THERMODYNAMIC PROPERTIES OF AQUEOUS MIXTURES OF LiCl AND Li₂SO₄ AT DIFFERENT TEMPERATURES

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Abstract

Emf measurements were made on the cell without liquid junction:

$$\text{Li-ISE LiCl}(m_1), \text{Li}_2\text{SO}_4(m_2)\ \text{Ag/AgCl}.$$

The performances of the electrode pairs constructed in our laboratory were tested and exhibited near-Nernstian behavior. The mean activity coefficients of LiCl for the system $\text{Li}^+\text{-Cl}^-\text{-SO}_4^{2-}\text{-H}_2\text{O}$ have been investigated by the emf values at temperatures of 0, 15, 35°C and constant total ionic strengths of 0.05, 0.1, 0.5, 1.0, 2.0, 3.0 and 5.0 mol·kg⁻¹. The activity coefficients decrease with increasing temperature and the ionic strength fraction of Li_2SO_4 in the mixtures. The thermodynamic properties are interpreted by use of Harned's empirical equations and Pitzer's ion interaction approach including the contribution of higher order electrostatic terms. The experimental results obey Harned's rule and are described by using Pitzer equations satisfactorily. The activity coefficients of Li_2SO_4, the osmotic coefficients and the excess free energies of mixing for the system in the experimental temperature range were reported.

Keywords: aqueous mixtures of LiCl and Li₂SO₄, thermodynamic properties

Introduction

In recent years, the ion-interaction model of Pitzer and co-workers has been successfully applied for predictions of thermodynamic properties and solubilities in sea water system (Na–K–Ca–Mg–Cl–SO₄–H₂O) of high ionic strengths and in wide temperature ranges from 0 to 300°C. A considerable number of thermodynamic data for the ternary subsystems of the sea water system at different temperatures have been reported [1–6].

However, the studies of thermodynamic properties for the salt lake system (Li–K–Na–Mg–Ca–Cl–SO₄–H₂O) and the ternary subsystem containing lith-
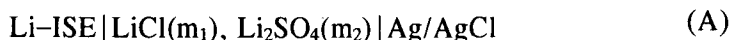
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ium ion at different temperatures are very rare. Filippov *et al.* studied the os-
motic coefficients and evaluated Pitzer parameters for the aqueous mixture of
Li$_2$SO$_4$–K$_2$SO$_4$ at 25°C [7]. Holmes reported the isopiestic studies of aqueous
solutions for the system NaCl–LiCl–H$_2$O at elevated temperatures [8]. In our
previous work, the investigations on the activity and osmotic coefficients at
25°C for the systems LiCl–MgCl$_2$–H$_2$O, Li$_2$SO$_4$–MgSO$_4$–H$_2$O, LiCl–KCl–H$_2$O
and LiCl–Li$_2$SO$_4$–H$_2$O by isopiestic and emf methods have been reported
[9–13]. The results by the emf method using a cell consisting of lithium ion-se-
lective electrode and silver –silver chloride for the system LiCl–Li$_2$SO$_4$–H$_2$O at
25°C are in good agreement with those by the isopiestic method, and indicate
the reliability of the emf method [13], but thermodynamic quantities for aque-
ous solutions of LiCl–Li$_2$SO$_4$ are rare at temperatures below and above 25°C.
Hence we extended and supplemented the emf measurements for a wider range
of temperatures.

Experimental

Deionized, redistilled water was used for preparing all solutions. Analytical
grade lithium chloride and lithium sulfate were recrystallized twice from the
distilled water. The concentrations of the stock solutions were determined by
gravimetric chloride and sulfate analysis for LiCl and Li$_2$SO$_4$ respectively, and
triplicate analyses were in agreement within ±0.05%. All cell solutions were
made by weighing the appropriate stock solutions and the redistilled water using
the Sartorius analytical electronic balance made in Germany. Weights were ac-
curate to ±0.0001 g. Also, all dilutions were made by use of weight burettes.
All the experimental solutions were saturated with AgCl.

The Ag/AgCl electrodes were the thermal electrode type, and were prepared
according to the directions given by Bates [14]. PVC membrane-Lithium ion se-
lective electrodes based on non-cyclic polyether trisamides were constructed in
our laboratory and its performance showed near-Nernstian behavior and good
selectivity [10, 13, 15], see Fig. 1.

The cell consisted of a Li ion-selective electrode and an Ag/AgCl electrode
in mixture of LiCl and Li$_2$SO$_4$ solutions placed in a double-walled glass vessel
whose temperature was maintained constant within ±0.02°C by circulation of
water from a thermostat, stirred magnetically at constant rate. The cell may be
represented as

$$\text{Li–ISE} \,|\, \text{LiCl}(m_1),\ \text{Li}_2\text{SO}_4(m_2) \,|\, \text{Ag/AgCl} \qquad\qquad \text{(A)}$$

The potentials of cell were measured from $I = 0.05$ to 5.0 mol·kg^{-1} at 0, 15,
35°C using an Orion Microprocessor Ionalyzer (model 901), reading directly
to 0.1 mV, and were recorded every 6 min until equilibrium was attained. Typi-

cally the emf remained constant with ±0.1 mV after 30 min of equilibrium at all ionic strengths.

More than three potential readings of cell A with molality of Li$_2$SO$_4$ equal to 0 mol·kg^{-1} were taken for mixed solutions at each ionic strength, and these potentials were plotted against lna_{LiCl} to calibrate the electrode pair of Li–ISE and Ag/AgCl. The activity coefficients of pure LiCl solutions at different temperatures were taken from [16]. The empirical standard potential E°, response slope k and the standard deviations for each ionic strength in all temperature range are shown in Fig. 1.

Results and discussion

Mean activity coefficients

The results of emf measurements in cell (A) along with the compositions of solutions are summarized in Table 2. Mean activity coefficients of LiCl ($\gamma_{\pm LiCl}$) in the mixtures are derived by the Nernst equation:

$$E = E^\circ + k\ln\left[a_{\pm LiCl}^2 + K_{Cl,SO_4}^{pot}\, a_{\pm LiCl}^{3/2}\right] \qquad (1)$$
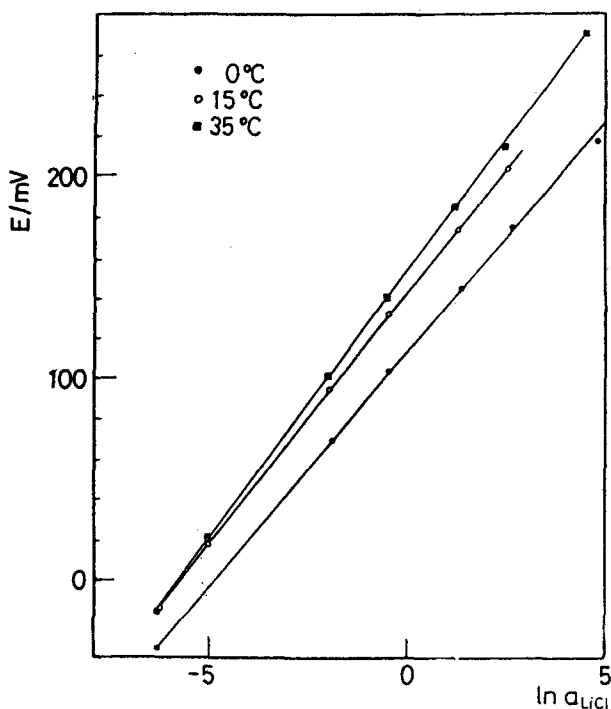

Fig. 1 Linear near-Nernstian response of the electrode pairs

where k is the Nernst slope and K is the selectivity coefficient of Ag/AgCl electrode for SO_4^{2-} ion. The values of K at 25°C reported in [13] were 1×10^{-4}. Therefore, the second term within brackets on the right side of Eq. (1) was neglected. Thus the experimental activity coefficients of LiCl at all ionic strengths and temperatures were calculated by Eq. (2):

$$E = E^\circ + k\ln\left[\gamma_{\pm LiCl}^2 \cdot m_1 \, (m_1 + 2m_2)\right] \quad (2)$$

The mean activity coefficients of LiCl at different values of y_B are also summarized in Table 2 where

Table 1 Results of calibration of electrode pairs at different temperature

I / mol·kg^{-1}	E°/mV	k	SD/mV
		0°C	
0.05	113.9	23.43	0.05
0.5	114.7	23.71	0.26
1.0	113.6	23.43	0.26
2.0	112.5	23.61	0.01
3.0	112.8	23.56	0.18
5.0	108.9	22.60	0.27
		15°C	
0.05	143.0	24.59	0.17
0.1	143.0	24.59	0.17
0.5	143.7	24.69	0.41
1.0	143.0	24.43	0.42
2.0	142.5	24.31	0.36
3.0	142.5	24.31	0.36
5.0	143.2	24.02	0.16
0.05–5.0	142.3	24.38	0.49
		35°C	
0.05	154.2	26.45	0.03
0.1	155.0	26.62	0.44
0.5	154.4	26.43	0.07
1.0	152.4	25.40	0.07
2.0	152.8	26.18	0.04
3.0	152.6	26.17	0.31
5.0	152.6	26.17	0.31
0.05–5.0	153.0	26.0	0.44

Table 2 Emf of cell A and mean activity coefficients of LiCl in mixtures from 0 to 35°C

I/mol·kg^{-1}	$y_{Li_2SO_4}$	E/mV	$\gamma_{\pm LiCl}$	I/mol·kg^{-1}	$y_{Li_2SO_4}$	E/mV	$\gamma_{\pm LiCl}$
				0°C			
	0.0	−35.0	0.8345		0.0	143.2	0.9585
	0.2079	−44.1	0.7916		0.2006	133.4	0.9006
0.05	0.4152	−50.5	0.8230	2.0	0.4003	122.0	0.8477
	0.6000	−62.6	0.8179		0.6016	106.9	0.7848
	0.7919	−79.4	0.8206		0.7990	84.8	0.7232
0.50	0.0	68.6	0.7536		0.0	174.4	1.2297
	0.1987	59.9	0.7280		0.2014	161.9	1.0948
	0.4014	50.8	0.7180	3.0	0.4003	148.5	0.9871
	0.5999	39.2	0.7159		0.6000	131.3	0.8729
	0.8001	19.6	0.7031		0.8001	107.8	0.7830
1.0	0.0	102.4	0.7918		0.0	217.8	2.2358
	0.2000	93.9	0.7615		0.2001	202.8	1.8489
	0.4011	84.2	0.7403	5.0	0.4000	185.8	1.5205
	0.5999	71.1	0.7145		0.6000	165.7	1.2421
	0.8000	50.2	0.6753		0.7997	138.0	0.9935
				15°C			
0.05	0.0	−12.8	0.8294		0.0	173.4	0.9363
	0.2024	−20.1	0.8309		0.2015	162.9	0.8802
	0.4362	−29.3	0.8120	2.0	0.4000	150.6	0.8189
	0.5989	−42.3	0.8184		0.6006	134.8	0.7547
	0.7984	−61.7	0.8118		0.7998	112.2	0.6990
0.1	0.0	18.7	0.7966		0.0	204.0	1.1863
	0.2020	11.2	0.7852		0.2001	191.5	1.0588
	0.4030	1.9	0.7804	3.0	0.3993	177.9	0.9570
	0.6036	−9.5	0.7904		0.5995	160.7	0.8561
	0.8005	−28.8	0.7802		0.8020	135.3	0.7583
	0.0	94.7	0.7466		0.0	256.0	2.0895
	0.2029	87.1	0.7376		0.2004	240.7	1.7628
0.5	0.4025	77.5	0.7253	5.0	0.4014	223.8	1.4851
	0.6003	64.4	0.7084		0.6012	202.7	1.2250
	0.8000	43.7	0.6839		0.8000	174.2	0.9963
1.0	0.0	130.6	0.7816				
	0.2007	122.2	0.7560				
	0.3938	111.6	0.7315				
	0.6002	97.9	0.7026				
	0.7990	77.1	0.6760				

Table 2 Continued

I/mol·kg^{-1}	$y_{Li_2SO_4}$	E/mV	$\gamma_{\pm LiCl}$	I/mol·kg^{-1}	$y_{Li_2SO_4}$	E/mV	$\gamma_{\pm LiCl}$
0.05	0.0	−13.8	0.8250		0.0	183.6	0.9014
	0.20244	−22.0	0.8196		0.2015	172.6	0.8442
	0.4362	−29.3	0.8412	2.0	0.3999	159.3	0.7846
	0.5990	−45.2	0.8176		0.6006	142.8	0.7302
	0.7984	−66.1	0.8105		0.7998	118.9	0.6820
			35°C				
0.1	0.0	20.2	0.7896		0.0	215.8	1.1229
	0.2020	11.5	0.7752		0.2001	202.8	1.0085
	0.4030	2.0	0.7781	3.0	0.3993	188.1	0.9106
	0.6036	−10.1	0.7910		0.5995	169.8	0.8180
	0.8005	−30.6	0.7853		0.8020	142.9	0.7306
0.5	0.0	101.5	0.7342		0.0	270.5	1.8980
	0.2029	92.7	0.7203		0.2004	254.0	1.6081
	0.4025	82.4	0.7094		0.4014	235.9	1.3628
	0.6003	68.5	0.6965		0.6012	213.6	1.1390
	0.8000	46.9	0.6826		0.8000	183.4	0.9415
1.0	0.0	138.6	0.7632				
	0.2007	129.8	0.7413				
	0.3938	118.4	0.7119				
	0.6002	104.1	0.6830				
	0.7990	81.7	0.6472				

$$y_B = 3m_{Li_2SO_4} / (m_{LiCl} + 3m_{Li_2SO_4}) \qquad (3)$$

Figures 2 and 3 indicate the activity coefficients of LiCl decrease with increasing temperature and ionic strength fraction of Li$_2$SO$_4$ in the mixtures.

Harned coefficients

The form of Harned's rule can be expressed by the experimental activity coefficients of LiCl in the mixtures:

$$\log\gamma_A = \log\gamma_A^o - \alpha_{12}y_B - \beta_{12}y_B^2 \qquad (4)$$

where γ_A^0 is the mean activity coefficients of LiCl in pure solutions at the same total ionic strength as the mixture and α_{12} is the Harned interaction coefficient for LiCl. Harned's rule is obeyed for the system from $I=0.05$ to $I=5.0$ in all
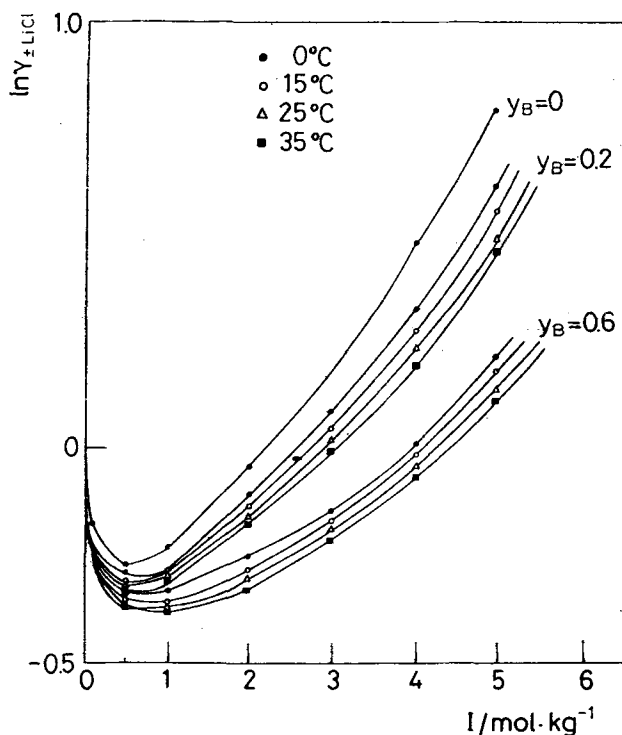
Fig. 2 Activity coefficients of LiCl in mixtures with Li$_2$SO$_4$ at different temperatures

temperature ranges. The nonlinear terms of the complete Harned Eq. 4 were not needed to fit the data within the experimental error. Table 4 lists the values of the Harned coefficients at 0, 15, 35°C and the standard deviations. The ionic strength (I>0.1) dependencies of the Harned coefficients at 0, 15 and 35°C are expressed by linear Eqs (5), (6) and (7) with the standard deviations of 0.0051, 0.0064, 0.0049 respectively.

$$\alpha_{A1} = 0.07157 + 0.003310I \tag{5}$$

$$\alpha_{A2} = 0.08237 - 0.0005039I \tag{6}$$

$$\alpha_{A3} = 0.0830 - 0.001569I \tag{7}$$

The ionic strength coefficients of the Harned coefficient $\delta\alpha_A/\delta I$ are then 0.003310, −0.000504, −0.00157 respectively. The results indicate that the effect of the ionic strength on the α_A changes from positive to negative with changing temperatures from 0 to 35°C.
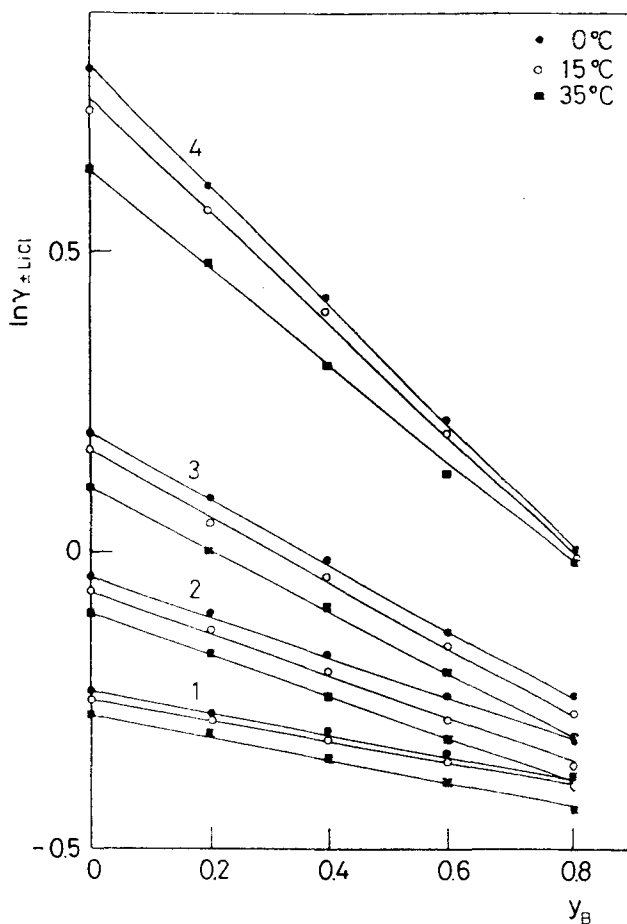
Fig. 3 Plot of $\ln\gamma_{\pm LiCl}$ vs. y_B at different ionic strengths and temperatures

Pitzer parameters

Pitzer mixing interaction parameters were evaluated by fitting Pitzer equations, including the contributions of higher order electrostatic terms to the experimental data given in Table 2, using multiple linear regression techniques. For details of calculation, see [1], [3], [17] and [18]. Pitzer's pure-electrolyte parameters for LiCl and Li₂SO₄ at 0, 15 and 35°C were taken from [19] and [20] reported by Holmes. The values of mixing interaction parameters at the three temperatures are listed in Table 4 along with the deviations of the fittings, and presented in Fig. 4.
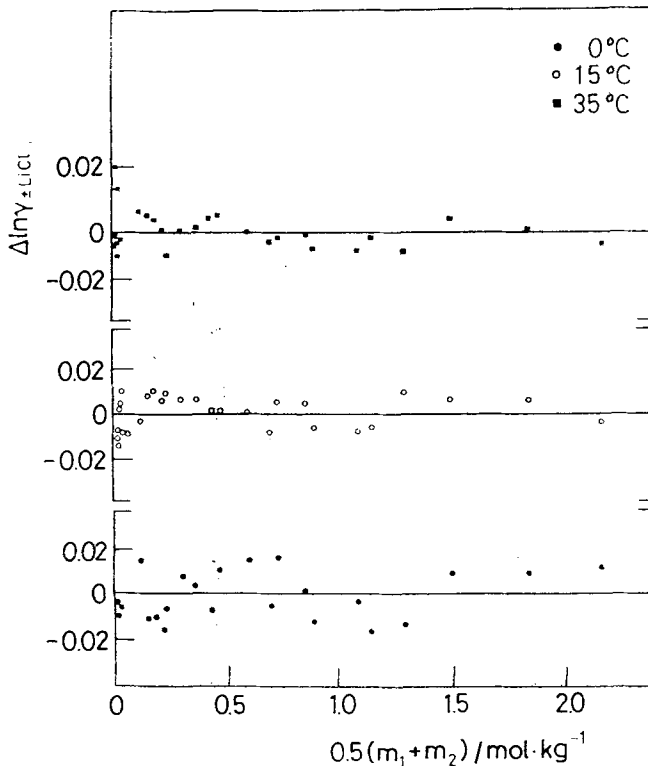
Table 3 Parameters of the harned equation for LiCl–Li$_2$SO$_4$ mixture from 0 to 35°C

I mol·kg^{-1}	0°C			15°C			35°C		
	$-\log\gamma_1^0$	α_{12}	$SD\times10^3$	$-\log\gamma_1^0$	α_{12}	$SD\times10^3$	$-\log\gamma_1^0$	α_{12}	$SD\times10^3$
0.05	0.07934	0.2063	1.3	0.08046	0.2657	2.2	0.08385	0.1654	0.90
0.1				0.1012	0.0749	2.7	0.1066	0.01965	3.4
0.5	0.1270	0.06741	3.2	0.1238	0.0938	2.8	0.1341	0.07796	0.5
1.0	0.1002	0.08292	2.9	0.1061	0.0790	0.80	0.1143	0.0894	2.6
2.0	0.01538	0.07601	3.1	0.02549	0.08014	2.3	0.04421	0.07630	0.82
3.0	-0.08987	0.08178	1.5	-0.07466	0.08031	2.0	-0.0508	0.07702	1.1
5.0	-0.3494	0.08780	4.0	-0.3254	0.08022	5.2	-0.2818	0.07596	3.6

Table 4 Pitzer mixing parameters for LiCl–Li$_2$SO$_4$ mixtures (with $^E\theta$ and $^E\theta'$ included)

	0°C	15°C	35°C
$^s\theta_{Cl, SO_4}$	0.04934	0.01229	0.01015
ψ_{Li, Cl, SO_4}	−0.000125	0.01795	0.01772
σ_{fit}	0.0094	0.0064	0.0051

The different values of θ_{Cl,SO_4} and ψ_{Li,Cl,SO_4} at 25°C evaluated using the experimental data taken from [13] are listed in Table 6. It indicates the differences in the values of the mixing parameters due to differences in the pure-electrolyte parameters taken from different literatures.

Fig. 4 Deviations of the fit of experimental activity coefficients to Pitzer equations

The activity coefficients of Li$_2$SO$_4$ and the osmotic coefficients for the system at different temperatures were calculated by the Pitzer equations with obtained mixing parameters. The results are listed in Table 5.

Table 5 Activity coefficients of Li_2SO_4 and osmotic coefficients for the system $Li-Cl-SO_4-H_2O$

$I/mol·kg^{-1}$	$y_{Li_2SO_4}$	$\gamma_{\pm Li_2SO_4}$	φ	$I/mol·kg^{-1}$	$y_{Li_2SO_4}$	$\gamma_{\pm Li_2SO_4}$	φ
			0°C				
0.01	0.2071	0.8149	0.9658	2.0	0.2006	0.4009	1.1031
	0.4053	0.8155	0.9608		0.4003	0.3769	1.0390
	0.6000	0.8167	0.9550		0.6016	0.3527	0.9665
	0.8002	0.8173	0.9473		0.7990	0.3293	0.8823
0.05	0.2079	0.6714	0.9415	3.0	0.2011	0.4390	1.2344
	0.4152	0.6705	0.9306		0.4003	0.3959	1.1444
	0.6000	0.6733	0.9197		0.6000	0.3558	1.0453
	0.7917	0.6723	0.9047		0.8001	0.3184	0.9304
0.50	0.1987	0.4465	0.9447	4.0	0.2008	0.5055	1.3781
	0.4014	0.4415	0.9170		0.4005	0.4352	1.2603
	0.5999	0.4361	0.8848		0.5998	0.3739	1.1322
	0.8001	0.4301	0.8451		0.8001	0.3200	0.9854
1.0	0.2000	0.4044	0.9897	5.0	0.2001	0.6018	1.5333
	0.4010	0.3939	0.9496		0.4000	0.4925	1.3849
	0.5999	0.3829	0.9034		0.6000	0.4025	1.2244
	0.8001	0.3707	0.8477		0.7997	0.3285	1.0441
			15°C				
0.01	0.2426	0.8077	0.9634	1.0	0.2007	0.3991	0.9841
	0.4315	0.8093	0.9586		0.3938	0.3912	0.9450
	0.6356	0.8043	0.9506		0.6002	0.3807	0.8987
	0.7982	0.8138	0.9464		0.7990	0.3702	0.8450
0.05	0.2024	0.6677	0.9406	2.0	0.2015	0.3917	1.0935
	0.4362	0.6634	0.9277		0.3999	0.3702	1.0306
	0.5989	0.6709	0.9192		0.6006	0.3483	0.9587
	0.7984	0.6710	0.9040		0.7998	0.3265	0.8750
0.1	0.2020	0.5963	0.9313	3.0	0.2001	0.4291	1.2222
	0.4030	0.5969	0.9180		0.3993	0.3898	1.1377
	0.6036	0.5969	0.9020		0.5995	0.3519	1.0404
	0.8005	0.5955	0.8822		0.8020	0.3158	0.9239
0.5	0.2029	0.4432	0.9412	5.0	0.2004	0.6152	1.5240
	0.4025	0.4397	0.9142		0.4014	0.5067	1.3946
	0.6003	0.4357	0.8831		0.6012	0.4135	1.2416
	0.8000	0.4304	0.8452		0.8000	0.3367	1.0646

Table 5 Continued

$I/\text{mol·kg}^{-1}$	$y_{Li_2SO_4}$	$\gamma_{\pm Li_2SO_4}$	φ	$I/\text{mol·kg}^{-1}$	$y_{Li_2SO_4}$	$\gamma_{\pm Li_2SO_4}$	φ
			35°C				
0.01	0.2426	0.8017	0.9621	1.0	0.2007	0.3840	0.9761
	0.4315	0.8034	0.9572		0.3938	0.3772	0.9374
	0.6356	0.7984	0.9489		0.6002	0.3678	0.8916
	0.7982	0.8081	0.9445		0.7990	0.3585	0.8384
0.05	0.2024	0.6584	0.9382	2.0	0.2015	0.3713	1.0791
	0.4362	0.6542	0.9250		0.4000	0.3526	1.0176
	0.5989	0.6619	0.9163		0.6006	0.3332	0.9474
	0.7984	0.6621	0.9008		0.7998	0.3137	0.8656
0.1	0.2020	0.5857	0.9284	3.0	0.2001	0.4004	1.200
	0.4030	0.5865	0.9149		0.3993	0.3663	1.1180
	0.6036	0.5866	0.8986		0.5995	0.3331	1.0235
	0.8005	0.5854	0.8783		0.8020	0.3010	0.9105
0.5	0.2029	0.4301	0.9358	5.0	0.2004	0.5509	1.4812
	0.4025	0.4270	0.9089		0.4014	0.4601	1.3565
	0.6003	0.4236	0.8777		0.6012	0.3808	1.2092
	0.8000	0.4189	0.8398		0.8000	0.3142	1.0387

Table 6 Pitzer mixing parameters for LiCl–Li₂SO₄–H₂O at 25°C

	$^s\theta_{Cl, SO_4}$	ψ_{Li, Cl, SO_4}	SD	Pure salt para. from	
				LiCl	Li₂SO₄
Wang[13]	−0.006146	0.004444	0.0077	Kim[17]	Kim[17]
Present	−0.012774	−0.001532	0.0074	Kim[17]	Holmes[20]
Present	0.02319	−0.001508	0.0069	Holmes[19]	Holmes[20]

Excess free energies of mixing

The excess free energies of mixing were calculated using equations:

$$\Delta_m G^E = 2m_A RT \left[\ln (\gamma_{\pm A}/\gamma_{\pm A}^o) + Y_A(\varphi_A - \varphi) \right] +$$

$$+ 3m_B RT \left[\ln (\gamma_{\pm B} /\gamma_{\pm B}^o) + Y_B (\varphi_B - \varphi) \right]$$

where $\gamma_{\pm A}^o$ and φ_A are respectively the mean activity coefficient and osmotic coefficient of LiCl in pure solution at the same total ionic strength as the mixture,

Table 7 Excess free energies of mixing for the LiCl–Li₂SO₄–H₂O system at 0, 15 and 35°C

I mol·kg^{-1}	y_B	$\Delta_m G^E$/J·kg^{-1}		
		0°C	15°C	35°C
0.05	0.2	0.7499	0.7744	0.8429
	0.4	0.8162	0.8341	0.9195
	0.6	0.1834	0.1756	0.2074
	0.8	−0.7573	−0.7772	−0.8500
0.5	0.2	13.50	12.23	13.05
	0.4	10.91	8.564	9.376
	0.6	−6.338	−9.128	−9.493
	0.8	−26.98	−29.32	−30.87
3.0	0.2	152.4	162.0	164.2
	0.4	32.52	41.86	37.28
	0.6	−297.8	−302.7	−319.8
	0.8	−606.3	−629.6	−658.0

Y_A is the mole fraction of A in the mixture, B represents Li₂SO₄. The results are listed in Table 7.

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Zusammenfassung — Die Leistungsfähigkeit eines in unserem Labor entwickelten Elektrodenpaares wurde getestet und zeigte ein fast Nernst'sches Verhalten. Die Hauptaktivitätskoeffizienten von LiCl für das System Li^+–Cl^-–SO_4^{2-}–H_2O wurden anhand der EMK-Werte bei der Temperatur 0°C, 15°C und 35°C und bei konstanter Gesamt-Ionenstärke von 0.05, 0.1, 0.5, 1.0, 2.0, 3.0 und 5.0 mol/kg untersucht. Die Aktivitätskoeffizienten nehmen mit steigender Temperatur und der Ionenstärkefraktion von Li_2SO_4 in den Gemischen ab. Die thermodynamischen Eigenschaften werden unter Anwendung der empirischen Gleichungen von Harned und der Pitzer'schen Näherung der Ionenwechselwirkung einschließlich des Beitrages elektrostatischer Ausdrücke höherer Ordnung interpretiert. Die experimentellen Ergebnisse folgen der Harned'schen Regel und werden durch die Anwendung von Pitzer'schen Gleichungen zufriedenstellend beschrieben. Es werden die Aktivitätskoeffizienten von Li_2SO_4, die osmotischen Koeffizienten und die freien Überschußmischungsenergien des Systemes im experimentellen Temperaturbereich angegeben.