

The Phase Diagram $\text{CuCl}_2\text{—LiCl—KCl}$

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The systems $\text{CuCl}_2\text{—LiCl}$ and $\text{CuCl}_2\text{—LiCl—KCl}$ were studied by DTA. $\text{CuCl}_2\text{—LiCl}$ is a simple eutectic system, while $\text{CuCl}_2\text{—LiCl—KCl}$ contains one congruent melting compound, KCuCl_3 . In a subsequent publication, the ternary phase diagram has been calculated on the basis of the conformal ionic solution theory, and there is good agreement between the experimental and calculated phase diagram.

As part of a phase study of systems of interest as oxychlorination catalysts, the phase diagram $\text{CuCl}_2\text{—LiCl—KCl}$ was determined. The phase diagram can also be calculated by the use of the conformal ionic solution theory^{1–6} and it was possible to extend the calculation to the present charge-asymmetric additive ternary system.⁷ This gave a satisfactory description of the phase diagram except in the area where the compound $\text{KCuCl}_3(\text{s})$ was present, as this compound was not taken into consideration by the model. In a subsequent publication the conformal solution model is expanded to include compound formation.⁸

EXPERIMENTAL

Chemicals. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ('Baker Analyzed' REAGENT, min. 99.0% $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, J. T. Baker, Holland) was dried by heating to 400 °C in a stream of HCl gas, whereupon Cl_2 gas was bubbled through the melt to prevent reduction to CuCl.

LiCl ('Baker Analyzed' REAGENT, min. 99.1% LiCl, J. T. Baker, Holland) was heated gradually to melting under a stream of HCl gas, and then filtered.

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KCl (*p.a.*, E. Merck, Germany) was dried in vacuum at 400 °C, and was afterwards melted in a nitrogen atmosphere. After cooling, clear crystals were picked out and used.

The DTA samples were made by weighing out about 2 g of the chlorides in a dry-box under nitrogen atmosphere, and transferring the mixture to a quartz tube. This was evacuated to 10^{-4} Torr and then filled with Cl_2 gas to ca. 350 Torr before it was sealed. All samples were equilibrated at about 500 °C for 12 h and then quenched in water, before DTA.

Al_2O_3 (E. Merck, Germany), the reference material for DTA, was heated to 1200 °C, and was then cooled and filled into a quartz tube. This was evacuated to 10^{-4} Torr and sealed.

DTA equipment. The specimen-holder assembly is shown in Fig. 1. The quartz ampoules containing the sample and reference materials were placed in wells in a copper block, covered by a copper lid. The thermocouples were Pt/Pt10%Rh with the junctions in the cavities in the bottom of the specimen holders. The temperature was measured at the bottom of the sample holder. The specimen-holder assembly was mounted in a vertical Kanthal A-wired laboratory furnace. The furnace temperature was controlled by an Eurotherm temperature programmer, *via* a chromel-alumel thermocouple. The temperature signal was fed to a recorder *via* a Fluke DC differential voltmeter, which was used as a reference voltage supply. The differential signal was amplified by a Leeds & Northrup microvolt indicating amplifier. The recorder was a Yokogawa dual-channel line recorder. Gas of composition 94% N_2 , 6% H_2 was passed through the furnace during all runs. Both heating and cooling curves were recorded. Typical heating and cooling rates were 1.6 °C/min. The DTA temperatures were calibrated using the following transition or melting points: KNO_3 (128 °C), Sn(232 °C), KClO_4 (300 °C), Ag_2SO_4 (412 °C), Zn(420 °C) and AgCl(455 °C). The corrections found were $+3 \pm 3$ °C for the heating curves

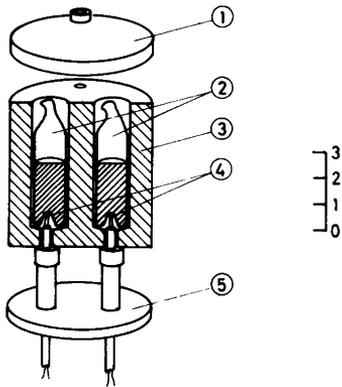


Fig. 1. Cross section of the specimen-holder assembly for DTA. 1. Copper lid. 2. Sample and reference quartz ampoules. 3. Copper block. 4. Pt/Pt 10% Rh thermocouples. 5. Radiation shield.

and $+7 \pm 3$ °C for the cooling curves. The main reason for these rather large discrepancies is probably the poor heat conductance through the walls of the quartz ampoules. These walls had a thickness of about 1.2 mm, but at the bottom, where the thermocouple junctions are placed, they were often thicker due to the sealing-off process.

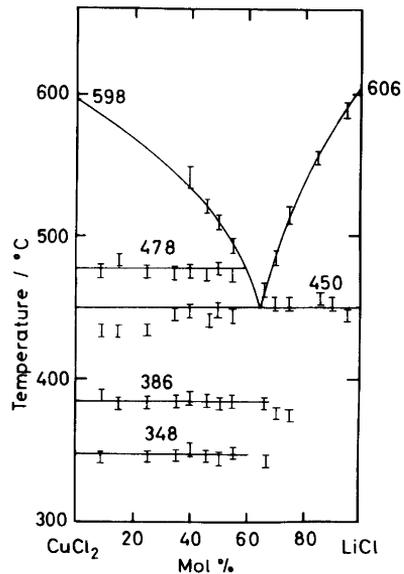


Fig. 2. Experimental phase diagram of the system CuCl_2 - LiCl .

RESULTS AND DISCUSSION

The experimental phase diagram of the system CuCl_2 - LiCl is shown in Fig. 2. This is a simple eutectic system with the eutectic point at 36 mol %

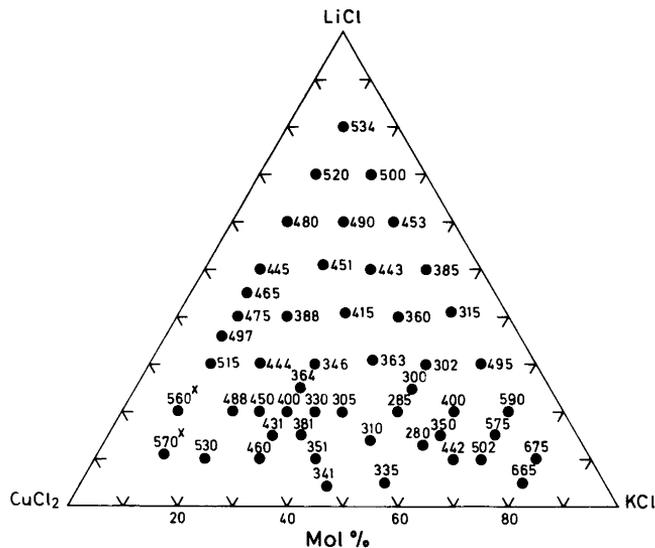


Fig. 3. Experimental liquidus temperatures (in °C) in the system CuCl_2 - LiCl - KCl . x, Points found by extrapolation.

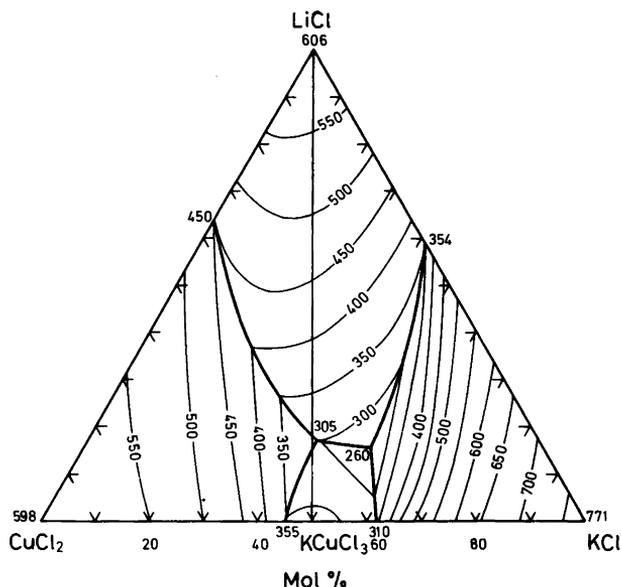


Fig. 4. Phase diagram of the system $\text{CuCl}_2 - \text{LiCl} - \text{KCl}$. Temperatures are in $^{\circ}\text{C}$.

CuCl_2 , 450°C . Because the ampoules holding CuCl_2 -rich samples tended to explode at temperatures above 560°C , the liquidus temperatures were not recorded in this region. The liquidus line was extrapolated from below 550°C to the melting point found by Vorobei and Skiba,⁹ 598°C . The melting point of LiCl , 606°C , was taken from Aukrust *et al.*^{10a,b} The reaction at 478°C is a solid-state transition in CuCl_2 , as reported previously in other systems.⁹ The reactions at 348°C and 386°C have not been identified. They are probably reactions in the ternary system $\text{CuCl}_2 - \text{LiCl} - \text{CuCl}$, as some CuCl will be formed by the reaction



The ampoules were filled with Cl_2 in order to depress this reaction, but even so it will take place to some extent in the CuCl_2 -rich region.

The experimental liquidus temperatures of the system $\text{CuCl}_2 - \text{LiCl} - \text{KCl}$ are shown in Fig. 3. On the basis of these values and data for the component binary systems $\text{CuCl}_2 - \text{LiCl}$ (present work), $\text{LiCl} - \text{KCl}$ (Aukrust *et al.*^{10a,b}) and $\text{CuCl}_2 - \text{KCl}$ (Vorobei and Skiba⁹) the phase diagram in Fig. 4 was constructed.

There are some inherent uncertainties in these measurements, mainly due to a strong tendency to

undercooling in the system, especially in KCl -rich samples. The magnitude of this undercooling was not reproducible; it might vary from a very few to $30-40$ degrees. Another source of error is the formation of CuCl . Analysis of $\text{CuCl}_2 - \text{LiCl} - \text{KCl}$ samples gave a CuCl content between 1 and 5 mol % CuCl .

The ternary phase diagram was constructed by plotting several quasi-binary sections and smoothing the liquidus curves. By this method the errors due to undercooling were reduced, and the uncertainties in the liquidus temperatures given in Fig. 4 are estimated to be less than $\pm 10^{\circ}\text{C}$.

The phase diagram (Fig. 4) shows a peritectic point ($\text{CuCl}_2(\text{s}) + \text{liq.} = \text{KCuCl}_3(\text{s}) + \text{LiCl}(\text{s})$) at 40% $\text{CuCl}_2 - 18\%$ $\text{LiCl} - 42\%$ KCl , 305°C and a eutectic point at 31% $\text{CuCl}_2 - 16\%$ $\text{LiCl} - 53\%$ KCl , 260°C .

As demonstrated by a subsequent publication⁸ the present phase diagram lends itself to a satisfactory calculation by use of the conformal ionic solution theory.

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