Research Paper

Phase Diagrams of ThCl₄ Systems Containig NaCl, KCl and LiCl and the Limitation of the Congruently Melting Compounds Formation

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The phase diagrams of NaCl-ThCl₄, KCl-ThCl₄, and LiCl-ThCl₄ are determined. These systems show the congruently melting compounds (CMC) such as Na₂ThCl₆, K₂ThCl₇, and KThCl₅. However, no compound exists in LiCl-ThCl₄ system.

The present author proposes a new method for the estimation of the limitation of the congruently melting compound formation. This method is applied to the above systems and other two components systems, containing the alkali metal chloride. In this method the polarization power of cation plays the important role.

When the congruently melting compound is formed, P_2/P_1 may be within 66%, where P_1 is the value of the polarization power of the host cation and P_2 is the mean value of the polarization power of the next nearest neighbor cations.

1 Introduction

It would be obvious that the polarization power¹⁾ (Ze/r^2 , Z : valency of ions, r : ionic radius) plays the important role for the formation of some melting compound containing ionic components by the reason that the most important interaction between ions is the coulombic interaction.

The present author tries to estimate the limitation of the congruently melting compound formation by comparing the polarization power between ions. This new method of analysis shall be applied to the systems NaCl-ThCl₄, KCl-ThCl₄, and LiCl-ThCl₄, which have been determined by the present author, and to the other systems containing alkali chloride.

2 Experimental

ThCl₄ was prepared as previously reported²⁾. NaCl and KCl were prepared as single crystal by Kyropoulos method. LiCl was prepared by bubbling dry N₂ gas into melt, then solidified in vacuum after having kept about 5 hrs. under vacuum.

Rates of cooling were kept as approximately 1°C/min at 800°C and 0.5°C/min at 400°C. From the obtained cooling curve the freezing point was determined.

3 Results

The phase diagrams of NaCl-ThCl₄, KCl-ThCl₄, and

LiCl-ThCl₄ systems are determined. The results are shown in Fig. 1, 2 and Fig. 3, respectively.

For the NaCl-ThCl₄ system, except for small differences in detail, the general form of the phase diagram is similar to that published by Tanii³⁾.

For the KCl-ThCl₄ system, the form of the phase diagram is quite different from the one published by Tanii³⁾ and by Desyatnik⁴⁾.

The above two systems show the congruently melting compounds such as Na₂ThCl₆, K₂ThCl₇, and KThCl₅.

For the LiCl-ThCl₄ system, the form of the phase diagram is a little different from the one determined by Tanii³⁾, and the phase diagram of the LiCl-ThCl₄ system shows no congruently melting compound.

The above results of compound formation seem to suggest that, the polarization power of the host and that of the added cation play the important role for the melting compound formation.

The present author desires to propose a new method which uses the polarization power of cation for the estimation of "the limitation of the congruently melting compound formation" of two component systems containing the alkali chloride.

Let us assume, as the first approximation, the structure of these systems are of NaCl type in which the numbers of the next nearest neighbor ions are twelve considering that one of the component is alkali chloride.

The formation and the stability of the congruently melting compound are estimated by comparing the

Fig. 1 Phase diagram of NaCl-ThCl₄ system Fig. 2 Phase diagram of KCl-ThCl₄ system Fig. 3 Phase diagram of LiCl-ThCl₄ system

value of the polarization power of the central cation (P_1) which has the larger polarization power and the mean value of the polarization power of the next nearest neighbor cations (P_3) in the NaCl type structure.

As we have assumed the random distribution of cations over NaCl type structure, P_3 may be given as follows, where X is the number of the host cations (same as central cation) in the twelve neighbors,

$$P_3 = \frac{XP_1 + (12-X)P_2}{12} \quad (1)$$

and P_2 is the value of the polarization power for the other cation.

This formula is equivalent to $P_3 = xP_1 + (1-x)P_2$, where x is the mole fraction of the host cation chloride.

The limitation of congruently melting compound of the NaCl-ThCl₄, the KCl-ThCl₄ and the LiCl-ThCl₄ systems obtained above are estimated by using Eqn. (1).

Here the values of the polarization power of Na⁺, K⁺, Li⁺ and Th⁴⁺ are 1.04, 0.57, 1.64 and 3.31, respectively.

For NaCl-ThCl₄ system which has Na₂ThCl₆ compound the values of P_3 and $P_3/P_1 \times 100$ (%) are

$$P_3 = \frac{8 \times 1.04 + 4 \times 3.31}{12} = 1.79 \quad (2)$$

$$P_3/P_1 \times 100 = 54 \text{ (\%)}$$

For KCl-ThCl₄ system which has K₃ThCl₇ and KThCl₅ compounds, the larger values of P_3 and $P_3/P_1 \times 100$ are

$$P_3 = \frac{6 \times 0.57 + 6 \times 3.31}{12} = 1.94 \quad (3)$$

$$P_3/P_1 \times 100 = 59 \text{ (\%)}$$

However, in the LiCl-ThCl₄ system the congruently melting compound is not observed. Since Li⁺ has large value of polarization power (Li⁺: 1.64) and small radius it tends to destroy the crystal field stabilization of Th⁴⁺ compound.

We have calculated $P_3/P_1 \times 100$ for other 34 systems containing alkali chloride. The results are shown in Table 1.

From these results we can say about the limitation of the congruently melting compound with a few exceptions (about 10%), as follows:

"When the congruently melting compounds are usually formed and stable for two component systems containing alkali chloride, the values of P_3/P_1 may be less than 66%".

However, for KCl-PbCl₂ system⁵⁾ with KPb₂Cl₅ compound the values of P_3 and $P_3/P_1 \times 100$ are

$$P_3 = 1.20 \quad (4)$$

$$P_3/P_1 \times 100 = 79 \text{ (\%)}$$

This may be caused by the fact that polarizability, being the other important property for the C.M.C. formation, of Pb (3.6 Å³)* is much larger than of K⁺

* Calculated

Table 1 P_1, P_2, P_3 and $P_3/P_1 \times 100$ of the systems containing alkali chloride

Systems	C.M.C.	P_1^*	P_2^*	P_3^*	$P_3/P_1 \times 100(\%)$
LiCl- UCl_4	Li_2UCl_6	3.64(U^{4+})	1.64(Li^+)	2.31	63
NaCl- ZrCl_4	Na_2ZrCl_6	5.28(Zr^{4+})	1.04(Na^+)	2.45	46
NaCl- HfCl_4	Na_2HfCl_6	6.58(Hf^{4+})	1.04(Na^+)	2.89	44
NaCl- UCl_4	Na_2UCl_6	3.64(U^{4+})	1.04(Na^+)	1.91	52
KCl- MgCl_2	KMgCl_3	3.29(Mg^{2+})	0.57(K^+)	1.93	59
KCl- SrCl_2	K_2SrCl_4	1.24(Sr^{2+})	0.57(K^+)	0.79	64
KCl- MnCl_2	KMnCl_3	2.42(Mn^{2+})	0.57(K^+)	1.50	62
KCl- FeCl_2	KFeCl_3	2.90(Fe^{2+})	0.57(K^+)	1.74	60
KCl- ZnCl_2	K_2ZnCl_4	2.90(Zn^{2+})	0.57(K^+)	1.35	46
KCl- CdCl_2	KCdCl_3	1.88(Cd^{2+})	0.57(K^+)	1.23	65
KCl- TiCl_3	KTiCl_4	6.30(Ti^{3+})	0.57(K^+)	3.44	55
KCl- LaCl_3	K_3LaCl_6	2.01(La^{3+})	0.57(K^+)	1.05	52
KCl- CeCl_3	K_2CeCl_5	2.15(Ce^{3+})	0.57(K^+)	0.97	45
KCl- NdCl_3	K_3NdCl_6	2.27(Nd^{3+})	0.57(K^+)	1.00	44
KCl- PuCl_3	K_3PuCl_6	2.94(Pu^{3+})	0.57(K^+)	1.16	40
KCl- ZrCl_4	K_2ZrCl_6	5.28(Zr^{4+})	0.57(K^+)	2.14	41
KCl- HfCl_4	K_2HfCl_6	6.58(Hf^{4+})	0.57(K^+)	2.57	39
KCl- UCl_4	K_2UCl_6	3.64(U^{4+})	0.57(K^+)	1.59	44
KCl- PbCl_2	KPb_3Cl_5	1.52(Pb^{2+})	0.57(K^+)	1.20	79
RbCl- PbCl_2	RbPbCl_3	1.52(Pb^{2+})	0.45(Rb^+)	0.99	65
RbCl- MgCl_2	RbMgCl_3	3.29(Mg^{2+})	0.45(Rb^+)	1.87	57
RbCl- TiCl_3	RbTiCl_4	6.30(Ti^{3+})	0.45(Rb^+)	3.38	53
RbCl- UCl_3	Rb_3UCl_6	2.78(U^{3+})	0.45(Rb^+)	1.03	37
RbCl- ZnCl_2	RbZn_2Cl_6	2.90(Zn^{2+})	0.45(Rb^+)	2.08	72
CsCl- MgCl_2	CsMgCl_3	3.29(Mg^{2+})	0.37(Cs^+)	1.83	56
CsCl- AlCl_3	CsAlCl_4	9.23(Al^{3+})	0.37(Cs^+)	4.30	47
CsCl- UCl_4	Cs_2UCl_6	3.64(U^{4+})	0.37(Cs^+)	1.46	44
CsCl- LaCl_3	Cs_3LaCl_6	2.01(La^{3+})	0.37(Cs^+)	0.778	39
CsCl- NdCl_3	Cs_3NdCl_6	2.27(Nd^{3+})	0.37(Cs^+)	0.846	37
CsCl- HfCl_4	Cs_2HfCl_6	6.58(Hf^{4+})	0.37(Cs^+)	2.44	37
CsCl- CeCl_3	Cs_2CeCl_5	2.15(Ce^{3+})	0.37(Cs^+)	0.782	36
CsCl- ZrCl_4	Cs_2ZrCl_6	5.28(Zr^{4+})	0.37(Cs^+)	2.01	38
CsCl- CuCl	CsCu_2Cl_3	1.09(Cu^+)	0.37(Cs^+)	0.87	79
CsCl- ZnCl_2	CsZn_2Cl_6	2.90(Zn^{2+})	0.37(Cs^+)	2.05	71

The ionic radius of cations are of Goldschmidt.

But the radius of Cu^+ is of Pauling, and those of Pu^{3+} and of U^{3+} are of Zachariasen.

* By Goldschmidt, arbitrary unit.

($1.00 \text{ \AA}^3$)⁹.

This means that when the mean polarization power of the next nearest neighbor cations is larger than about 66% of the polarization power of the central one, complex compounds which are composed of a central cation and of the surrounding anions will not exist.

The existence of the Na_2ThCl_6 compound in NaCl-ThCl_4 system, of K_3ThCl_6 and of KThCl_5 compounds in KCl-ThCl_4 and no existence of any Li^+ compound in LiCl-ThCl_4 system show that the complex compounds are stabilized with decreasing the polarization power from Li^+ to K^+ .

As for the case of Rb^+ and Cs^+ , the complex compounds are stabilized with increasing the polariza-

tion power from Rb^+ to Cs^+ .

The formation of the complex ions in fused salts may be inferred by using the phase diagram.

Since it might be considered that same coordination of Th^{4+} occur in both solid and liquid states of alkali-chloride, for example, the NaCl-ThCl_4 system in solid state shows congruently melting compound as Na_2ThCl_6 and in the liquid state complex ion as $2\text{Na}^+ + [\text{ThCl}_6]^{2-}$.

The $[\text{ThCl}_6]^{2-}$ is in agreement with the result obtained through the study of e.m.f.⁷⁾ of conductivity¹⁾ and of density measurements⁹⁾.

Then for the melt of the KCl-ThCl_4 system, the complex ions $[\text{ThCl}_5]^-$ and $[\text{ThCl}_4]^{3-}$ will be expected and no complex ions are formed for the LiCl-KCl

system.

When Th^{4+} is surrounded by anions in the melt as Na^+ in NaCl crystal, the coordination of Th^{4+} compounds becomes 5 or 6 or 7 according to the concentration of Th^{4+} . This tendency is also affected strongly by the polarization of the co-existing cation.

4 Conclusion

- 1) The phase diagrams of NaCl-ThCl_4 , KCl-ThCl_4 and LiCl-ThCl_4 systems are determined.
- 2) The limitation of the congruently melting compound formation is confirmed for many systems containing alkali chloride by the new method proposed by the present author.
- 3) When the congruently melting compound is formed in the above systems, the values of P_3/P_1 may be within 66%.

- 4) This means that complex compounds in melt which are composed of a cation surrounded by anions will be able to exist when the mean polarization power of the next nearest neighbor cations is less than about 66% of the polarization power of the central one.

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Research Paper

Electrolytic Preparation of Metanilic Acid

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The Electrochemical reduction of sodium salt of *m*-nitrobenzene sulphonic acid in sulphuric acid solution to metanilic acid was studied using the rotating electrode technique. Among the various materials, copper and deposited tin appeared to be the best cathode materials for the reduction. It was also found that metanilic acid separated out easily in the cell when about 50% of the theoretical current was passed using a nearly saturated solution of the sodium salt of the *m*-nitrobenzene sulphonic acid. The paper deals with the conditions of electrolysis, the isolation of the product and the reuse of the electrolyte.

1 Introduction

Metanilic acid is a valuable intermediate for the synthesis of a number of dyes and for the preparation of PAS (para-aminosalicylic acid) a powerful anti tuberculosis drug. The total demand in India is estimated at 300 tons/year. The actual production is not known but major requirements are still met by imports.

Metanilic acid is usually prepared by the reduction of *m*-nitrobenzene sulphonic acid by the classical Behamp process. In this method, dilute solutions of *m*-nitrobenzene sulphonic acid is reduced and metanilic acid is isolated after concentrating the solution. The

product so isolated is not suitable for synthesis of dyes or drugs because of the iron contamination and requires elaborate purification techniques.

It is well known that in the electrochemical synthesis, the purity of the chemicals prepared are quite high as compared to the chemical synthesis, although the yields may be almost similar. In such cases, electrochemical process may be preferred as compared to the chemical process and since absolute purity is essential in the process of dye making and drugs, the electrochemical synthesis will score above the conventional chemical synthesis. For this particular synthesis, studies on the electrochemical synthesis was taken up with a view to ascertain its advantages over the conventional