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The phase diagram of $LiNO_3$–KNO_3

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Abstract

The binary phase diagram of $LiNO_3$–KNO_3 are studied by means of differential scanning calorimeter (DSC). The convincing evidence for the identification of new phase has been presented. The phase diagram indicates an intermediate compound $KLi(NO_3)_2$, which melts congruently at 428 K. The coordinates of two eutectic points are 420 K, 47 mol% KNO_3 and 410 K, 54 mol% KNO_3. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phase diagram; $LiNO_3$–KNO_3 system; Congruently melting compound

1. Introduction

The system of $LiNO_3$–KNO_3 is usually regarded as a simple eutectic one [1,2], although some researchers [3] have noted that in addition to the eutectic point at $x(\mathrm{Li}^+) = 0.41$, there was another discontinuity at $x(\mathrm{Li}^+) = 0.45$ which was tentatively attributed to an intermediate incongruently melting compound. This observation seems to have been neglected by some investigators using the liquid mixtures of $LiNO_3$–KNO_3 [2,4]. No further thermal measurements have been attempted to explore the origin of the discontinuity. Raman spectroscopic studies [5,6] indicated that a congruently melting compound $KLi(NO_3)_2$ was formed. The new compound can be prepared from quenched samples.

In this work, we determined the phase diagram of $LiNO_3$–KNO_3 by differential scanning calorimetry and calculated their phase diagram.

2. Experimental

The thermal analyses were carried out on a Perkin-Elmer DSC-7 differential scanning calorimeter. The calibration of the instrument was made by high purity indium and zinc as standard samples.

Reagent grade potassium nitrate and lithium nitrate were recrystallized from redistilled water and dried in the oven at approximately 378 K for 3 days. The dried chemicals were weighed at definite ratios, mixed well in a mortar and transferred to quartz crucibles. The mixtures were dried for 3 days, first at 333 K, then 378 K, and finally at 403 K. Then the temperature was gradually raised until the mixtures were completely melted. The samples were kept in molten state for at least 12 h to achieve well-mixed and homogenous compositions for the mixtures. Then the quenched samples were ground into a fine powder and stored over desiccant.

At least three successive runs were carried out for each sample. Generally, the results of the third run were in agreement with those of the second run (indicating equilibrium conditions) and only third data are reported here. The heating and cooling rates are 10 K min^{-1}, and

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the dry N_2 sweep rate through the DSC assembly was ~20 $cm^3\ min^{-1}$, the samples (5–20 mg) were placed in open aluminum pans.

3. Thermodynamic relationships

For equilibrium between a solid and a liquid phase in a binary system with components A and B, the Gibbs energy of fusion of A may be expressed as

$$-\Delta_{\mathrm{fus}}G_{\mathrm{A}} = RT\ln\frac{x_{\mathrm{A}}(\ell)}{x_{\mathrm{A}}(\mathrm{s})} + G_{\mathrm{A}}^{\mathrm{E}}(\ell) - G_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s}) \qquad (1)$$

where $x_A(\ell)$ and $x_A(s)$ are the mole fractions of A on the liquidus and solidus at temperature T respectively, and R is the gas constant. $G_A^E(\ell)$ and $G_A^E(s)$ are the partial excess Gibbs energies of A in the liquid and solid. In this system the excess entropy $S^E(\ell)$ and $S^E(s)$ were set to equal zero. So $G^E = H^E$. The partial properties can be obtained from the integral property from the following equation:

$$G_i^{\mathrm{E}} = H_i^{\mathrm{E}} = H^{\mathrm{E}} + (1 - x_i)\frac{\mathrm{d}H^{\mathrm{E}}}{\mathrm{d}x_i} \qquad (2)$$

where i = A or B.

H^E may be expanded as ploynomials in the mole fractions as follows [10]:

$$H^{\mathrm{E}} = x_{\mathrm{A}}x_{\mathrm{B}}(h_0 + h_1x_{\mathrm{B}} + \cdots + h_ix_{\mathrm{B}}) \qquad (3)$$

where the h_i is empirical coefficients.

4. Results and discussion

Fig. 1 shows the DSC profiles for the salt mixtures of the $LiNO_3$–KNO_3 system. The DSC profile of 1:1 mixture (mole fraction of KNO_3, $x = 0.5$) shows the typical of the congruently melting compound $KLi(NO_3)_2$. To determine the eutectic composition, the sharpness of the DSC peaks (expressed by the ratio of peak height to half the width) were compared from sample to sample in the composition range $x = 0.4$–0.6 at 1% intervals. The sharpest peaks were observed for the sample of $x = 0.47$ and $x = 0.54$. The eutectic temperatures were determined from the heating and cooling profiles of these compositions.

The data for solidus and for liquidus are listed in Table 1 and graphically displayed in Fig. 2. The phase diagram clearly indicates the occurrence of intermediate compound $KLi(NO_3)_2$, which melts congruently at 428 K. The coordinates of two eutectic points are 420 K, 47 mol% KNO_3 and 410 K, 54 mol% KNO_3.

None of the investigations has reported the solid solubility, although some solubility of $LiNO_3$ and KNO_3 may be expected. Solid solutions have not been examined in this work too. Earlier, the calculations about the system were performed by one simple eutectic system [2,7]. Those calculation values were below the experimental values. In the present work, calculations were performed under the assumption of zero solid solubility and the intermediate compound $KLi(NO_3)_2$ was used.

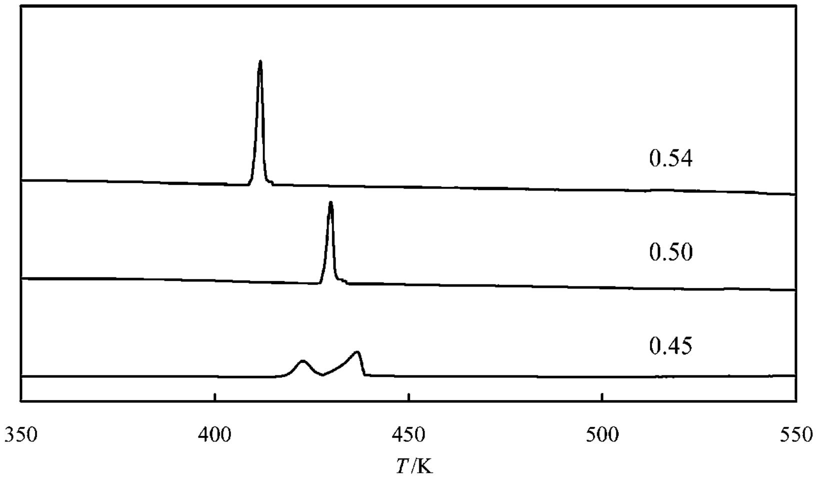

Fig. 1. DSC profiles of the mixture of KNO_3 and $LiNO_3$.

Table 1
DSC data of the system $LiNO_3$–KNO_3

Mole fraction KNO_3	Eutectic temperature, T (K)		Liquidus tempeature, T_L (K)
	1	2	
0.0			527.5
0.1			514.3
0.2			497.7
0.3	420		477.9
0.4	420		450.6
0.45	420		431.5
0.47	420		420.1
0.49	420		425.3
0.50			428.0
0.52		410	418.6
0.54		410	410.0
0.56		410	419.1
0.58		410	428.6
0.60		410	437.6
0.7		410	481.2
0.8			527.4
0.9			570.1
1.0			608.0

The excess enthalpy (in J mol^{-1}) was measured at 618 K in solid–liquid mixing experiments by Kleppa and Hersh, and the results are used here [8]:

$$H^{E}(\ell) = x_A x_B(-7352.6 - 363.7x_A - 1935.3x_A x_B) \tag{4}$$

The system was dealt with two simple eutectic portions. For each portion, under the assumption that $G^{E}(\ell)$ is given by Eq. (4), a phase diagram was calculated. At the eutectic temperatures of 410 and 420 K, the calculated liquidus compositions were $x_B = 0.47$ and $x_B = 0.54$, in very good agreement with the experiment eutectic compositions. The calculated Gibbs energy of fusion (in J mol^{-1}) of the compound $KLi(NO_3)_2$ is

$$\Delta_{fus}G^{\circ} = 19410 - 23.120T \tag{5}$$

The calculated liquidus is displayed by a solid line in Fig. 2. Probable maximum inaccuracy in calculated liquidus is 5 K. The broken line indicates that the compound $KLi(NO_3)_2$ is unstable. The congruently melting compound $KLi(NO_3)_2$ could only exist in a narrow composition range at the equimolar point and in a short temperature range just below the solidus. Standing at room temperature, $KLi(NO_3)_2$ decomposed gradually into $LiNO_3$ and KNO_3.

For the series of lithium nitrate with the other alkali metal nitrates, the size difference between the cations in $LiNO_3$–$RbNO_3$ is sufficiently large to permit formation of the congruently melting compound $RbLi(NO_3)_2$ [1,9]. There seems to be little debate about the phase diagram $LiNO_3$–$RbNO_3$. For $LiNO_3$–$CsNO_3$ the early investigations [1] indicated eutectic or solid solution formation but these sugges-

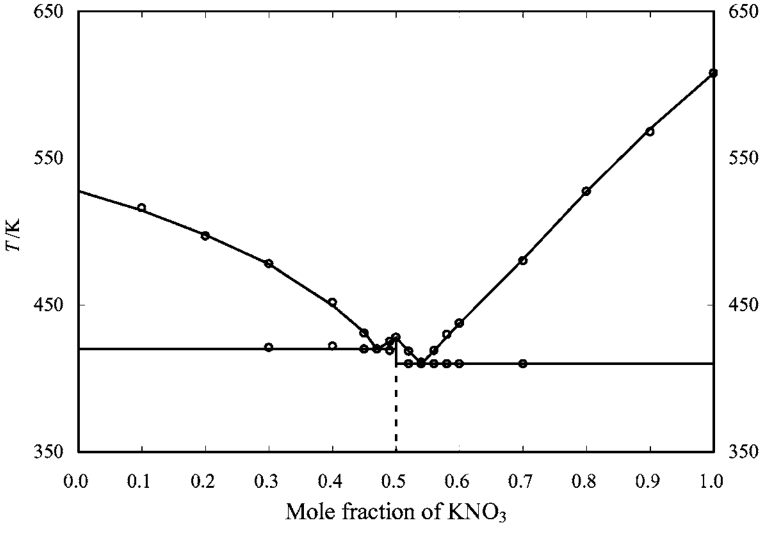

Fig. 2. The phase diagram for the $LiNO_3$–KNO_3 system.

tions were questioned [9] since the congruently melting compound had already been observed for $LiNO_3$–$RbNO_3$. Bol'shakov et al. [9] reinvestigated the binary nitrates and a congruently melting compound $CsLi(NO_3)_2$ was detected at 467 K. The existence of the compound was confirmed by other authors [10,11]. $LiNO_3$–KNO_3 is usually regarded as a eutectic system, although a discontinuity at $x(Li^+) = 0.45$ in the liquidus was observed in the phase diagram by some early researchers [3,12], No further studies have been attempted to explore the origin of the discontinuity.

Complete disappearance of the Raman features of the two initial components implies absence of the structure of either $LiNO_3$ or KNO_3. Although no crystallographic data are available, the new features in Raman spectrum of the quenched sample indicated that an entirely new structure, being very similar to those congruently melting compound $RbLi(NO_3)_2$ or $CsLi(NO_3)_2$, had been created in the equimolar $LiNO_3$–KNO_3 solid [5,6]. The new structure corresponds to the compound $KLi(NO_3)_2$ which has been overlooked previously by thermal analysis.

In binary systems with a common anion, and involving lithium salts, the occurrence of intermediate compounds is not surprising, in view of the small cation Li^+. The second cation, a larger one, can thus easily coordinate the anions around it. This may lead to formation of a new compound. The function of larger K^+, Rb^+ or Cs^+ appears to make it possible for the already existing coordination between lithium and nitrate ions to be retained in the crystal when the temperature decreased and the congruently melting compound formed. As was noted previously, the compounds $KLi(NO_3)_2$ had broad bands over the whole spectrum and a strong Rayleigh wing. This is typical for polymeric structures. It seems likely that the nitrate ions remained bridging the lithium ions to form polymeric complexes in the congruently melting compounds.

5. Conclusions

The convincing evidence for the identification of new phase has been presented in our work. This studies suggested that a congruently melting compound $KLi(NO_3)_2$ was formed in the system of $LiNO_3$–KNO_3 formerly regarded as a simple eutectic system, and the $KLi(NO_3)_2$ forms eutectic mixtures with the end members. This result is identical with thermodynamic calculation.

Acknowledgements

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