

Immiscibility Gap in the System: LiCl-KCl-AlCl₃

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The system LiCl-KCl-AlCl₃ was found to exhibit an immiscibility gap extending over a temperature range of from 350° to 775° C. The composition extent of the binodal surface has been defined by isothermic-isobaric sections at 450°, 525°, 625°, 715°, and 770° C. The cause of immiscibility is discussed in qualitative terms.

MOLTEN MIXTURES of LiCl, KCl, and AlCl₃ were investigated during a search for useful solvents for application in current pyrochemical processing studies. This system exhibited a substantial region of immiscibility. This property is potentially of value in pyrochemical processing and the decision was made to define the limits of the immiscibility gap.

The phase diagrams for the completely miscible binary systems: LiCl-KCl (5), KCl-AlCl₃ (5), and LiCl-AlCl₃ (4) have been reported and were not further investigated here. The latter two exhibit a nearly flat region on the AlCl₃ rich side which has been interpreted as an incipient tendency toward phase separation. Kendall (4) has reported numerous binary systems containing AlCl₃ or AlBr₃ which exhibit this tendency or actually show separation into two phases.

Grothe and Peil (3) have reported an immiscibility gap in the LiCl-KCl-AlCl₃ system, but the limits were defined in a qualitative way. These authors, however, stress the significance of the compound KAlCl₄ whose presence is indicated by convergence of the tie lines at this composition. Fischer and Simon (2) also emphasize the stability of the compound KAlCl₄ in their investigation of the system: NaCl-KCl-AlCl₃. They report this system exhibits an immiscibility gap near the AlCl₃ apex. They also observed immiscibility in the system BaCl₂-KCl-AlCl₃.

During the course of this work the importance of the compound KAlCl₄ was revealed very early. KAlCl₄ melts congruently, is immiscible with LiCl, and exhibits immiscibility in varying degree with many heavy metal chlorides. A variety of metal chlorides was qualitatively tested for miscibility with KAlCl₄ with results to follow.

EXPERIMENTAL

Weighed mixtures were prepared which would exhibit two phases on melting. These were allowed to equilibrate and were then sampled at the test temperature by withdrawing portions of each phase with preheated pipets. The pipetted samples were analyzed flame photometrically for Li and K and titrimetrically for Al. Materials of C.P. reagent grade were used without extensive purification other than drying. Since AlCl₃ is too hygroscopic to handle conveniently, it was reacted with KCl to form the much less hygroscopic complex salt KAlCl₄. Chlorine was bubbled through the salt at 400° C., to free it from moisture and from organic impurities which separate as a carbonaceous precipitate. The final product was poured as a melt into 90% silica test tubes. After solidification of the contents, these were sealed and stored in desiccators over anhydrous until needed. LiCl was dried by sparging with Cl₂ at 650°-700° C. It was also cast into test tubes for storage.

These materials could be weighed in air as coarse lumps without serious moisture contamination. After melting, the KAlCl₄ phase would gradually become turbid, particularly

with AlCl₃-rich compositions. This was due to Al₂O₃ formation. Since the Al₂O₃ formed very slowly and remained insoluble upon subsequent dissolution of samples in dilute HCl (and was filtered off), its formation had little effect upon results reported here.

The materials were equilibrated in open 96% silica test tubes (200 × 25 mm.) heated by a large resistance furnace controlled by a Wheelco pyrometer controller. Temperature was monitored continuously using a Chromel-Alumel thermocouple, protected by thin wall quartz tubing, immersed directly in the sample. By opposing a portion of the thermocouple signal with a potentiometer, the remaining signal could be measured with a recorder (2 mv. full scale) to ±0.02 mv.—i. e., ±0.5° C.

Duplicate samples were taken 15 to 20 minutes apart at each composition and test temperature. Taking into account the precision of the analytical data, the agreement is such as to warrant the conclusion that equilibrium was closely approached in all cases.

RESULTS AND DISCUSSION

The phase composition data are presented in the form of isothermic sections through the isobaric prism. Each section represents a set of experimental measurements at the specified temperature. These data, plotted on triangular coordinates, are illustrated by Figures 1 to 5.

In those figures, the binodal curves are drawn through circled points derived from duplicate measurements of the phase compositions. Tie lines are drawn connecting these

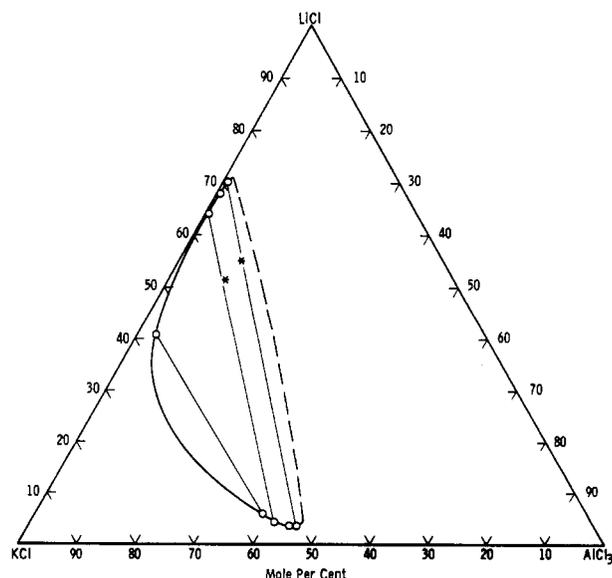


Figure 1. Isothermic section at 450° C.

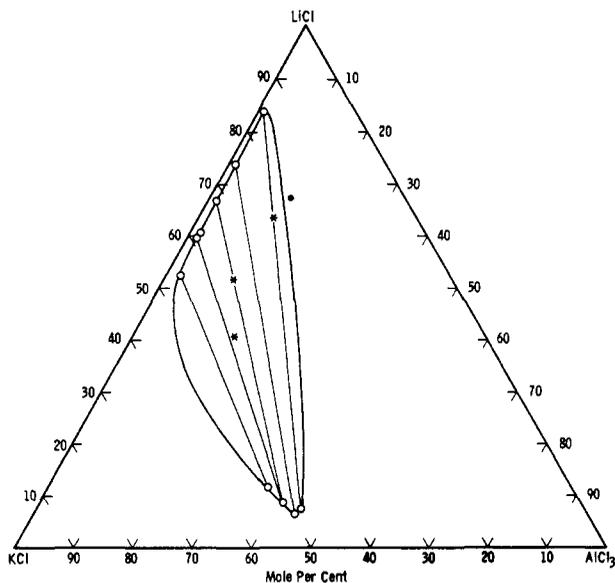


Figure 2. Isothermic section at 525° C.

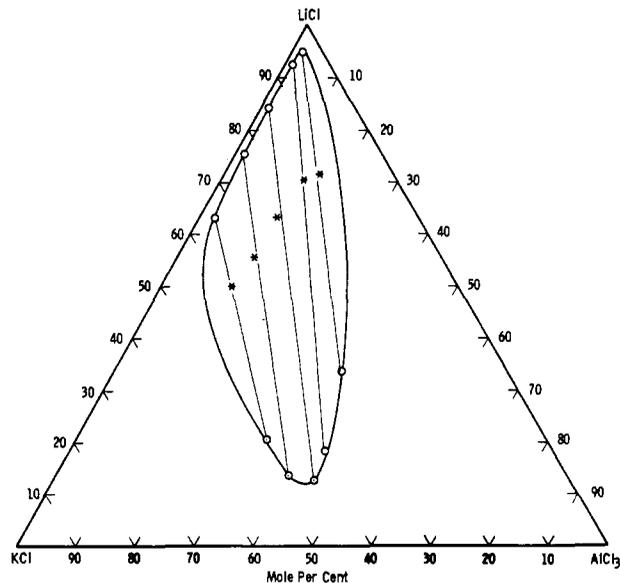


Figure 3. Isothermic section at 625° C.

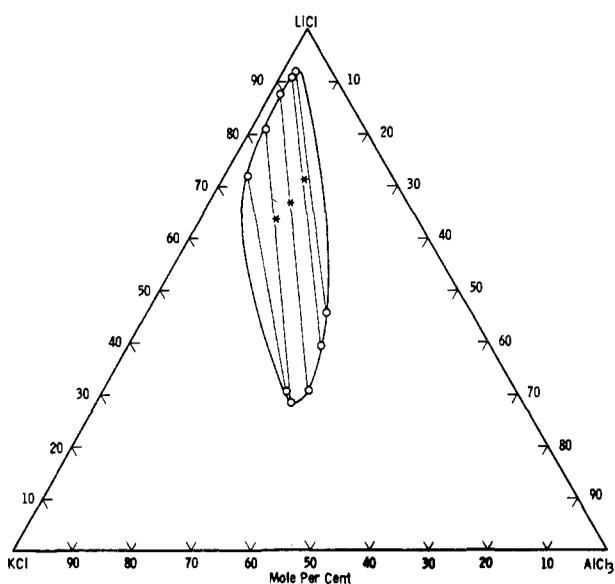


Figure 4. Isothermic section at 715° C.

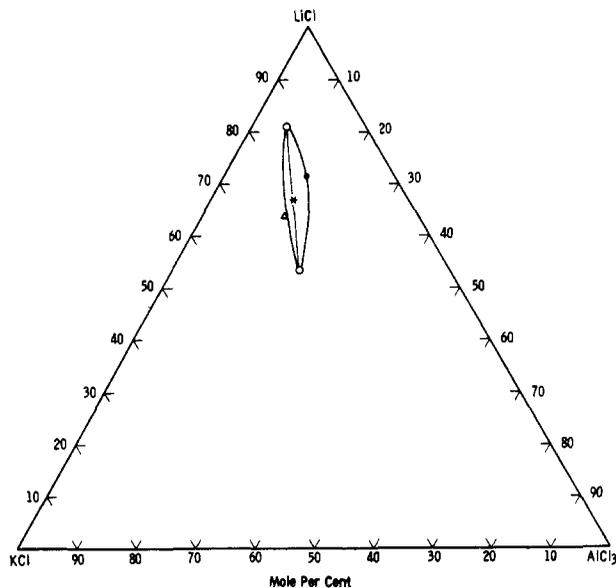


Figure 5. Isothermic section at 770° C.

points and passing through the initial composition (marked by an asterisk) from which the two phases were derived. Points on the binodal curve are average values. The estimated precision, P , of these data (95% confidence level) in mole per cent units is:

	Precision, Mole %
LiCl	± 1.8
KCl	± 1.6
AlCl ₃	± 1.3

In a few cases, sampling and adjustment of composition were conducted in sequence, so the initial composition corresponding to points on the binodal curve was not precisely known. For these data no initial composition is indicated.

In Figures 1 and 2, the segment of the binodal curve on the low KCl side was difficult to locate accurately as a result of a tendency for the LiCl rich phase to solidify. As drawn in Figure 2, the curve passes between a point (solid circle) at 67.3 mole % LiCl, 19.2 mole % KCl, and

13.1 mole % AlCl₃, a composition which shows appreciable solid separation in the LiCl phase, and the asterisk at 63.5 mole % LiCl, 24.0 mole % KCl and 12.5 mole % AlCl₃. The latter composition yields two phases, as shown, with no solid separation. The position of the binodal curve in this region is thus bracketed within narrow limits.

The high freezing point of the LiCl rich phase accounts for the compression of the immiscibility gap at low temperatures. For this reason the areas of the isothermal sections at 525° and at 450° C. are less than that at 625° C. Above 625° C. compression of the immiscibility gap occurs as a result of the increasing solubility of one phase in the other. The system exhibits a true ternary critical point at 775° C. The surface near the critical point is gently curving, and the critical temperature, therefore, is difficult to determine accurately. The value 775° C. is believed correct to within $\pm 2^\circ$ C. and occurs at the composition: 66.9 mole % LiCl, 19.3 mole % KCl, and 13.8 mole % AlCl₃.

The low temperature limit of the immiscibility gap was very difficult to locate, due to the tendency for a solid

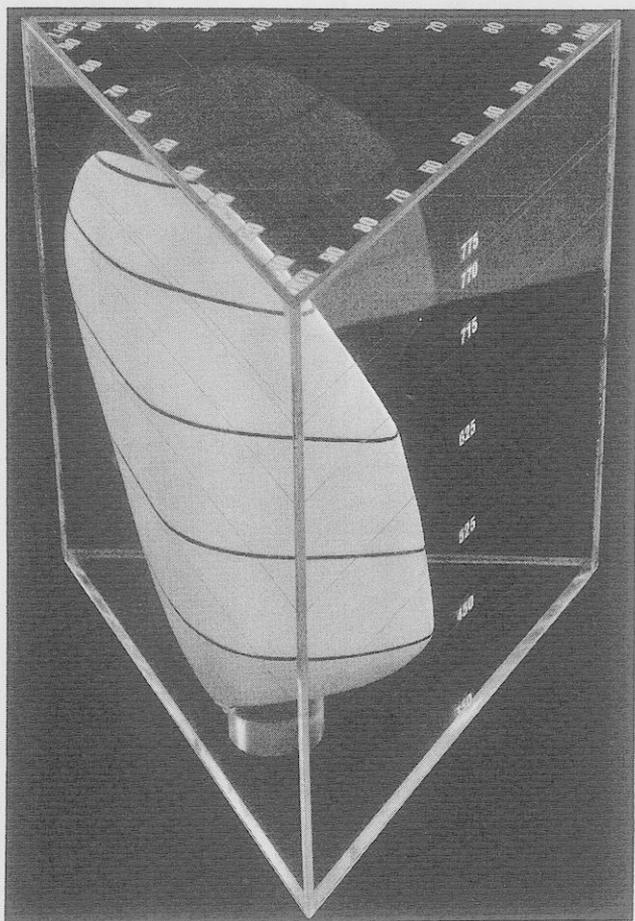


Figure 6. Photograph of the isobaric prism facing the KCl apex

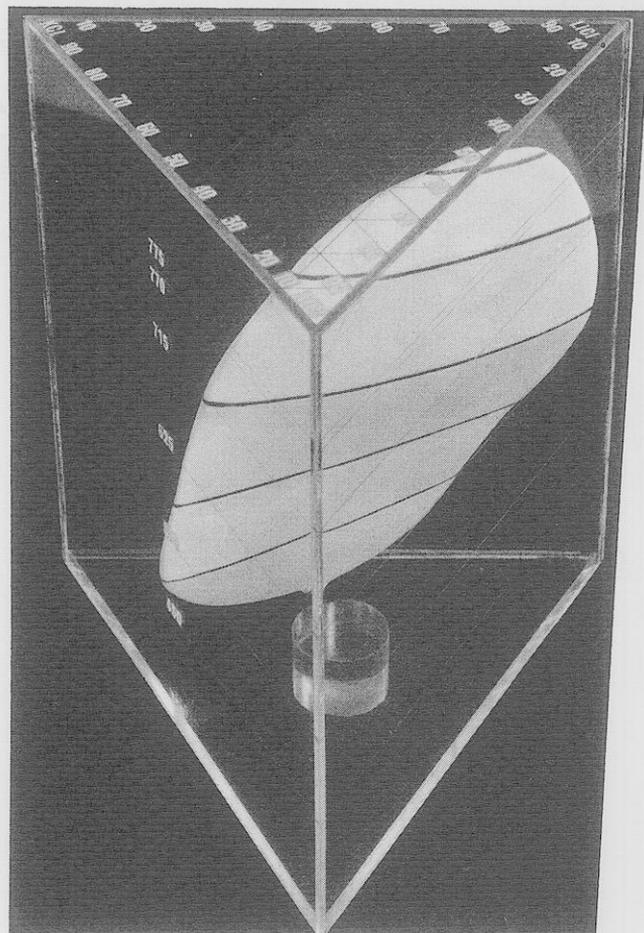
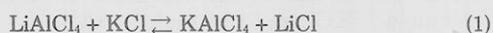


Figure 7. Photograph of the isobaric prism facing the AlCl₃ apex

phase to appear in one or both of the immiscible phases. The lowest temperature at which two phases could be obtained with no solid separation in either phase was 350° C. This temperature was measured when the gross composition was 40.9 mole % LiCl, 49.1 mole % KCl, and 10.0 mole % AlCl₃. Compositions randomly selected a few per cent away from this composition were found to yield solids in one or both phases at higher temperatures than this. Since no unequivocal method for locating this low temperature limit could be devised, this value and the corresponding composition cited should be considered tentative.

Figures 6 and 7 show two views of a model of the three-dimensional phase diagram showing the immiscibility gap enclosed within the isobaric prism. The vertical axis of the prism is a linear centigrade temperature scale, and sections through the prism, shown as curving lines on the surface of the immiscibility gap, correspond to the isothermic sections of Figures 1 to 5. The top surface of the prism is ruled as a conventional triangular composition diagram.

The slope of the tie lines and tendency toward convergence (Figures 1 to 5) at an equimolar KCl-AlCl₃ composition strongly implies that the formation of KAICl₄ (rather than LiAlCl₄) is important in the phase separation phenomenon. The stability of KAICl₄ as a compound is evident from vapor pressure considerations which show that AlCl₃ as such, is almost nonexistent in equimolar KCl-AlCl₃. (At 650° C., the estimated vapor pressure of pure AlCl₃ is about 10 atm.; that of KCl-AlCl₃ is <0.02 atm.). Stated in another way, the position of the equilibrium for the reaction



lies markedly to the right.

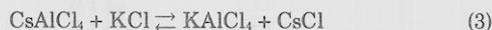
Fischer and Simon (4) report that the equilibrium for the reaction



also lies to the right. Thus, KCl is a better chloride ion donor than either LiCl or NaCl.

The addition of NaCl to the LiCl-KCl-AlCl₃ system results in partitioning of the NaCl between the LiCl-rich and KAICl₄-rich phases. The partition coefficient (KAICl₄/LiCl) for NaCl is 0.56 at 625° C. (mole fraction basis). Based on the average of two determinations, NaCl exhibits a preference for the LiCl phase.

Addition of CsCl to the LiCl-KCl-AlCl₃ system results in quite a different phenomenon. In this case CsCl partitions so as to markedly favor the KAICl₄ (rich) phase. A partition coefficient of 18.2, computed as above, is observed. Further, as addition of CsCl is continued, it is evident that KCl is being progressively displaced from the KAICl₄ phase. Apparently, the position of the equilibrium for the reaction



lies markedly to the left. Thus, CsCl is a better chloride ion donor than KCl.

This relative order of chloride donor ability, increasing from LiCl to CsCl, stands in reciprocal relation to the relative polarizing power of the cation. Of these alkali metal cations, lithium can be considered to compete most successfully with AlCl₃ for chloride ions. The complex ion, AlCl₄⁻, should therefore be less stable in the presence of lithium ions than in the presence of sodium, potassium, or cesium ions.

This concept may provide a basis for understanding the more fundamental question of why this system exhibits immiscibility. Qualitatively, a molten KAlCl_4 solution can be regarded as a quasi lattice of AlCl_4^- tetrahedral with interstitial K^+ ions in numbers sufficient for electrical neutrality. This solution will not exhibit the long range order of a solid crystal, but considerable short range order should persist. Simple Li^+ ions should neutralize the AlCl_4^- tetrahedral as effectively as K^+ ions, in which case complete miscibility would prevail. When faced with the obvious fact of immiscibility, one is forced to conclude that few simple Li^+ ions exist in this system.

The polarizing power of lithium is such that a molten LiCl salt may consist almost entirely of complex poly-ions, Li_2Cl^+ , LiCl_2^- , Li_3Cl_2^+ , etc. The Li_2Cl^+ or Li_3Cl_2^+ ions would not readily enter the AlCl_4^- quasi lattice in competition with K^+ ions, and the system would tend to separate into two immiscible phases.

Berkowitz and Chupka (1) have shown that complex poly-ions of the type proposed above do, in fact, exist in the vapor of LiCl as the predominant species. They also show that the simpler ions become increasingly important in going from NaCl through KCl to CsCl . This latter fact is important in that failure to observe immiscibility (of consequence) in the system NaCl-KCl-AlCl_3 , NaCl-CsCl-AlCl_3 , or KCl-CsCl-AlCl_3 is therefore to be expected. X-ray and neutron diffraction studies have also shown that cation-anion distances contract whereas cation-cation and anion-anion distances increase on going from the solid to the molten state (6).

As indicated earlier, Fischer and Simon (4) report a region of immiscibility in the system NaCl-KCl-AlCl_3 near the AlCl_3 apex. This was not confirmed in these laboratories although no compositions containing more than 66 mole % AlCl_3 were tested. A composition of 16.5 mole % NaCl , 19.5 mole % KCl , and 64.0 mole % AlCl_3 melted near 100°C . and boiled at $200^\circ\text{--}210^\circ\text{C}$. Any region of immiscibility at compositions richer in AlCl_3 than this must exhibit a very narrow range of stability.

The systems NaCl-CsCl-AlCl_3 and KCl-CsCl-AlCl_3 have also been tested over a moderate range of compositions and temperature. No indications of immiscibility were found. The system LiCl-CsCl-AlCl_3 exhibits immiscibility for reasons similar to those advanced for the system LiCl-KCl-AlCl_3 .

The compound KAlCl_4 displays varying degrees of immiscibility with a number of chlorides. In making tests

Table I. Qualitative Survey of Materials Miscible and Immiscible With KAlCl_4

Miscible Compd.	Immiscible Compd.	Remarks
NaCl KCl	LiCl AgCl	Also immiscible with NaAlCl_4 and CsAlCl_4
CsCl TlCl CuCl		
HgCl_2	CaCl_2 BaCl_2 ZnCl_2 CdCl_2 PbCl_2 SnCl_2 MnCl_2	Reference 2 Monophasic above 550°C . Also immiscible with NaAlCl_4 Monophasic above 340°C .
BiCl_3 FeCl_3	LaCl_3	

for immiscibility, the approximately 1 to 1 KCl-AlCl_3 salt was combined with the anhydrous salt to be tested in 2 to 1, 1 to 1, and 1 to 2 weight ratios after which the mixtures were melted and observed over a range of temperatures. This procedure would miss cases of immiscibility in some instances, so a negative finding is not necessarily conclusive. Results are shown in Table I and are arranged according to valence.

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