31] G. Scatchard, S.S. Prentiss, *J. Am. Chem. Soc.* 55 (1933) 4355–4362.
- [32] J.P. Simmons, H. Freimuth, H. Russell, *J. Am. Chem. Soc.* 58 (1936) 1692–1695.
- [33] W. Birnthal, E. Lange-Erlangen, *Z. Elektrochem., Ber. Bunsen-Ges. Phys. Chem.* 44 (1938) 679–693.
- [34] V.P. Blidin, *Zh. Obsch. Khim.* 17 (1947) 1590–1594.
- [35] D.A. Boryta, *J. Chem. Eng. Data* 15 (1970) 142–144.
- [36] W. Raatschen, *Thermophysikalische Eigenschaften von Methanol/Wasser-Lithiumbromid Lösungen*, Aachen, 1985.
- [37] R. Peters, R. Busse, J.U. Keller, *Int. J. Thermophys.* 14 (1993) 763–775.
- [38] K. Murakami, *Proceedings of the Asian Conference on Refrigeration and Air Conditioning*, Kobe, Japan, 2002.
- [39] K. Murakami, N. Kondo, *Proceedings of the Fifteenth Symposium on Thermophysical Properties*, Boulder, CO, USA, 2003.
- [40] P. Kremers, *Ann. Phys. Chem.* 99 (1856) 25–57.
- [41] P. Kremers, *Ann. Phys. Chem.* 103 (1858) 57–68.
- [42] S. Arrhenius, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 2 (1888) 491–505.
- [43] M. Engel, *Ann. Chim. Phys.* 13 (1888) 370–387.
- [44] E.H. Loomis, *Ann. Phys. Chem.* 60 (1897) 523–546.
- [45] H. Jahn, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 50 (1905) 129–168.
- [46] Cheneveau, *Ann. Chim. Phys.* 12 (1907) 145–228.
- [47] H. Jahn, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 59 (1907) 31–40.
- [48] E.W. Washburn, D.A. MacInnes, *J. Am. Chem. Soc.* 33 (1911) 1686–1713.
- [49] S. Piña de Rubies, *An. Soc. Esp. Fis. Quim.* 11 (1913) 422–435.
- [50] A.C.D. Rivett, *Z. Phys. Chem. Stöchiom. Verwandtschaftsl.* 82 (1913) 253–254.
- [51] W.H. Rodebush, *J. Am. Chem. Soc.* 40 (1918) 1204–1213.
- [52] F.A. Schreinemakers, G.M.A. Kayser, *Chem. Weekblad* 15 (1918) 120–121.
- [53] F.A. Schreinemakers, A.C. Noorduy, *Chem. Weekblad* 15 (1918) 118–120.
- [54] O. Klein, K. Svanberg, *Sven. Vetenskapsakad. Medd. Nobel-inst.* 4 (1920) 13.
- [55] M.N. Demassieux, *Ann. Chim.* 20 (1923) 233–296.
- [56] A. Smits, J. Elgersma, M.E. Hardenberg, *Rec. Trav. Chim. Pays-Bas* 43 (1924) 671–677.
- [57] G.E.R. Deacon, *J. Chem. Soc.* 129 (1927) 2063–2065.
- [58] S. Palitzsch, *Z. Phys. Chem. Abt. A* 138 (1928) 379–398.
- [59] J.A.N. Friend, A.T.W. Colley, *J. Chem. Soc.* 133 (1931) 3148–3149.
- [60] H. Bassett, I. Sanderson, *J. Chem. Soc.* 134 (1932) 1855–1865.
- [61] S.C. Collins, F.K. Cameron, *J. Chem. Soc.* 32 (1932) 1705–1716.
- [62] J.N. Pearce, A.F. Nelson, *J. Am. Chem. Soc.* 54 (1932) 3544–3555.
- [63] A. Lannung, *Z. Phys. Chem. Abt. A* 170 (1934) 134–144.
- [64] H. Benrath, *Z. Anorg. Allg. Chem.* 220 (1934) 145–153.
- [65] J.N. Friend, R.W. Hale, S.E.A. Ryder, *J. Chem. Soc.* 139 (1937) 970.
- [66] H. Benrath, *Z. Anorg. Allg. Chem.* 240 (1938) 87–96.
- [67] R.A. Robinson, *Trans. Faraday Soc.* 41 (1945) 756–758.
- [68] E.J. Johnson, M.C. Molstad, *J. Phys. Colloid Chem.* 55 (1951) 257–281.
- [69] A.V. Novoselova, G. Sosnovskaya, *Zh. Obsch. Khim.* 21 (1951) 813–817.
- [70] V.P. Blidin, *Dokl. Akad. Nauk. SSSR* 84 (1952) 947–950.
- [71] V.P. Blidin, *Dokl. Akad. Nauk. SSSR* 88 (1953) 457–459.
- [72] V.P. Blidin, *Izv. Akad. Nauk. SSSR Ser. Khim.* (1954) 400–409.
- [73] V.P. Blidin, V.I. Gordienko, *Dokl. Akad. Nauk. SSSR* 94 (1954) 1081–1084.
- [74] A.N. Campbell, E.M. Kartzmark, *Can. J. Chem.* 34 (1956) 672–678.
- [75] V.E. Plyushchev, G.P. Kuznetsova, S.B. Stepina, *Zh. Neorg. Khim.* 4 (1959) 1449–1453.
- [76] M.I. Ravitch, L.F. Yastrebova, *Zh. Neorg. Khim.* 8 (1963) 202–207.
- [77] S. Hasaba, T. Uemura, Y. Higuchi, *Refrigeration* 39 (1964) 636–650.
- [78] I.N. Belyaev, L.E. Tyuk, *Zh. Neorg. Khim.* 11 (1966) 1919–1925.
- [79] A.D. Sheveleva, *Uch. Zap. Permsk. Im. A.M. Gorkogo* (1966) 3–14.
- [80] V.G. Shevtchuk, M.I. Vaisfeld, *Zh. Neorg. Khim.* 12 (1967) 1064–1068.
- [81] F. Momicchioli, O. Devoto, G. Grandi, G. Cocco, *Ber. Bunsen-Ges. Phys. Chem.* 71 (1970) 59–66.
- [82] R. Vilcu, F. Irenei, *An. Univ. Bucuresti Chim.* 20 (1971) 103–111.
- [83] H.F. Gibbard, A. Fawaz, *J. Sol. Chem.* 3 (1974) 745–755.
- [84] V.G. Skvortsov, *Zh. Neorg. Khim.* 20 (1975) 3149–3151.
- [85] V.K. Filipov, K.N. Mikhelson, *Zh. Neorg. Khim.* 22 (1977) 1689–1694.
- [86] E.M. Kartzmark, *Can. J. Chem.* 55 (1977) 2792–2798.
- [87] M.I. Vaisfeld, M.K. Onishchenko, V.G. Shevtchuk, *Zh. Neorg. Khim.* 22 (1977) 1994–1998.
- [88] N.M. Lazorenko, N.N. Kisel, D.A. Storozhenko, V.G. Shevtchuk, *Zh. Neorg. Khim.* 27 (1982) 1575–1577.
- [89] A.S. Sharina, S.N. Tyutina, L.V. Chernykh, *Zh. Neorg. Khim.* 28 (1983) 3171–3173.
- [90] P. Claudy, J.M. Letoffe, J.J. Counieux, R. Cohen-Adad, *J. Therm. Anal.* 29 (1984) 423–431.
- [91] M.K. Khripun, A.Yu. Efimov, L.S. Lilitch, M.L. Kutuzova, *Zh. Neorg. Khim.* 31 (1986) 2659–2664.
- [92] A. Apelblat, *J. Chem. Therm.* 25 (1993) 63–71.
- [93] V. Gomis, F. Ruiz, J.C. Asensi, P. Cayuela, *Fluid Phase Equilib.* 119 (1996) 191–195.