JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 78A, No. 4, July–August 1974

The System $NaCl-AlCl_3$

Ernest M. Levin

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

and

J. F. Kinney,* R. D. Wells,* and J. T. Benedict

Fairleigh Dickinson University, Teaneck, New Jersey 07666

(March 14, 1974)

The system $NaCl-AlCl_3$ has been restudied by DTA, visual observation, and x-ray diffraction powder techniques for identification of crystalline phases. It was confirmed that the system contains one intermediate compound $NaAlCl_4$ with an incongruent mp of 153 ± 0.5 °C and a region of liquid immiscibility extending from 80.25 to 99.6 mol percent $AlCl_3$ at 191.3 °C, the monotectic temperature.

Key words: Immiscibility; $NaAlCl_4$; phase equilibrium; system $AlCl_3-NaCl$; system $NaCl-AlCl_3$.

1. Introduction

A summary of the pertinent data in previous studies [1–5][1] of the system is given in table 1. In addition, Boud [6] in 1904 reported compound compositions of $3NaCl \cdot AlCl_3$, $NaCl \cdot AlCl_3$, and $NaCl \cdot 2AlCl_3$. The compound $NaAlCl_4$ with an incongruent melting point at ~153 °C seems well established and its crystal structure has been determined [7], using a Weissenberg camera. It is orthorhombic (space group $P2_12_12_1$), with $Z = 4$ and d (x-ray) = 2.00 g/cm^3. However, the existence of additional compounds and the occurrence of a stable two liquid region of immiscibility are questionable.

2. Experimental Procedure

The general nature of the diagram was first established with a commercial DTA apparatus[2], using a microholder with Al_2O_3, as a reference material and a 10°/min heating rate. The final diagram (fig. 1) was refined by determining the liquidus and solidus curves by visual observation. The chlorides of aluminum and sodium were obtained as Reagent Grade. The NaCl was analyzed to be 99.7 ± 0.1 percent pure. The $AlCl_3$ was resublimed at 135–150 °C under vacuum from molten $NaCl \cdot AlCl_3$ mixtures containing Al-metal strips [8]. The final purity of $AlCl_3$ was analyzed to be 99.8 ± 0.1 percent. Atomic absorption analysis for Na confirmed a content of < 0.1 percent Na in the $AlCl_3$. To prevent hydration of $AlCl_3$, various mixtures of NaCl and $AlCl_3$ were prepared in glove bags flushed with anhydrous N_2 and sealed under vacuum in Pyrex tubes. Compositions not forming two liquids, i.e., those below 80 mol percent $AlCl_3$, were subjected to three cycles of grinding and sealing in the glove box, followed by heating to promote homogeneity. Samples which had been reground several times appeared pure white in color; but when they were heated to the appropriate invariant temperature of either 153 or 107 °C, they turned sharply to a gray hue.

The two liquid region of the diagram was studied visually by introducing the sealed sample into a nichrome-wound Pyrex tube furnace (40 mm O.D.) insulated by an outer Pyrex tube. Sealed samples with 80 mol. percent $AlCl_3$ and less were studied visually in a silicone oil bath, stirred with a magnetic stirrer. Heat control was accurate enough to permit heating and cooling rates of 6 °C per hour or less. The liquidus temperatures were determined by observing under a magnifying glass the disappearance of tiny crystals approximately 0.5 mm in their largest dimension. Several determinations were averaged, and all temperatures are estimated accurate to ± 0.5 °C. The Chromel-Alumel thermocouple was calibrated using pure Sn (mp 231.89 °C) and the normal freezing and boiling points of water. At times a calibrated Hg thermometer was used also in the oil bath.

*Now with Avon Products Inc., Research and Development Division, Suffern, New York 10901.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Certain commercial materials and equipment are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

TABLE I. *Phase studies in the system* NaCl–$AlCl_3$

Investigator	Methods of Study	Incong. mp of $NaAlCl_4$	Location of $NaAlCl_4$–$AlCl_3$ Eutectic		Two Liquid Region		Notes
					Extent	Temp.	
		°C	Mol % $AlCl_3$	Temp. °C	Mol % $AlCl_3$	°C	
Kendall, et al. (1923) [1]	Visual observation in sealed tubes	152	~ 61	115	82.0 – > 99.8	193.5	Compound XNaCl · Y$AlCl_3$ under two liquids.
Plotnikov and Shvartsman (1936) [2]	Heating and cooling curves automatically recorded; sealed	—	61	108			Only studied between 50.2 and 80.8 mol % $AlCl_3$.
Shvartsman (1940) [3]	Heating and cooling curves automatically recorded, sealed	152	61	108	80.8 – 100	190.0	
Cretien and Lous (1943) [4]	Cooling curves in N_2 atm; Chem. analysis	155	65	105	None detected		
Midorikawa (1955) [5]	Cooling curves	154	62	112			Only studied between 48.1 and 70.7 mol % $AlCl_3$.
Present study	DTA; visual observation in sealed tubes; x ray	153 ± 0.5	61.4	107.2	80.25 – 99.6	191.3	

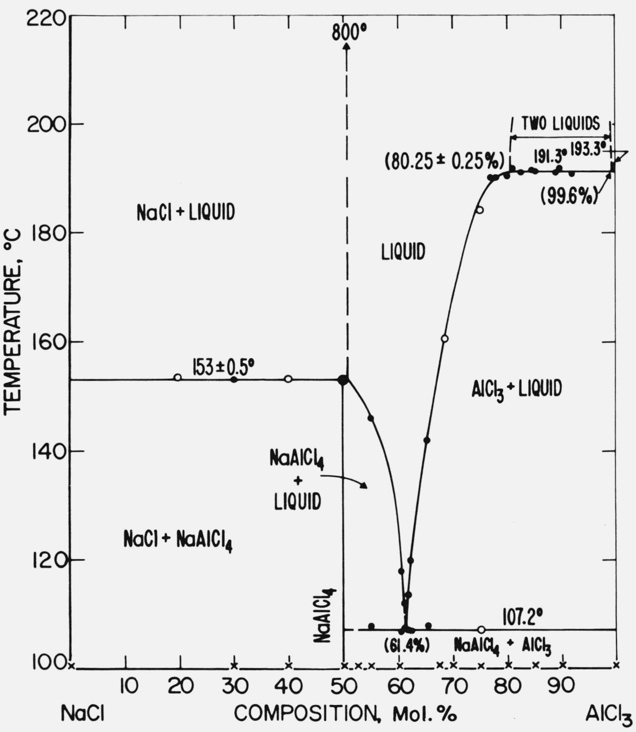

FIGURE 1. *The system* NaCl–$AlCl_3$.

o – Visual observation.
O – DTA.
X – X-ray examination at room temperature.

The solid phases were identified by x-ray diffraction powder techniques, using a dry mount with $Mg(ClO_4)_2$ as desiccant. All compositions could be interpreted in terms of the components NaCl and $AlCl_3$, and one intermediate compound $NaAlCl_4$. The x-ray powder pattern of $NaAlCl_4$ was indexed on the basis of an orthorhombic cell [7], with $a = 10.33$ Å, $b = 9.91$ Å, $c = 6.18$ Å, within a few hundreths Ångstroms of the dimensions reported by Baenziger [7] and Semenenko et al. [9]. Small irregular variations in interplanar spacings with different compositions are attributed to hydration effects rather than to an indication of slight solid solubility of $AlCl_3$ in $NaAlCl_4$.

A two liquid region, as reported by Kendall et al. [1], and Shvartsman [3], was found to exist between a composition of 80.25 ± 0.25 and 99.6 mol percent $AlCl_3$ at 191.3 °C. Two liquids were observed visually to form in several samples containing 80.5 mol percent $AlCl_3$ or greater (fig. 1). In repeated experiments, two liquids were never observed in samples of 80.0 mol percent $AlCl_3$ or less, i.e., 79.5, 77.9, and 75 percent. Atomic absorption analysis for Na in the upper liquid segregated at ~192 °C revealed the composition to be 0.4 mol percent NaCl. The composition of the $AlCl_3$-rich liquid, therefore, is 99.6 mol percent $AlCl_3$.

Several attempts were made to study the closure of the two-liquid dome. Samples of composition 80.6 and 90.2 mol percent $AlCl_3$ were heated in sealed glass tubes to form two liquids. After heating at a rate of 5 °C/day and reaching temperatures of above

210 °C, the tubes burst. The triple point of $AlCl_3$ is reported [10] at 193.3 °C and 2.33 atm.

3. Conclusion

In conclusion, a restudy of the system $NaCl-AlCl_3$ has shown it to contain only one intermediate compound and a definite region of liquid immiscibility. Also, temperatures and compositions of invariant points have been closely defined.

4. References

[1] Kendall, J., Crittenden, E. D., and Miller, H. K., J. Am. Chem. Soc. **45,** 963 (1923); also, Fig. 3107 in Phase Diagrams for Ceramists, published by the Am. Ceram. Soc., Inc. (1969).

[2] Plotnikov, V. O., and Shvartsman, U. I., Western Inst. Chem., Akad. Nauk URSR **3,** 387 (1936).

[3] Shvartsman, U. I., Western Inst. Chem., Akad, Nauk URSR **7,** 1 (1940); also, Fig. 1314 in Phase Diagrams for Ceramists, published by the Am. Ceram. Soc., Inc. (1964).

[4] Chrétien, A., and Lous, E., Compt. Rendu **217,** 451 (1943).

[5] Midorikawa, R., J. Electrochem. Soc. Japan **23,** 72 (1955).

[6] Boud, A., Ann. Chim. Phys. **1,** 8 (1904).

[7] Baenziger, N. C., Acta Cryst. **4,** 216–19 (1951).

[8] Uhr, D., Master's Thesis, 1970, Fairleigh Dickinson Univ., Teaneck, N.J. 07666.

[9] Semenenko, K. N., Surov, V. N., and Kedrova, N. S., Russ. J. Inorg. Chem. (English Transl.) **14,** [4] 481–83 (1969).

[10] Treadwell, W. D., and Terebesi, L., Helv. Chim. Acta **15,** 1053–66 (1932).

(Paper 78A4–830)