Thermochimica Acta, 97 (1986) 29–35
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

$LiCl–ZnCl_2$ PHASE DIAGRAM

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(Received 17 June 1985)

ABSTRACT

The $LiCl–ZnCl_2$ binary phase diagram has been determined because of its presence as a binary component of several ternary systems under study. At LiCl–(10 mol%)$ZnCl_2$ (835 K) the polymorhous lithium chloride phase change was found, and at LiCl–(40 mol%)$ZnCl_2$ (610 K) the peritectic corresponding to incongruent melting of Li_2ZnCl_4 was present. Two eutectics were observed at LiCl–(78 mol%)$ZnCl_2$ (548 K) and LiCl–(91 mol%)$ZnCl_2$ (560 K). The compound $LiZn_5Cl_{11}$ (LiCl–(83 mol%)$ZnCl_2$ (659 K)), was found and supported by the results of X-ray diffraction analysis.

INTRODUCTION

There is considerable interest in the application of molten salt reactions using zinc chloride and an important aspect is the determination of phase diagrams. Previous experimental studies on the $KCl–CaCl_2–ZnCl_2$ ternary system have been carried out in this laboratory [1] and the $LiCl–ZnCl_2$ system is the latest in the series. Interest in this binary arises from the possible future application of the $LiCl–KCl–ZnCl_2$ ternary system as a molten salt solvent extraction system. The possibility of liquid–liquid immiscibility in $LiCl–KCl–ZnCl_2$ is suggested by analogy with $LiCl–KCl–AlCl_3$ and the covalent nature of zinc chloride. The component binary phase diagrams of LiCl–KCl [2] and $KCl–ZnCl_2$ [1] are well known but the $LiCl–ZnCl_2$ binary diagram has not been extensively investigated.

The only reference to the $LiCl–ZnCl_2$ phase diagram (Fig. 1) was published in a Russian compilation [3] from data by Evseeva and Bergman [4] as part of the $LiCl–ZnCl_2–Li_2SO_4–ZnSO_4$ system. Other evidence suggests that complex anion formation [5] occurs at high zinc chloride concentrations which was not observed in the phase diagram. The calculated excess free energies of the system $LiCl–ZnCl_2$ [6] deviated markedly from expected

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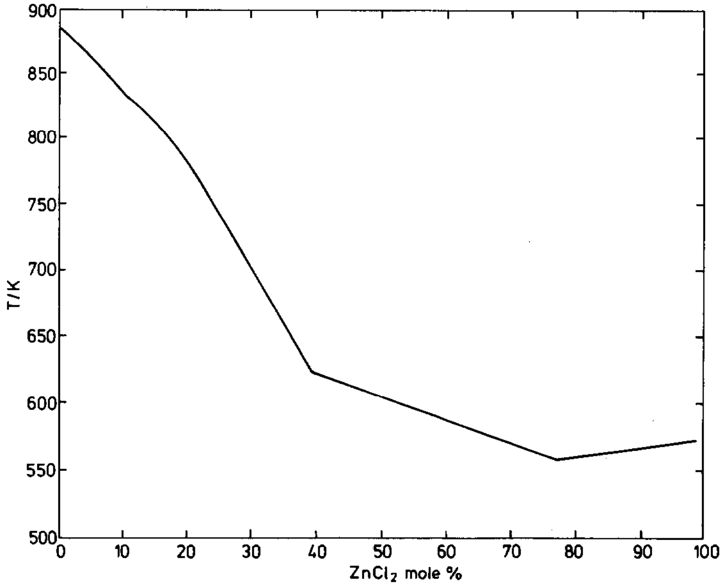

Fig. 1. LiCl–$ZnCl_2$ liquidus diagram [3,4].

values at high $ZnCl_2$ concentrations, also implying complex formation. The present study was undertaken to resolve these anomalies in the LiCl–$ZnCl_2$ phase diagram.

EXPERIMENTAL

Materials

Anhydrous lithium chloride was obtained from the Aldrich Chemical Co. and had a melting point of 608°C (cf. 610°C [7]). Anhydrous, vacuum-sublimed zinc chloride was supplied by Andersons Physics Laboratories (m.p. 308°C, cf. 318°C [8]). Both reagents were dried at 100°C under vacuum for at least 24 h before use.

Method

The LiCl–$ZnCl_2$ phase diagram was determined by the thermal arrest method which has previously been described [1].

X-ray powder diffraction analysis

X-ray diffraction analysis was carried out using the following technique. A powdered sample was prepared by crushing in an agate mortar in a dry box, and a thin-walled (0.01 mm) silica capillary tube (0.3–0.5 mm ID) was loaded with the sample and sealed at both ends. The sample tube was loaded into a Straumanis-Ievins type Debye–Scherrer powder camera, the sample was exposed for 2½ h to Cu-*Kα* radiation, and the resulting diffraction pattern measured with a calibrated ruler to give spacings directly. The diffraction pattern was compared with standard patterns for zinc chloride and lithium chloride.

RESULTS

The LiCl–ZnCl$_2$ phase diagram is shown in Fig. 2 and Table 1 gives the line intensities and spacings of the diffraction patterns. An important feature of the series of diffraction patterns was the degree of absorption due to the inability of grinding the sample to a sufficiently fine power which results in splitting into a strong and weak line. The clearest example is the zinc chloride line at 4.8 on the JCPDS standard pattern which was observed as two lines (4.75 (strong) and 4.9 (weak)) in this work.

Despite this effect there is good agreement between the patterns observed for lithium chloride and zinc chloride and the standard patterns. Photographic film shrinkage has not been taken into account and consequently may lead to a slight displacement of the lines between different samples.

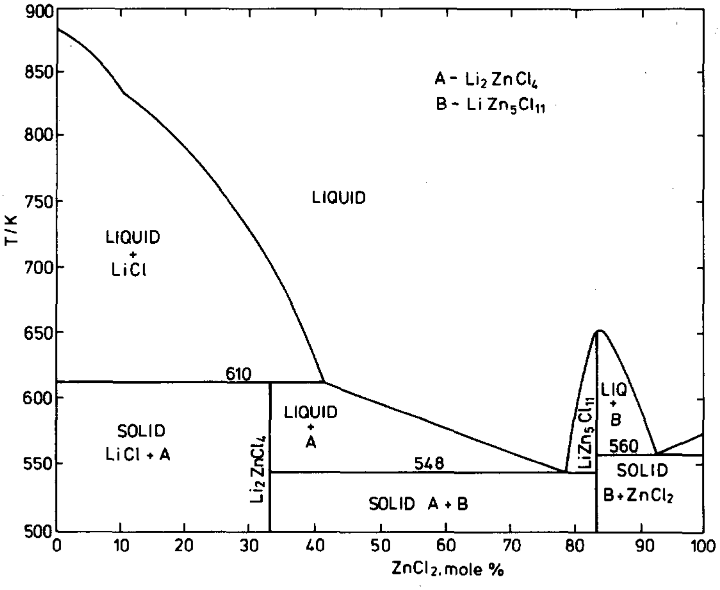

Fig. 2. LiCl–ZnCl$_2$ liquidus diagram.

TABLE 1

X-ray powder diffraction *d* spacings for LiCl–$ZnCl_2$ mixtures

LiCl JCPDS [a] 40664	LiCl	60 mol% LiCl– 40 mol% $ZnCl_2$	40 mol% LiCl– 60 mol% $ZnCl_2$	17 mol% LiCl– 83 mol% $ZnCl_2$	5 mol% LiCl– 95 mol% $ZnCl_2$	$ZnCl_2$	α-$ZnCl_2$ JCPDS [a] 15-452
		6.4	6.4				
		5.5	5.6 }	5.0			
			5.4 }				
		4.9	4.9	4.9	4.9	4.9	
		4.8					
		4.7	4.65	4.7	4.75	4.75	4.79
		4.4	4.4		4.5		
			3.8	3.81	3.81		
		3.69	3.69				
				3.32	3.30		
			3.28	3.29			
		3.19	3.19	3.195	3.20		
		3.15					
				3.09	3.10	3.11	
		3.03	3.03	3.03	3.08	3.03	3.08
	2.98						
2.967		2.95	2.94	2.95	2.93		
	2.94		2.89	2.89	2.895	2.895	2.903
		2.82	2.81	2.81			
	2.70	2.72	2.72	2.65	2.71		
	2.58						
2.570		2.58	2.595	2.595	2.595		
	2.55						
		2.48	2.48				

				2.38	2.37		
		2.33	2.35	2.35	2.35	2.35	2.351
		2.30					
					2.225		
		2.21	2.22	2.23	2.20		
		2.20	2.20	2.20	2.13		
		2.10	2.12	2.11	2.11		
		2.05	2.06				
		2.00	2.00	2.00	2.00		
		1.95	1.96	1.955	1.975	1.97	1.975
				1.92			
			1.92			1.93	1.928
				1.91			
		1.89				1.905	1.910
		1.85	1.86	1.86	1.86	1.86	1.866
	1.82						
1.817		1.84	1.845				
	1.81						
					1.77	1.77	1.773
			1.73	1.74	1.74		
		1.71	1.715	1.72	1.73		
		1.64	1.67	1.68	1.68		
			1.645	1.65	1.65		
		1.62	1.63	1.63	1.62	1.62	1.621
		1.595	1.59	1.595	1.595	1.595	1.595
		1.57	1.57		1.568	1.565	1.569
1.550	1.549	1.55	1.55	1.55			
		1.53	1.53	1.52	1.52		

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[a] Joint Committee on Powder Diffraction Standards.

DISCUSSION

The region 75–100 mol% $ZnCl_2$ shows considerable variation from the data of Evseeva and Bergman [4] where only a single eutectic at LiCl–(77 mol%)$ZnCl_2$ (560 K) was observed. Two eutectic compositions were found in the present study at LiCl–(78 mol%)$ZnCl_2$ (548 K) and LiCl–(91 mol%)$ZnCl_2$ (560 K). A peak in the liquidus curve, indicative of compound formation, was observed at LiCl–(83 mol%)$ZnCl_2$ (659 K) corresponding to the compound $LiZn_5Cl_{11}$.

The cooling curve of the LiCl–(83 mol%)$ZnCl_2$ composition did not give a single temperature arrest, as expected for a congruently melting compound. This may be due to instability of the compound and the problem of obtaining complete mixing of the highly viscous melt. The duration of the first temperature of arrest increased the longer the melt was held at temperature, indicating that the concentration of the compound was increasing. However, the melt could not be held at temperature for more than 3 h because of volatilisation of zinc chloride. Some X-ray powder diffraction studies were made to confirm the existence of this compound. The compositions LiCl–(40 mol%)$ZnCl_2$, LiCl–(60 mol%)$ZnCl_2$, LiCl–(82 mol%)$ZnCl_2$, LiCl–(83 mol%)$ZnCl_2$, LiCl–(85 mol%)$ZnCl_2$ and LiCl–(91 mol%)$ZnCl_2$ were examined. None of the X-ray diffraction patterns of these compositions showed any lines due to lithium chloride because of the presence of the incongruently melting compound Li_2ZnCl_4. The diffraction pattern of the proposed compound has lines which are not present in those of zinc chloride, lithium chloride or the LiCl–(40 mol%)$ZnCl_2$ composition. It is inferred from these results that another high molecular weight solid phase is present. This new phase was assigned as the $LiZn_5Cl_{11}$ compound on the basis of the phase diagram data. The zinc chloride line at 3.05 is present throughout the range of compositions studied, even at the composition of the proposed compound, supporting the evidence of the cooling curve that the compound exists in equilibrium with free zinc chloride and Li_2ZnCl_4.

The X-ray powder diffraction results, with the previous evidence [5,6] support the phase diagram and the existence of a compound in the $ZnCl_2$-rich region. This disagrees with the Russian version of this system [3].

CONCLUSIONS

Experimental determination of the LiCl–$ZnCl_2$ phase diagram was carried out. At LiCl–(10 mol%)$ZnCl_2$ (835 K), the polymorphous lithium chloride solid phase change occurs and at LiCl–(40 mol%)$ZnCl_2$ (610 K) a peritectic corresponding to the incongruent melting of the Li_2ZnCl_4 compound was present. Two eutectic compositions were observed: LiCl–(78 mol%)$ZnCl_2$ (548 K) and LiCl–(91 mol%)$ZnCl_2$ (560 K). A congruently melting compound, $LiZn_5Cl_{11}$ (LiCl–(83 mol%)$ZnCl_2$ (659 K)) was found and supported by the results of X-ray diffraction studies. This compound was not found in a previous Russian study of this phase diagram.

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