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LiCl–$ZnCl_2$ PHASE DIAGRAM

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ABSTRACT

The $ZnCl_2$-rich region of the LiCl–$ZnCl_2$ phase diagram has been re-investigated following differences in other published reports. The eutectics at LiCl–(78 mol%)$ZnCl_2$ (548 K) and LiCl–(91 mol%)$ZnCl_2$ (560 K), and the formation of the compound $LiZn_5Cl_{11}$ (LiCl–(83 mol%)$ZnCl_2$) are confirmed when dried salts are used. Whenever undried salts are used the compound is not observed, but there is no experimentally proven explanation for this.

INTRODUCTION

The LiCl–$ZnCl_2$ binary phase diagram determined by Macdonald et al. [1] in 1985 (Fig. 1) differed considerably from an earlier determination by

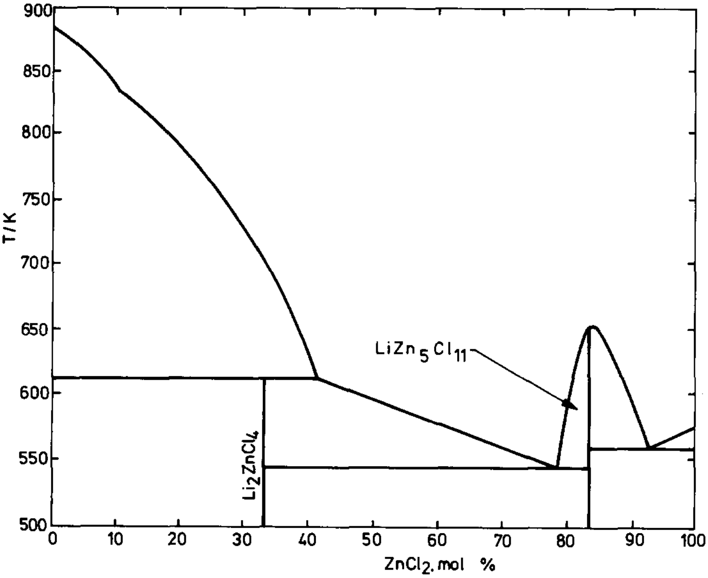

Fig. 1. LiCl–$ZnCl_2$ liquidus diagram [1].

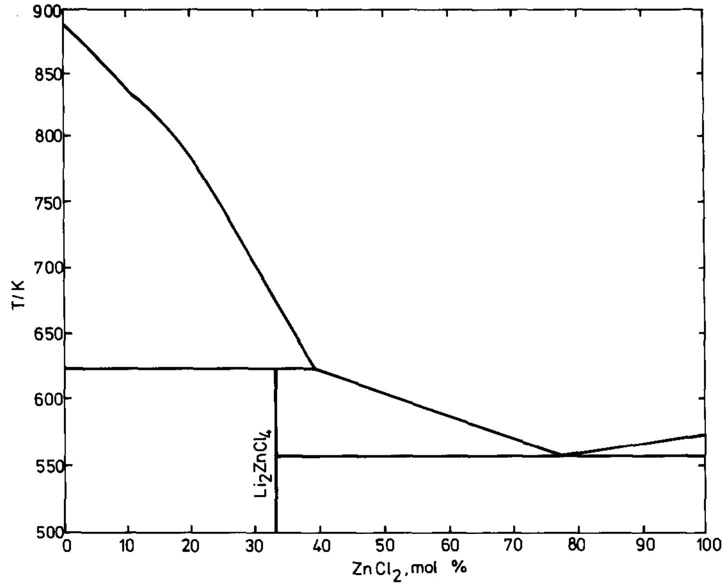

Fig. 2. LiCl–$ZnCl_2$ liquidus diagram [2].

Evseeva and Bergman (Fig. 2) [2]. Macdonald et al. [1] found two eutectics, one peritectic, an LiCl phase change and $LiZn_5Cl_{11}$, a congruently melting compound (melting point 659 K) whose formation was supported by X-ray evidence. However, it did not give a single temperature arrest, as would be expected for a congruently melting compound: three temperature arrests were observed. Evseeva and Bergman, on the other hand, reported only one

TABLE 1

Literature results for the LiCl–$ZnCl_2$ binary phase diagram

Reference	$ZnCl_2$ (mol%)	Temperature (K)	Remarks
Macdonald et al. [1]	10.2	830	α–β LiCl
	45	610	Peritectic
	78	548	Eutectic
	91	560	Eutectic
	83	659	Compound
Evseeva and Bergman [2]	9.6	847	α–β LiCl
	44.4	625	Peritectic
	77	567	Eutectic
	(93)	(575)	(Eutectic?)
	(89)	(582)	(Compound?)
Liu et al. [3]	42.2	598	Peritectic
	69.8	562	Eutectic

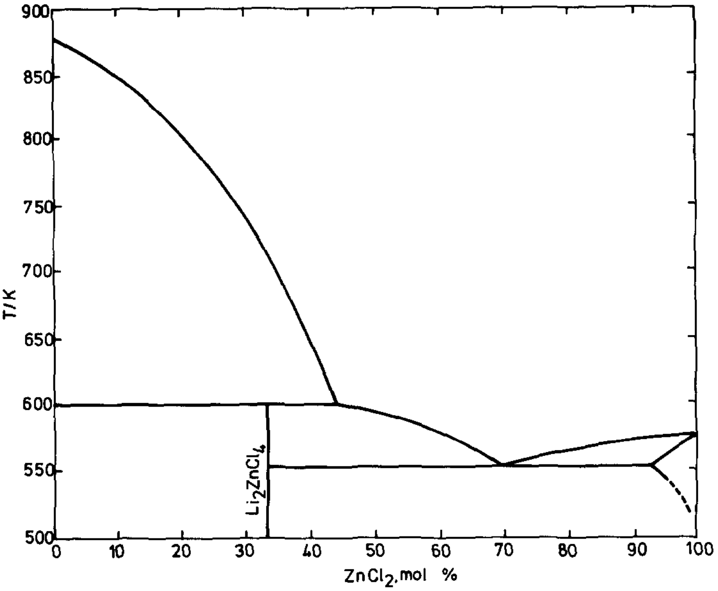

Fig. 3. LiCl–$ZnCl_2$ liquidus diagram [3].

eutectic, the peritectic and the phase change. These results are summarized in Table 1.

A recent study (Fig. 3) [3] found the peritectic at 42.2 mol% $ZnCl_2$ (melting point 598 K) and one eutectic at 69.8 mol% $ZnCl_2$ (melting point 562 K). They did not find the phase change or the compound. Zhang [4] has suggested the compound $LiZn_5Cl_{11}$ may exist only in the solid phase at lower temperatures. It was therefore decided to re-investigate this system, in an attempt to resolve these differences.

EXPERIMENTAL

Materials

Anhydrous lithium chloride was obtained from the Aldrich Chemical Co. and had a melting point, after drying, of 880 K (cf. 883 K [5]). Polarographic grade zinc chloride was obtained from Anderson Physics Laboratories (APL) and had a melting point of 574 K. This salt was received in sealed glass ampoules and was used without further treatment. Ultrapure grade zinc chloride was obtained from Ventron GmbH and had a melting point, after drying, of 567 K. The capillary tube method on the same material gave a value of 586 ± 1 K and DTA measurements gave 578 ± 5 K. Reviews on the melting point of $ZnCl_2$ [6,7] have quoted a wide range of values from 512 to 638 K. Craw and Rogers [7] obtained 591 ± 4 K using the capillary tube method, which showed good agreement with previous work. A DTA study by Takagi and Nakamura [8] gave a value of 586.3–589.3 K for the melting of crystalline $ZnCl_2$.

Salt drying

The Ventron $ZnCl_2$ and Aldrich LiCl were dried by the method below. The salt was weighed in a nitrogen atmosphere dry box ($<$ 25 ppm water vapour) and transferred to the salt-drying apparatus described previously [1]. The apparatus was purged with nitrogen from a liquid nitrogen container and the temperature raised to 150 °C. A stream of electronic grade HCl (2 l min^{-1}) was passed through the salt for 2 h. The temperature was increased until the salt was molten and the HCl passed through for a further 2 h. The apparatus was then purged with nitrogen for 30 min. The gas flow was reversed, forcing the molten salt through the sinter and removing any solid impurities. The salt was allowed to cool under nitrogen, then transferred to the dry box, crushed, and stored in the box in a sealed Kilner jar. Typically, undried $ZnCl_2$ contained 1.4% oxygen and dried $ZnCl_2$ contained 0.3% oxygen (by neutron activation analysis).

Methods

A 20-g sample of the required composition of LiCl and $ZnCl_2$ was weighed into a clean, dry silica test tube in the dry box. A chromel–alumel thermocouple, protected by a closed-end recrystallized alumina tube, was inserted into the salt mixture. Comparison of weights before and after the experiments indicated that $<$ 0.02 g of $ZnCl_2$ was lost by volatilization.

The salt was melted in a resistance furnace controlled by a West 2050 furnace controller which allowed the salt to be held molten for a specified time and cooled at a constant rate. The furnace was programmed, allowing the melt to cool at 1–2 K min^{-1} and the thermocouple output to be stored by a microcomputer. The thermocouples were calibrated against pure zinc metal (melting point 692 K) and corrections found to be unnecessary for results quoted to the nearest 1 K. The samples were stirred while molten and during cooling to ensure complete mixing and to reduce supercooling effects.

In ref. 1, it was shown that the duration of the first temperature arrest increased the longer the mixture was held molten. Therefore when the first arrest was not observed, the sample was reheated the next day and the melt held molten for a further fixed time before allowing it to cool. If necessary this was repeated a further two times.

RESULTS

Experimental data for mixtures of dried and undried salt in the composition range 80–86 mol% $ZnCl_2$ are shown in Table 2. The first temperature arrest was only seen when both salts were dried; in these cases three temperature arrests were seen. Other data outside the 80–86 mol% $ZnCl_2$ range are shown in Table 3.

DISCUSSION

The study of zinc chloride systems is complicated by the extremely hygroscopic nature of the salt, and it was thought that the differences observed in the phase diagram may be due to different methods of drying the salt. The workers in ref. 3 used commercially produced anhydrous $ZnCl_2$ and LiCl and melted them separately in an atmosphere of relative humidity < 50% to obtain transparent solutions. No impurity analysis was given.

From the results in Table 2 it can be seen that the first temperature arrest is difficult to obtain, and it was often necessary to reheat the sample on more than one occasion and to keep the mixture molten for 2 or 3 h in order to obtain a temperature arrest due to solid formation. This may be caused by incomplete mixing in the viscous melt.

Whenever salts were used that had not been dried the first temperature arrest was not found. The two arrests corresponding to the two eutectic temperatures were easily obtained, but the points were generally slightly lower, probably because of moisture and other impurities. When argon gas, known to contain traces of water vapour, was bubbled through a melt of dried salts no high temperature arrest was observed.

The results for compositions outside the 80–86 mol% $ZnCl_2$ range are shown in Table 3. For concentrations < 70 mol% they show agreement with ref. 1 and confirm the eutectic temperature of 548 K. The results for $ZnCl_2$ concentrations > 91 mol% give a eutectic temperature of 553 K, compared with 560 K found in ref. 1, but in the 78–91 mol% region the second arrest was around 560 K.

It was considered that these anomalies could be due to a miscibility gap. Binary and ternary salt mixtures normally show complete miscibility, with the structure consisting of two interpenetrating subquasi-lattices, the ions on each being distributed randomly [9]. Interactions in molten salts are largely Coulombic with only second-order perturbations caused by polarization effects. The thermodynamics of binary systems, as thermodynamic potential versus composition diagrams, indicate whether a particular system will form two immiscible liquids. However, calculation of specific thermodynamic potentials is difficult because many thermodynamic constants are unknown [10]. For immiscibility to occur the plot of free energy of mixing against composition is such that $(d^2G_m/dN_2^2)_{T,P} = 0$ at two points. When the overall composition is in the region of immiscibility the two layers each have a fixed composition at constant temperature according to the phase rule.

TABLE 2

Experimental data between 80 and 86 mol% $ZnCl_2$

LiCl (mol%)	$ZnCl_2$ (mol%)	LiCl treatment	$ZnCl_2$	$ZnCl_2$ treatment	Temperature arrests (K)			Comments
					1st	2nd	3rd	
14	86	Dried	Ventron	Dried		561	547.4	
						561.2	547.2	Held molten 2 h
					636.8	561.1	547.2	Held molten 3 h
17	83	Dried	Ventron	Dried		558.2	553.1	
						559.1	553.2	Held molten 2 h
						559.7	553.2	Held molten 3 h
					653.4	560.2	549.5	Held molten 3 h
20	80	Dried	Ventron	Dried	579.1	559.1	546.3	
			Mean value with dried salts			559.9	549.6	
17	83	Dried	Ventron	Undried		557.3	544.4	
						557.6	544.1	Held molten 2 h
						557.5	544.9	Held molten 3 h
						558.7	545.2	Held molten 3 h
14	86	Dried	Ventron	Undried		559.4	545.1	
						558.7	544.2	Held molten 2 h
						558.8	545.7	Held molten 2 h
						558.9	544.2	Held molten 3 h

17	83	Undried	Ventron	Dried	560.4	544.8	
					559.7	543.2	Held molten 2 h
					559.5	545.1	Held molten 3 h
					558.9	544.4	Held molten 3 h
14	86	Undried	Ventron	Dried	558.7	543.5	
					558.4	544.1	Held molten 2 h
					559.9	544.6	Held molten 3 h
					559.2	545.1	Held molten 3 h
17	83	Undried	Ventron	Undried	556.5	542.1	
					558.1	544.2	Held molten 2 h
					557.9	544.5	Held molten 3 h
					558.8	545.2	Held molten 3 h
14	86	Undried	Ventron	Undried	557.1	542.8	
					557.9	543.4	Held molten 2 h
					558.4	544.2	Held molten 3 h
					558	544.6	Held molten 3 h
17	83	Dried	Ventron	Dried	558.9	545.6	Dry argon 15 min
					558.6	546.2	Dry argon 15 min
17	83	Dried	Ventron	Dried	557.2	546.1	Wet argon 15 min
					558.1	545.9	Wet argon 15 min
			Mean value with undried salts		558.5	544.4	

TABLE 3

Experimental data outside 80–86 mol% $ZnCl_2$

LiCl (mol%)	$ZnCl_2$ (mol%)	LiCl treatment	$ZnCl_2$	$ZnCl_2$ treatment	Temperature arrests (K)			Comments
					1st	2nd	3rd	
2	98	Dried	APL	Dried		573.4		
						571.8		
3	97	Dried	Ventron	Dried		562.7		
						562.0		Held molten 2 h
						561.5		Held molten 3 h
4	96	Dried	APL	Dried		570.5	552.1	
						570.7	551.9	
7	93	Dried	Ventron	Dried		559.1		
						561.6		Held molten 2 h
						562.3		Held molten 3 h
7	93	Dried	APL	Dried		564.4	552.6	
						569.6	552.8	
9	91	Dried	Ventron	Dried		559.3		
30	70	Dried	Ventron	Dried		564.2	548.1	
						562.8	548.2	Held molten 2 h
						561.6	547	
40	60	Dried	Ventron	Dried		596	547.6	Held molten 2 h
						584.8	547.6	Held molten 3 h
45	55	Dried	Ventron	Dried		594.1	546.1	Held molten 2 h
						594.2	549.6	Held molten 3 h
50	50	Dried	Ventron	Dried		590.3	548.1	
						594.7	544.7	Held molten 2 h
						594.7	545.1	Held molten 3 h
			Mean value for eutectic				547.2	

In general for a miscibility gap to occur one phase should have a more covalent character, consisting of large, polarizable ‘soft’ ions, the other is more ionic, consisting of small, non-polarizable ‘hard’ ions [11]. Solutes then distribute between the phases according to their preference for a hard or soft environment. For most binary systems immiscibility does not occur between the two binary components but between a compound $n\mathrm{AX} \cdot m\mathrm{BX}$ and the less polar component [10,11]. It is the formation of complex compounds in binary systems which produced conditions favouring immiscibility. Thus, in this system, the immiscibility might be expected to occur between Li_2ZnCl_4 and $ZnCl_2$ in the region under investigation.

In a number of experiments the melt was visibly examined, but only a uniform melt could be seen. A small amount of nickel chloride was added to the molten mixture, dissolved and thoroughly shaken, allowed to stand molten, then rapidly cooled. The nickel chloride was found to be uniformly dispersed throughout the salt, suggesting a completely miscible system. Nickel chloride was used because it has a second ionization potential of 18.15 eV, compared with 17.96 eV for zinc [12], and an electronegativity of 1.90 compared with 1.81 on the Pauling scale [13], so it would be expected to partition preferentially into a $ZnCl_2$-rich layer.

Therefore, the treatment of the salt would appear to be critical to observing the liquidus temperature. It has been suggested that the compound $LiZn_5Cl_{11}$ may be unstable—it either reacts with any moisture present, or the presence of moisture catalyses its decomposition. At the moment these suggestions have not been proven experimentally.

CONCLUSION

This re-investigation of the $ZnCl_2$-rich region of the $LiCl$–$ZnCl_2$ phase diagram has confirmed the results of an earlier investigation. However, the present study has indicated that the pre-treatment of the constituent salts appears to be critical to observing the formation of the compound $LiZn_5Cl_{11}$, which appears to be unstable. There is no experimentally proven explanation for this.

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