

The Investigation of Conductivity of Liquid NdCl₃–LiCl–KCl System by Mixture Design

Zhang Yifeng,* Sui Dianpeng, Huang Xuebing, and Wang Shulan

Northeastern University, Shenyang 110006, P. R. China

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Scheffe' simplex centroid design and alternating electric bridge method have been used to design an experiment and to measure the conductivity of the rare earth molten salt system NdCl₃–LiCl–KCl. The results are presented in the form of a regression equation between composition and conductivity, as well as in the form of an isogram of conductivity for the ternary system.

Conductivity with viscosity, density, and surface tension are basic physicochemical properties of molten salts. Such measurements are important for the study of molten salt structure and for the electrolysis production of rare earth metal. But there are many difficulties in the measurement of such properties, especially in systems containing rare earth chloride and a multicomponent system such as difficulties in obtaining dehydrated salts of chloride, wasting time and high expense. Reports about properties of such systems are few. Mixture design¹⁾ is a new statistical method of design. Because it is efficient and economic, it has been widely used in experimental design in all fields. Its application to physicochemical areas can be seen in references.^{2–4)} In this paper, the conductivity of ternary system NdCl₃–KCl–LiCl has been studied by one of the methods of mixture design: Scheffe' simplex centroid design.⁵⁾ Only seven experimental points were employed for the regression equation between composition and conductivity and the isogram of conductivity. This kind of method of experimental design can be extended to the studies of systems with more compositions and to study of other properties.

Experimental

Preparation of Material. Dehydration of LiCl was performed by heating the mixture of LiCl and NH₄Cl at vacuum conditions. The melting point (mp) of LiCl obtained is 883 K. The mp of KCl after drying is 1045 K. NdCl₃ was obtained by the following process: Nd₂O₃ (99.5 wt%) was dissolved in hydrochloric acid to obtain NdCl₃·6H₂O, then this was heated in vacuum to dehydrate NdCl₃·6H₂O step by step in a dry HCl atmosphere. Its mp is 1033 K. All samples for measurements are made in a box containing P₂O₅.

Measurement of Conductivity. The conductivity has been measured by the Wheatstone' bridge method. The Quartz capillary cell is about 1 cm longer than the Pt electrode in order to increase the response resistance of the sample. The weight of the sample is about 15 g. Argon is used

as protecting atmosphere. The experimental temperature is 873 K and was controlled within ±2 K. One experimental design, simplex-centroid design,⁵⁾ adopts the fitting of the *q*th order centroid polynomial:

$$Y = \sum_{i=1}^q \beta_i X_i + \sum_{1 \leq i < j \leq q} \beta_{ij} X_i X_j + \sum_{1 \leq i < j < k \leq q} \beta_{ijk} X_i X_j X_k + \cdots + \beta_{12 \cdots q} X_1 X_2 \cdots X_q. \quad (1)$$

For the mixture design of three-component system, *q* = 3, Eq. 1 is written as follows:

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{123} X_1 X_2 X_3. \quad (2)$$

In order to determine the seven parameters in Eq. 2 one needs to design seven experimental points. Because the experimental temperature is 873 K, and lowers than melting points of all three pure components, then the concentration range of the seven experimental points of design is forced to be limited in some ranges melted at 873 K which are determined according to the NdCl₃–LiCl–KCl phase diagram⁶⁾ as follows: 10% ≤ NdCl₃ ≤ 80%, 20% ≤ LiCl ≤ 90% and 0 ≤ KCl ≤ 70%. *T* = 873 K. In a system with restraint conditions such as in this system, variables in the polynomial are not composition *X*, but fictitious variables which are some kind of combinations of the compositions. The polynomial with three components and third order conforming to this experimental condition is represented as follows:

$$Y = b_1 Z_1 + b_2 Z_2 + b_3 Z_3 + b_{12} Z_1 Z_2 + b_{13} Z_1 Z_3 + b_{23} Z_2 Z_3 + b_{123} Z_1 Z_2 Z_3. \quad (3)$$

Here *Z_i* is a fictitious variable. The restraint conditions for a practical variable are:

$$0 \leq a_i \leq X_i \leq b_i \leq 1 \quad i = 1, 2, 3, \cdots q. \quad (4a)$$

$$X_1 + X_2 + \cdots + X_q = 1. \quad (4b)$$

In the above equation, *a_i* and *b_i* are the lower and upper bounds of *X_i*, respectively. If all of upper and lower bounds satisfy the following Eq. 5 for each component:

$$b_i + \sum_{j \neq i}^q a_j = 1, \quad i = 1, 2, 3, \dots, q. \quad (5)$$

then the system degenerates into a system without restraint conditions. According to the equation transformation of X_i into Z_i , the upper bounds of the fictitious variable $Z_i^{\max}$ can be obtained:

$$Z_i^{\max} = (b_i - a_i)/R = [(1 - \sum_{j \neq i}^q a_j) - a_i]/R = 1 \quad (i = 1, 2, 3, \dots, q) \quad (6)$$

Here R is the conversion factor of equiform transformation. Figure 1 shows the experimental points of simplex-centroid design. Because the fictitious variable is only an invented variable, it must be reconverted into the original variable when in practical use.

Results and Discussion

Measured conductivities of $\text{NdCl}_3\text{--LiCl--KCl}$ at 873 K are presented in Table 1. Here Z_1 , Z_2 , and Z_3 are fictitious variables, and X_1 , X_2 , X_3 are practical variables which represent NdCl_3 , LiCl , and KCl mass fractions respectively. Y_1 and Y_2 are two measured results of conductivity of the same sample. After determining the seven parameters in the special third order polynomial Eq. 3, and converting the fictitious variable Z_i into the practical variable, X_i , the following regression equation has been obtained:

$$Y = 2.74X_1 - 1.03X_2 - 1.04X_3 + 18.17X_1X_2 + 15.60X_1X_3 + 15.81X_2X_3 - 82.92X_1X_2X_3. \quad (7)$$

The reason of the larger difference between two results of conductivity of No. 1 may be an inhomogeneous distribution of compositions in molten salts. The calculated correlation coefficient of Eq. 7, R_A is 0.99. Inserting values of practical values for an arbitrary point: $X_1=0.209$, $X_2=0.146$, and $X_3=0.645$, into Eq. 7, $Y=2.26 \Omega^{-1} \text{cm}^{-1}$ is obtained; its conductivity has also been measured to be $2.29 \Omega^{-1} \text{cm}^{-1}$ (see No. 8 in Table 1) and the relative error of point No. 8 is 1.3%.

Figure 2 (which is taken from Ref. 7) shows the conductivities of the system of $\text{NdCl}_3\text{--LiCl--KCl}$ as a func-

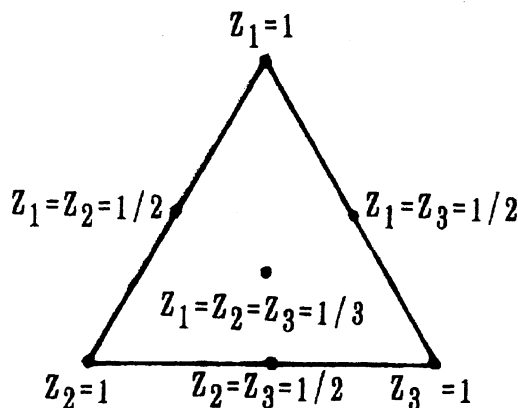


Fig. 1. Simplex-centroid design for three-component system.

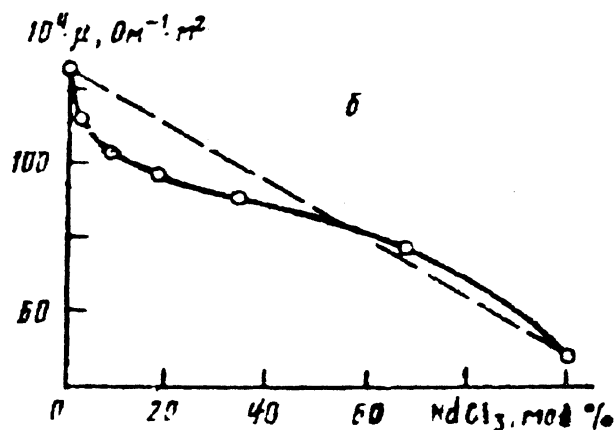


Fig. 2. The relation between mole conductivity and mol% NdCl_3 for eutectic composition of LiCl--KCl is fixed at 1050 K. (This curve is taken from Ref. 7).

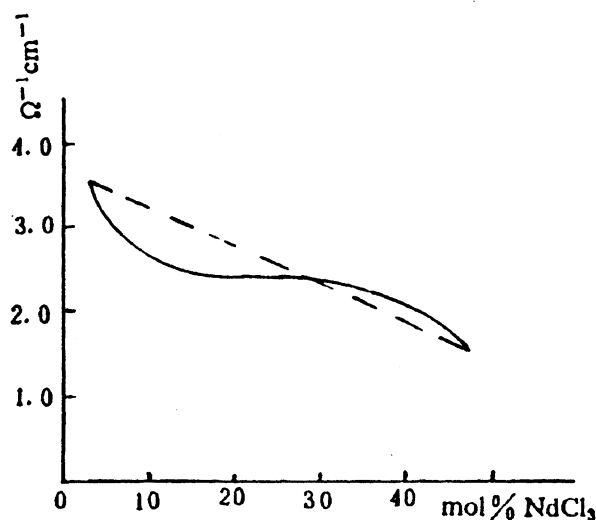


Fig. 3. The relation between conductivity and mol% NdCl_3 for eutectic composition of LiCl--KCl is fixed at 873 K.

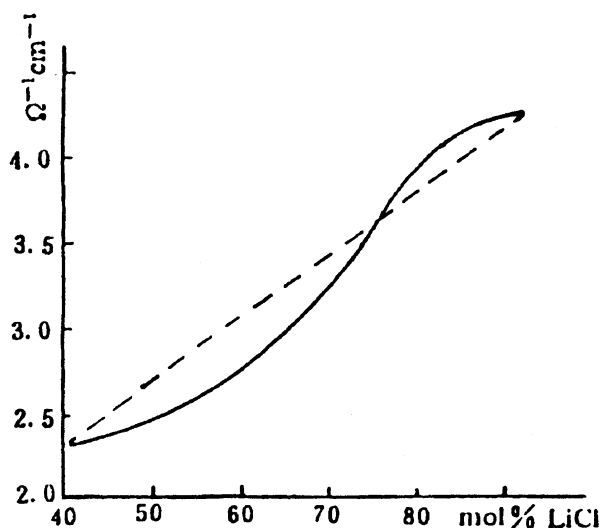


Fig. 4. The relation between conductivity and mol% LiCl .

Table 1. Fictitious Variable, Practical Variable, and Measured Values of Conductivity

No.	Fictitious variable			Practical variable (wt%)			Measured values of conductivity, Y_i ($\Omega^{-1} \text{cm}^{-1}$)		
	Z_1	Z_2	Z_3	X_1	X_2	X_3	Y_1	Y_2	Average
1	1	0	0	0.90	0.10	0.00	3.88	4.12	3.98
2	0	1	0	0.20	0.80	0.00	2.62	2.64	2.63
3	0	0	1	0.20	0.10	0.70	2.21	2.21	2.21
4	1/2	1/2	0	0.55	0.45	0.00	5.57	5.50	5.54
5	1/2	0	1/2	0.55	0.10	0.35	4.00	4.00	4.00
6	0	1/2	1/2	0.20	0.45	0.35	2.33	2.33	2.33
7	1/3	1/3	1/3	0.433	0.333	0.233	3.26	3.20	3.23
8	/	/	/	0.209	0.146	0.645	2.28	2.30	2.29

Table 2. Activation Energy of Electroconductivity

	Temperature/K	Conductivity/ $\Omega^{-1} \text{cm}^{-1}$	Conductivity at 1071 K
LiCl	961—1133	11.5 exp $(-0.053/kT)$	6.5
KCl	1071—1213	7.1 exp $(-0.107/kT)$	2.2

tion of NdCl_3 wt% added to the eutectic mixture (46.0 wt% LiCl) of LiCl and KCl. It is to be noted that the curve in Fig. 2 is drawn simply from seven experimental data. In this paper, the conductivity of systems similar to those in Ref. 7 have been calculated with the regression equation (Eq. 7) (see solid line in Fig. 3). The very similar trend of concentration variation can be seen between Figs. 2 and 3.

Figure 4 shows the variation of conductivity with LiCl content when the ratio of KCl to NdCl_3 is fixed to be 47.17 wt% KCl, where KCl and NdCl_3 forms a congruent compound $3\text{KCl} \cdot \text{NdCl}_3$.

Figure 5 depicts the conductivity as a function of KCl concentration while the ratio of NdCl_3 to LiCl is kept at their eutectic composition (28.5 wt% LiCl).⁸⁾

Figure 6 illustrates the isogram of conductivity of ternary system NdCl_3 –KCl–LiCl. It is made from data calculated from the regression Eq. 7. From Figs. 4, 5, and 6, it can be seen that, with the increase

of concentration of KCl, the conductivity of system of KCl–LiCl– NdCl_3 decreases strikingly, and the effect of LiCl on conductivity of the system is just opposite to that of KCl. Therefore, Li^+ plays the main role in process of electrical conduction of this system. The data¹⁰⁾ of electrical conduction activation energy and conductivity for LiCl and KCl at temperatures near 1000 K in Table 2 also supports above conclusion. Values 0.053 and 0.107 eV in the above exponents are activation energy for LiCl and KCl, respectively. It can also be seen that the concentration (83.3 mol% LiCl) where maximum positive deviation appears (see Fig. 4) just corresponds to the composition of eutectic point of the pseudo binary system 3KCl – NdCl_3 –LiCl.⁶⁾ The effect of NdCl_3 on the conductivity of NdCl_3 –KCl–LiCl system is small, especially when NdCl_3 content exceeds 30 wt% and the ratio, KCl:LiCl, is fixed (The isogram is nearly vertical) compared with the effect of KCl. This tendency can also be seen in Fig. 3, in which in the middle of the curve, the slope is nearly zero. It can also be seen from the above Figures that all conductivity curves of systems containing NdCl_3 are not straight lines with concentration and reveal negative deviation in some ranges of composition and positive in others for the NdCl_3 –KCl–LiCl system. The reason why conductivity curves containing NdCl_3 in NdCl_3 –KCl–LiCl system are not straight lines is that there exists some equilibria relating to formation and destruction of complex ions in the molten salts and these equilibria may change complex ion concentration, which further affects conductivity behavior of the molten salts. But the reason why concentration range which has maximum conductivity in this system is not near pure LiCl but in the middle LiCl and dilute KCl concentration range (see Fig. 6) should be further investigated. Electron absorption spectrometry of molten salts containing ACl – NdCl_3 (A represents alkali metal) at 1103 K has

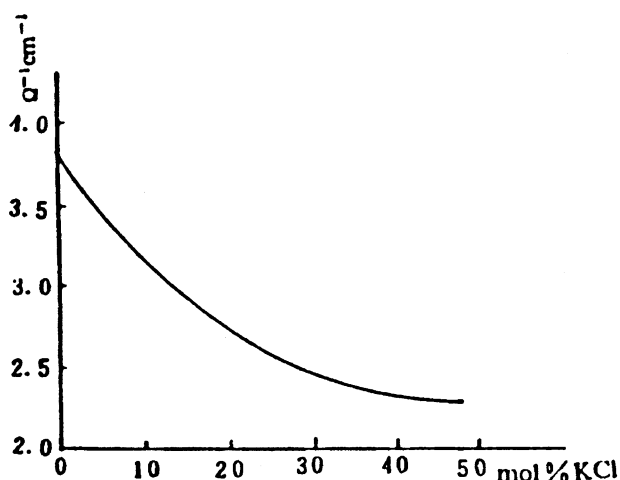
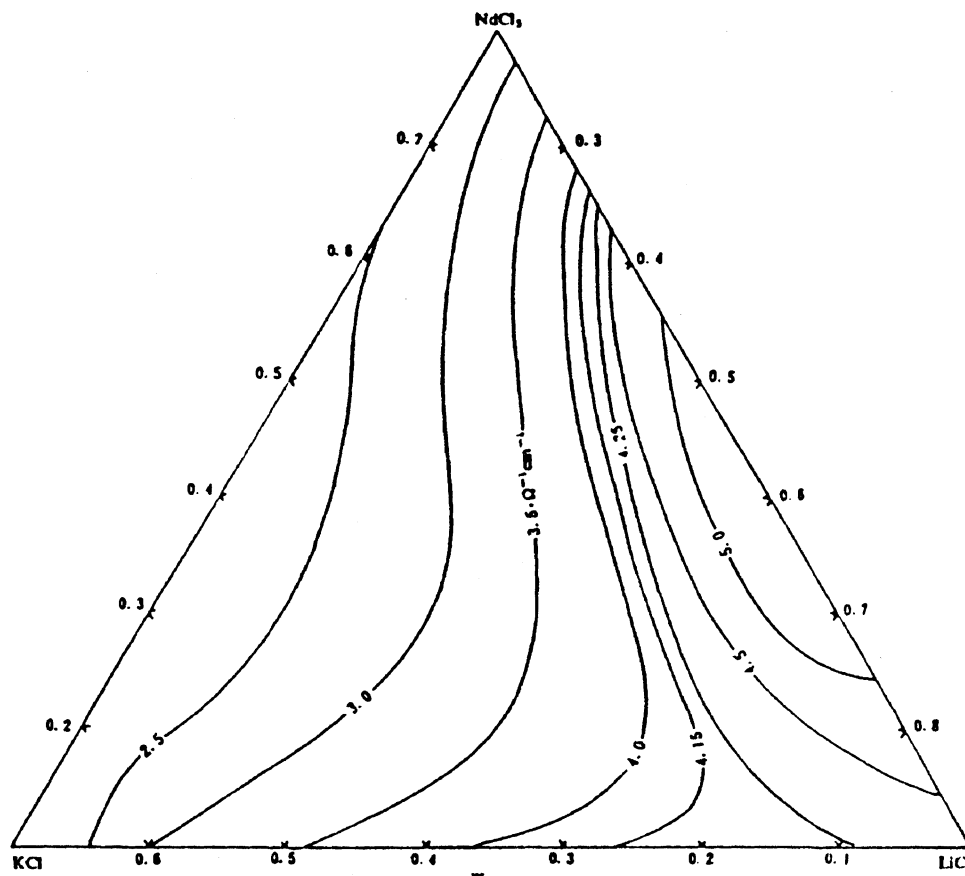


Fig. 5. The relation between conductivity and mol% KCl.

Fig. 6. Isogram of conductivity for ternary system $\text{NdCl}_3\text{--LiCl--KCl}$.

confirmed that the content of NdCl_6^{3-} increases progressively from LiCl to CsCl and there also exist NdCl_4^- and NdCl_6^{2-} ions in the molten salts at the same time. Such information about the formation and variation of complex ions in molten salts containing NdCl_3 can be seen in Ref. 9

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References

- 1) J. A. Cornell, "Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data," John Wiley, New York (1981).
- 2) J. W. Gorman and J. A. Cornell, *Technometrics*, **27**, 229 (1985).
- 3) J. A. Cornell, *J. Qual. Technol.*, **18**, 1 (1986).
- 4) Ф. С. Новик, Р. С. Минц, Ю. С. Малков Заводская лаборатория, **XXIX**, 840 (1967).
- 5) H. Scheff, *J. R. Statist. Soc.*, **B25**, 253 (1963).
- 6) Zhang Yifeng and Zheng Chaogui, *Acta Metall. Sin.*, (in Chinese), **24**, B243 (1988).
- 7) А. В. Ковалевский, В. И. Шишлов ЖФХ, **57**, 2597 (1983).
- 8) Zhang Yifeng and Zheng Chaogui, *Chem. Sin.*, (in Chinese), **47**, 14 (1989).
- 9) Duan Shuzhen and Qiao Zhiyu, "Molten Salt Chemistry-Principle and Application," Chap. 5, Sect. 1, Metallurgical Industry Publishing House, Beijing (1990).
- 10) W. A. Fischer and D. Janke, "Metallurgische Elektrochemie," Chap. 4, Sect. 2.