Miscibility of Liquid Metals with Salts. XI.
System Yttrium Metal-Yttrium Trichloride at High Temperatures

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A large miscibility gap from about 21 to 97 mol % yttrium in yttrium chloride was found at the monotectic temperature of 1480°C. This is contrary to data in the literature suggesting complete miscibility at temperatures below the melting point of yttrium (~1530°C). A consolute temperature above 1600°C is estimated for this system.

As a result of our previous work (*2*, *5*, *6*), we have been able to correlate solubilities of alkali and alkaline earth metals in their own halides both at temperatures near the melting points of the salts and at much higher consolute temperatures above which the systems are completely miscible. For the lanthanide systems the solubility of the metals in their halides is known in most cases only at temperatures within a few hundred degrees of the melting point of the salt (*2-4*). We have extended these measurements for the Y-YCl_3 system to much higher temperatures (~1550°C) in an attempt to find a consolute temperature for at least one trivalent salt-metal system. This system was chosen for study because vapor pressure measurements reported in the literature (*7*) indicated a solubility of 35 mol % for yttrium at about 1350°C, high enough to suggest the possibility of complete miscibility at all temperatures below the melting point of yttrium (~1530°C). If this were true, other lanthanide systems might have consolute temperatures below 1500°C since yttrium is less soluble than most of the lanthanide metals in the chloride at the eutectic temperature (*4*).

Experimental

The data shown in Figure 1 were obtained by the method of thermal analysis (heating and cooling curves). The apparatus has been described in detail previously (*6*). Briefly, a platinum-wound Marshall tube furnace was used to attain the necessary high temperatures. The tantalum capsules into which the salt and metal were loaded and sealed by welding in a helium drybox were mounted in a Morganite impervious recrystallized alumina tube in the furnace. A Pt-Pt 10% Rh thermocouple was placed in a well extending about 1.5 cm into the tantalum capsule from the bottom. The entire furnace assembly could be rocked about the horizontal position to obtain mixing.

The yttrium chloride was prepared by the reaction of yttrium oxide with a large excess of ammonium chloride. Upon completion of the reaction, the excess ammonium chloride was sublimed away at temperatures up to 500°C. The yttrium chloride was then sublimed under high vacuum at 800°C. The chloride contained less than 0.1% of other lanthanides and no significant quantities of foreign cations. The metal contained less than 0.5% of other lanthanides, no foreign cations, 120 ppm H_2, 140 ppm N_2, and 2000 ppm O_2. The melting and transition temperatures of the yttrium were found to be 1530° ± 5°C and 1505° ± 5°C as compared to 1525° ± 3°C and 1480° ± 2°C reported in the literature (*1*).

The thermocouple was checked during the course of the measurements against the melting point of lanthanum trifluoride. This was found to be 1494° ± 2°C in agreement with our previous measurements as well as with those in the literature (*6*).

Results and Discussion

As can be seen from Figure 1 our results are in disagreement with those of Polyachenok and Novikov (*7*). We find a large miscibility gap from about 21 to 97 mol % yttrium in yttrium chloride at the monotectic temperature of 1480°C. The second series of points at 1475°C are due to the transition in yttrium metal. Since the actual vapor pressure data from which the solubility data were derived are not given in ref. *7*, it is difficult to postulate the reason for the apparently higher solubility of yttrium reported by Polyachenok and Novikov. Their measurements were made "in quartz ampoules coated internally with a compact layer of metallic molybdenum." Whether the layer of molybdenum maintains its integrity and protects the quartz from attack from yttrium at such elevated temperatures is open to question.

From our data we estimate the consolute temperature to be above 1600°C. It appears unlikely that a consolute temperature can be measured with the present apparatus (maximum temperature about 1550°C) for any lanthanide metal-halide system with the exception of those involving the largely divalent europium and ytterbium metals and possibly samarium and thulium metals (*6*).

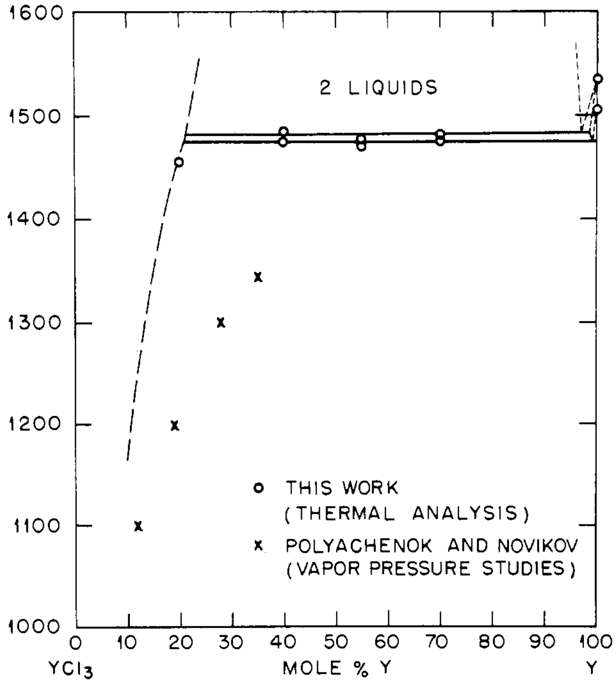

Figure 1. The system YCl_3-Y

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Surface Tension of LiCl–KCl Eutectic Mixture

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The surface tension of the eutectic composition of the binary molten salt system LiCl-KCl has been measured over the temperature range 375–600°C.

Even though the molten eutectic mixture of lithium and potassium chloride has been used extensively as a solvent in both electrochemical and chemical studies, very little is known of its physical properties—e.g., surface tension, viscosity. As a consequence of studying the binary molten salt system LiCl–KCl, we have measured the surface tension of the eutectic, and report our findings in this paper.

Of the numerous methods for determining the surface tension of molten salts, the maximum bubble pressure method was chosen for this investigation. This technique has been used to measure the surface tension of molten salts by numerous workers, and the theory and practice of this method have been extensively reviewed by Dahl *(3)*.

Experimental

The experimental details were essentially the same as those of Dahl and Duke *(4)* with the exception that the capillary was fabricated from pure gold and was 2.25 cm long with an orifice approximately 0.8 mm in diam. All measurements were made in a purified argon atmosphere on carefully purified salts. The temperature of the melt was measured with a chromel-alumel thermocouple and was maintained constant within ±0.5°C. The furnace was arranged in such a manner that the vertical temperature gradient of the melt was less than 1.0°C. A more detailed discussion of the experimental technique is given elsewhere *(8)*.

Both the lithium chloride and potassium chloride used in these experiments were of analytical reagent purity and were carefully vacuum-dried before use. The eutectic composition was made up by accurately weighing the dried materials directly into the container and, after the salts were melted, they were further purified by the use of chlorine and hydrogen chloride gas *(7)*. All weighing and other manipulations of the dried salts were done in an atmosphere whose water content was less than 100 ppm.

The exact composition of the eutectic in the LiCl–KCl system is a matter of some controversy *(1)*. For this work the eutectic composition was determined with the aid of a hot-stage microscope. A number of possible eutectic compositions were examined to obtain a sample exhibiting the eutectic properties. The composition of this sample was then determined by analyzing for both lithium and potassium by atomic absorption. Our results agree with those of Plyushchev and Kovalev *(9)*; the eutectic in this system lies at 41.8 ± 0.3 mol % KCl–58.2 ± 0.3 mol % LiCl and has a melting point of 352° ± 1°C.

Prior to determining the surface tension of the LiCl–KCl eutectic, we measured the surface tension of both $NaNO_3$ and KNO_3, and the agreement between our results and the accepted literature values *(5)*, shown in Table I, is quite good.

In all our calculations of the surface tension, appropriate correction was made for expansion of the capillary orifice *(2)*.

Results and Discussion

A total of 35 determinations of the surface tension of the eutectic LiCl–KCl mixture was made at different depths of immersion of the capillary and at various temperatures between 375° and 600°C. The resulting surface tension could be expressed as a linear function of the temperature by an expression of the form:

$$\gamma = 165.3 - 0.0780\, t$$

The standard deviation in these experiments was 0.2 dyn/cm. In calculating the surface tension, the density values of Van Artsdalen and Jaffee *(10)* were used.

To the best of our knowledge, the only other measurement of the surface tension of the LiCl–KCl system was that of Jaeger *(6)* at 447°C on the composition 40.5 mol % KCl–59.5 mol % LiCl, which is approximately the eutectic composition. His value of 123.6 dyn/cm is about 5% lower than our value, 130.4 dyn/cm.

While the surface tension does change with composition, the discrepancy between our results and those of Jaeger's cannot be accounted for on that basis. Measurements of the surface tension of other compositions in

Table I. Surface Tension Values for $NaNO_3$ and KNO_3

Salt	γ (lit.) (dyn/cm at t°C)	γ (exptl) (dyn/cm at t°C)
$NaNO_3$	$136.1 - 0.0573\, t$	$138.8 - 0.0613\, t$
KNO_3	$137.3 - 0.0727\, t$	$136.5 - 0.0705\, t$

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