Thermal Properties of Mixed Alkali Bis(trifluoromethylsulfonyl)amides

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Phase diagrams of binary mixtures of alkali bis(trifluoromethylsulfonyl)amides have been constructed, and their eutectic compositions and temperatures have been determined. It has been revealed that the molten salt electrolytes having the melting points in the intermediate temperature range (373 to 473) K are easily formed by simple mixing of two kinds of single alkali bis(trifluoromethylsulfonyl)amide salts. The 1:1 or 3:1 double salt is occasionally formed for some binary systems.

Introduction

Molten salts have excellent characteristics as electrolytes such as negligibly small volatility, nonflammability, high electrochemical stability, and high ionic conductivity.[1,2] Molten salts are roughly classified into two groups: high-temperature molten salts ($T > 673$ K) and room (or ambient) temperature molten salts ($T < 373$ K). There is a tradeoff between the features as electrolytes for high-temperature and room-temperature molten salts. High-temperature molten salts are generally superior in physicochemical properties such as high conductivities, wide electrochemical windows, and wide liquid temperature range. On the other hand, room-temperature molten salts, also called ionic liquids, have the advantages of an easy handling and wide range of application field.[3–6] Salts consisting of alkali metal cations and the bis(trifluoromethylsulfonyl)amide (Tf_2N) anion, MTf_2N (M = Li, Na, K, Rb, Cs), are solids at room temperature but have, or are expected to have, melting points at relatively low temperatures.[7,8] The Tf_2N anion is well-known as one of the major anions constituting room-temperature molten salts because of its high chemical and electrochemical stability.[9]

It would be possible to obtain molten salts having melting points of lower than those of the single MTf_2N salts from their mixture. These molten salt mixtures are expected to have melting points from (373 to 473) K and be used at intermediate temperatures (373 to 673) K, giving averaged characteristics of high-temperature and room-temperature molten salts. It is also expected that the alkali metal Tf_2N salts are promising as intermediate temperature molten salt electrolytes for electrochemical systems including a process of alkali metal depositions owing to the high electrochemical stability of the Tf_2N anion. For example, lithium metal is expected to deposit at the cathode limit of mixed MTf_2N molten salts containing $LiTf_2N$, and these molten salts are able to be used as electrolytes for lithium ion batteries operating at intermediate temperatures.

Many researchers have reported organic electrolytes for lithium ion batteries in which $LiTf_2N$ is dissolved as supporting electrolytes;[10–12] however, the properties reported for MTf_2N salts themselves are limited except for some crystal structures.[13] No reports are available on the physicochemical properties of the molten MTf_2N salts and their mixtures.

In this study, the thermal properties of the mixtures of the two MTf_2N single salts (M = Li, Na, K, Rb, Cs) were systematically investigated to construct phase diagrams and determine the composition giving the melting points in the intermediate temperature range.

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Table 1. Melting Temperature, *T*, and Decomposition Temperatures, T_d, of MTf_2N Single Salts

	$LiTf_2N$	$NaTf_2N$	KTf_2N	$RbTf_2N$	$CsTf_2N$
T/K(this study)	506	530	472	450	395
T/K(previous study)	507[7]	–	478[7]	–	388[8]
T_d/K	657	714	733	740	745

Experimental Section

Bis(trifluoromethylsulfonyl)imide, HTf_2N (Morita Chemical Industries, purity > 99 %), Na_2CO_3 (Wako Pure Chemical Industries, purity > 99.5 %), K_2CO_3 (Wako Pure Chemical Industries, purity 99.9 %), Rb_2CO_3 (Wako Pure Chemical Industries, purity 99.9 %), and Cs_2CO_3 (Aldrich, purity 99.9 %) were used for the syntheses of MTf_2N salts. $LiTf_2N$ (Morita Chemical Industries, purity > 99.0 %) was used as received. Melting points and thermal decomposition temperatures of single MTf_2N salts were measured by means of differential scanning calorimetry (DSC) and thermogravimetry (TG), respectively. Temperature was increased with a scan rate of 10 $K \cdot min^{-1}$. The phase diagrams of the binary MTf_2N salt mixtures were constructed by plotting the temperatures of endothermic peaks found on the DSC curves obtained in the heating process against the compositions of the salts. The transition temperatures were determined in a heating process to avoid uncertainty by supercooling. The liquidus and solidus curves were drawn by eye through experimental plots. The measurement was performed for every five mole percent of the entire composition range. Aluminum pans were used for the sample holders. Prior to the measurements, the sample was melted at 573 K to prepare homogeneous samples. The measurement was started after cooling the pretreated samples to room temperature. In this study, the accuracy of melting points is ± 5 K.

Results and Discussion

Melting and Thermal Decomposition Temperatures of Single MTf_2N Salts. The melting and thermal decomposition temperatures of MTf_2N single salts in this study are summarized in Table 1. Figure 1 shows the plots of the melting points of the single salts against the reciprocal radii of the cations. Coordination numbers of the cations ($LiTf_2N$, 6; $NaTf_2N$, 6;

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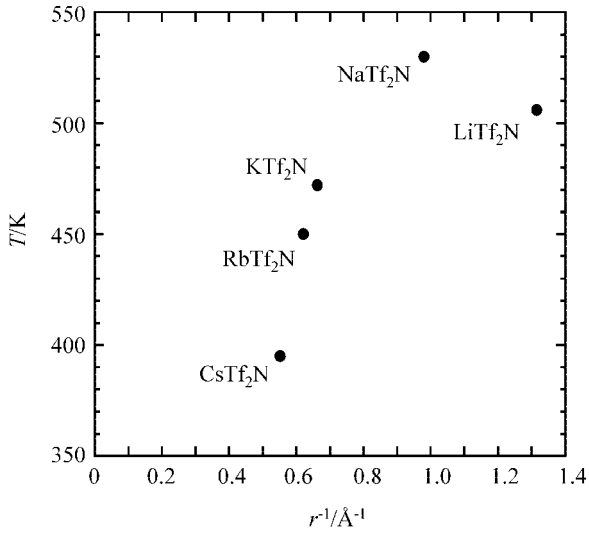

Figure 1. Plots of the melting temperature, T, against the reciprocal radius of the cations of the salts, r.

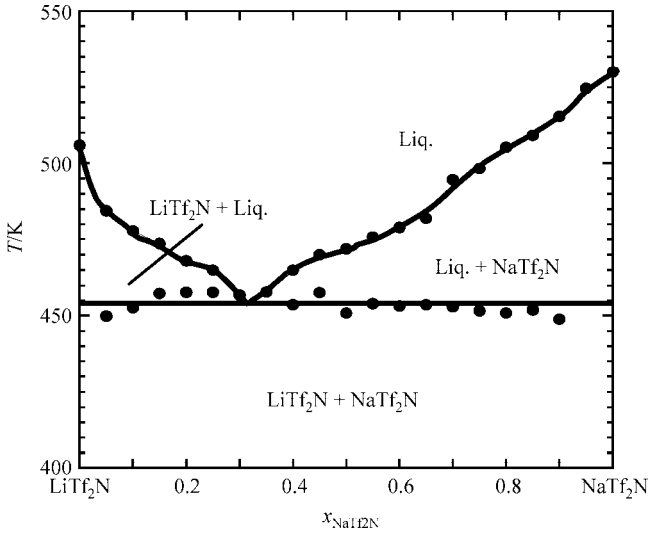

Figure 2. Phase diagram of $LiTf_2N + NaTf_2N$.

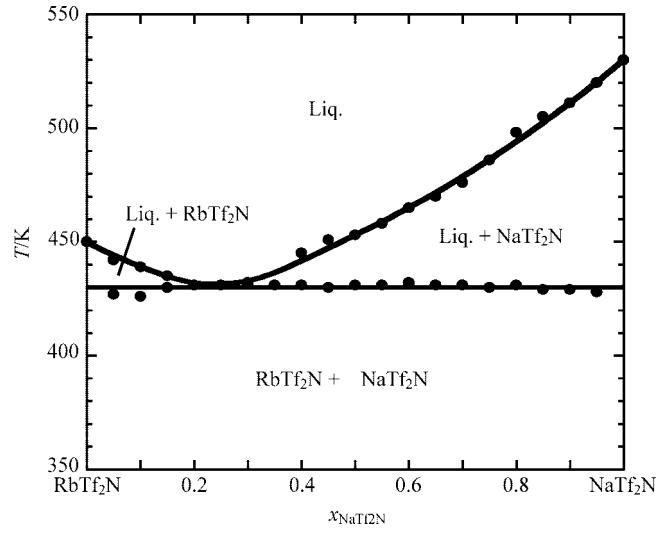

Figure 3. Phase diagram of $NaTf_2N + RbTf_2N$.

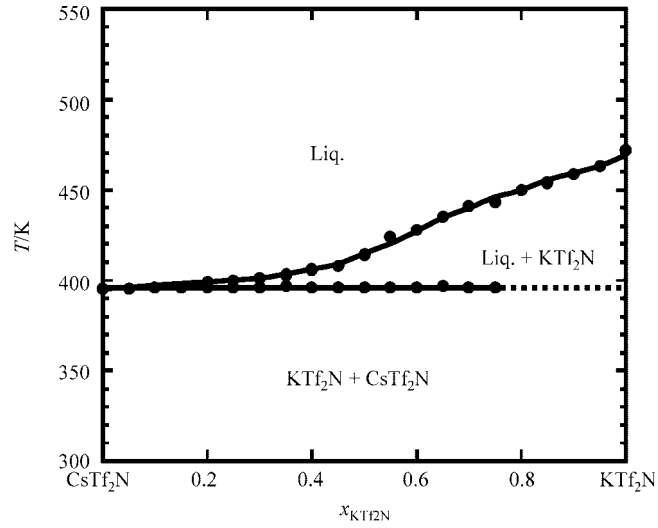

Figure 4. Phase diagram of $KTf_2N + CsTf_2N$.

KTf_2N, 8; $RbTf_2N$, 8; $CsTf_2N$, 10) from the previous study on the crystal structure of the MTf_2N salts[13] are used to estimate the Shannon's ionic radii of the cations. The melting point of the salt containing a smaller cation is generally higher, but it is found from the figure that the melting point of $LiTf_2N$ does not follow the trend, irregularly lower than that of $NaTf_2N$. This would be caused by the difference of the lattice energies of the salts with different structures containing a large organic anion in which the electrostatic interactions are more complicated than that in simple inorganic salts. The single MTf_2N salts are thermally stable to 700 K except for $LiTf_2N$, which has a decomposition temperature of 657 K. Thermal stability becomes higher with the increase of the size of the cation.

Phase Diagrams of the Binary MTf_2N Salt Mixtures. Figure 2 shows a phase diagram of the $LiTf_2N + NaTf_2N$ binary system that exhibits a simple binary eutectic system. Figure 3 shows a phase diagram of the $NaTf_2N + RbTf_2N$ binary system. The phase diagram is also a simple eutectic type. No binary compounds and structural phase transitions are observed. These two systems are a simple eutectic type in the binary MTf_2N systems examined here.

Figure 4 shows a phase diagram of $KTf_2N + CsTf_2N$. There are two endothermic peaks on the DSC curves at different temperatures at $x_{KTf_2N} \geq 0.25$. Although only one peak is observed at $x_{KTf_2N} \leq 0.20$, the system is considered to be a eutectic type. It is considered that the eutectic composition is very close to the $CsTf_2N$ side and that the eutectic temperature is almost equal to the melting point of neat $CsTf_2N$.

Figure 5 illustrates a phase diagram of the $LiTf_2N + RbTf_2N$ system. The endothermic peak found at the lowest temperature, 421 K, shifts by 5 K to a higher temperature, 426 K, at $x_{LiTf_2N} > 0.50$. At this composition, only one endothermic peak is observed at 432 K. This suggests the existence of a double salt, $LiRb(Tf_2N)_2$. As a result, this binary system has two eutectic points. A similar phase diagram is found for the $LiTf_2N + CsTf_2N$ binary system as shown in Figure 6. The endothermic peak at 385 K appears only at the compositions where the molar ratios of $LiTf_2N$ are 0.05 to 0.50, and this peak disappears for the higher $LiTf_2N$ compositions. This suggests the existence of a double salt, $LiCs(Tf_2N)_2$. As a result, this binary system has two eutectic points in common with $LiTf_2N + RbTf_2N$. Formation of 1:1 double salts is suggested for these two systems.

A phase diagram of the $LiTf_2N + KTf_2N$ binary system is shown in Figure 7. Two endothermic peaks are observed when the molar ratio of $LiTf_2N$ exceeds 0.75. These observations suggest the existence of the 3:1 double salt, $Li_3K(Tf_2N)_4$. A

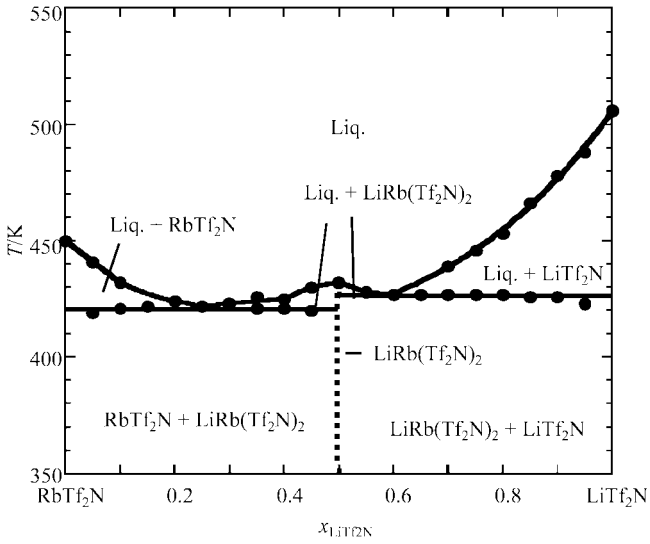

Figure 5. Phase diagram of $LiTf_2N$ + $RbTf_2N$.

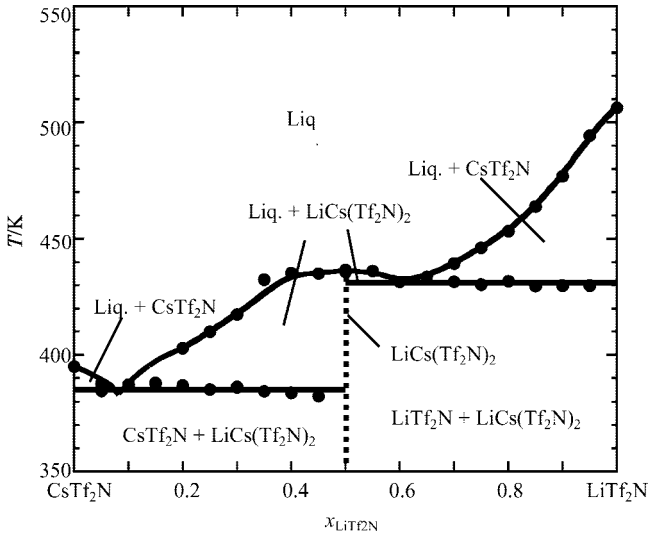

Figure 6. Phase diagram of $LiTf_2N$ + $CsTf_2N$.

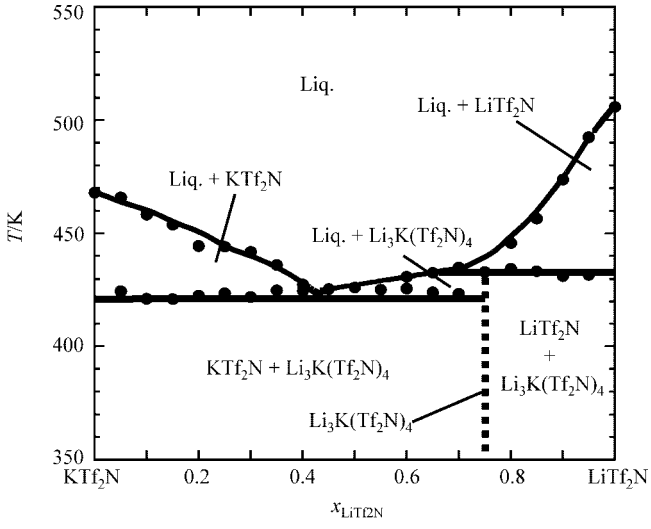

Figure 7. Phase diagram of $LiTf_2N$ + KTf_2N.

peritectic point should exist at $x_{LiTf_2N} \simeq 0.7$ with the temperature of 435 K. The eutectic point is found at $x_{LiTf_2N} = 0.43$ with the temperature of 423 K. A similar phase diagram is obtained for the $NaTf_2N$ + KTf_2N binary system and shown in Figure 8.

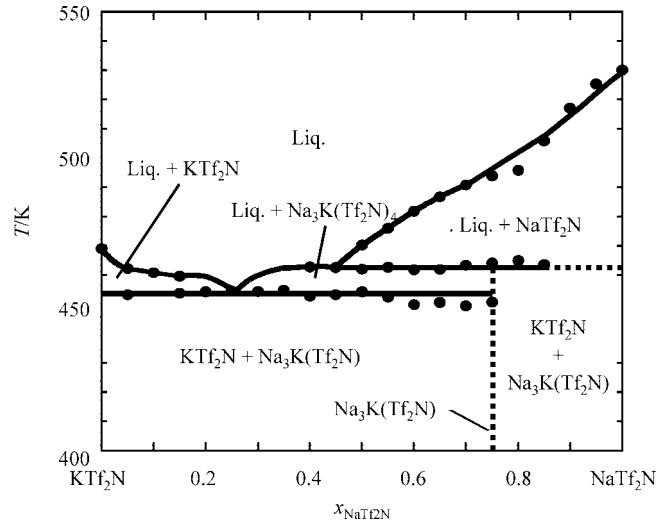

Figure 8. Phase diagram of $NaTf_2N$ + KTf_2N.

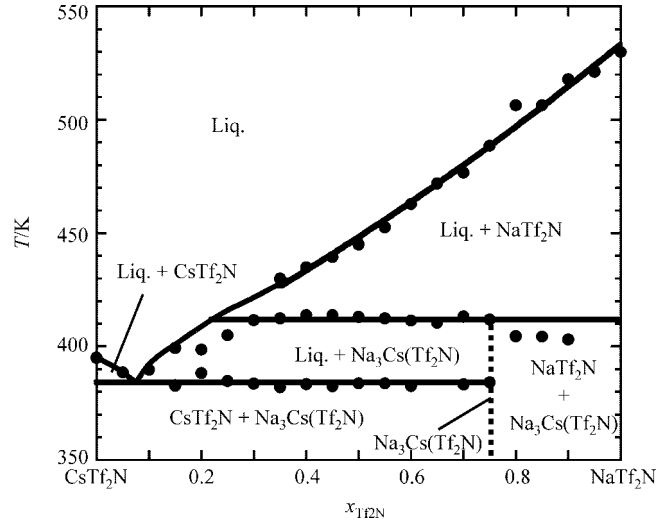

Figure 9. Phase diagram of $NaTf_2N$ + $CsTf_2N$.

Table 2. Eutectic Compositions, x_{eu}, and Temperatures, T_{eu}, of the Binary MTf_2N Salt Mixtures

system	x_{eu}	T_{eu}/K
$LiTf_2N$ + $NaTf_2N$	$x_{LiTf_2N} = 0.67$	453
$LiTf_2N$ + KTf_2N	$x_{LiTf_2N} = 0.43$	423
KTf_2N + $CsTf_2N$	−	395
$LiTf_2N$ + $RbTf_2N$	$x_{LiTf_2N} = 0.25$	421
	$= 0.60$	426
$LiTf_2N$ + $CsTf_2N$	$x_{LiTf_2N} = 0.07$	385
	$= 0.60$	432
$NaTf_2N$ + KTf_2N	$x_{NaTf_2N} = 0.25$	456
$NaTf_2N$ + $RbTf_2N$	$x_{NaTf_2N} = 0.25$	431
$NaTf_2N$ + $CsTf_2N$	$x_{NaTf_2N} = 0.07$	383

There is a peritectic point at $x_{NaTf_2N} = 0.45$ at a temperatures of 462 K. Three endothermic peaks also appear at $x_{NaTf_2N} \geq 0.45$. Similarly, it suggests the formation of a 3:1 double salt, $Na_3K(Tf_2N)_4$. Figure 9 illustrates a phase diagram of $NaTf_2N$ + $CsTf_2N$. The endothermic peak at 383 K disappears at $x_{NaTf_2N} \geq 0.75$. It suggests the formation of a 3:1 double salt, $Na_3Cs(Tf_2N)_4$. A peritectic point is found at $x_{NaTf_2N} = 0.22$ with the temperature of 411 K. Table 2 summarizes the eutectic compositions and temperatures of binary MTf_2N salt mixtures. Table 3 summarizes the intermediate compounds of binary MTf_2N salt mixtures.

In the case of the KTf_2N + $RbTf_2N$ binary system, as shown in Figure 10, only one endothermic peak is observed for entire

Table 3. Intermediate Compounds of the Binary MTf_2N Salt Mixtures

system	compound
$LiTf_2N + RbTf_2N$	$LiRb(Tf_2N)_2$
$LiTf_2N + CsTf_2N$	$LiCs(Tf_2N)_2$
$LiTf_2N + KTf_2N$	$Li_3K(Tf_2N)_4$
$NaTf_2N + KTf_2N$	$Na_3K(Tf_2N)_4$
$NaTf_2N + CsTf_2N$	$Na_3Cs(Tf_2N)_4$

compositions in the DSC curves. It is, thus, impossible to obtain the compositions having a lower melting point than neat $RbTf_2N$ by the mixing of KTf_2N and $RbTf_2N$. The $RbTf_2N + CsTf_2N$ system, as shown in Figure 11, is similar to the $KTf_2N + RbTf_2N$ system. In this binary system, again there is only one endothermic peak at different temperatures for all mole fractions. It is concluded that these two systems form solid solutions for all mole fractures. In these systems, it is considered that there are two-phase regions where liquid and solid solution exist between liquidus and solidus. However, the regions could not be detected in this measurement.

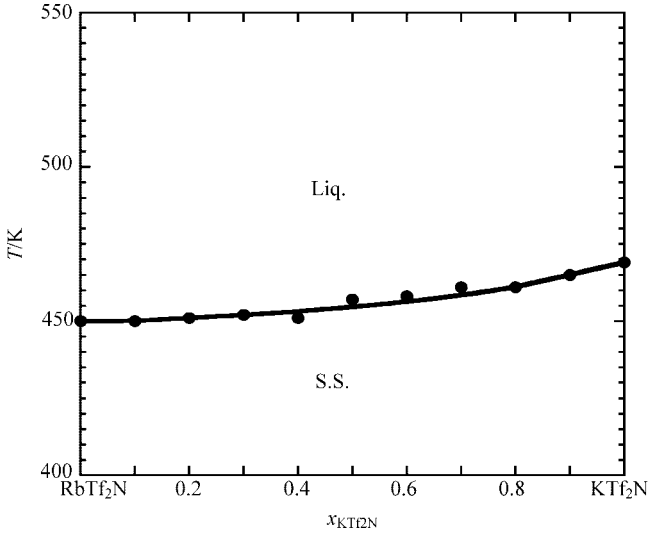

Figure 10. Phase diagram of $KTf_2N + RbTf_2N$.

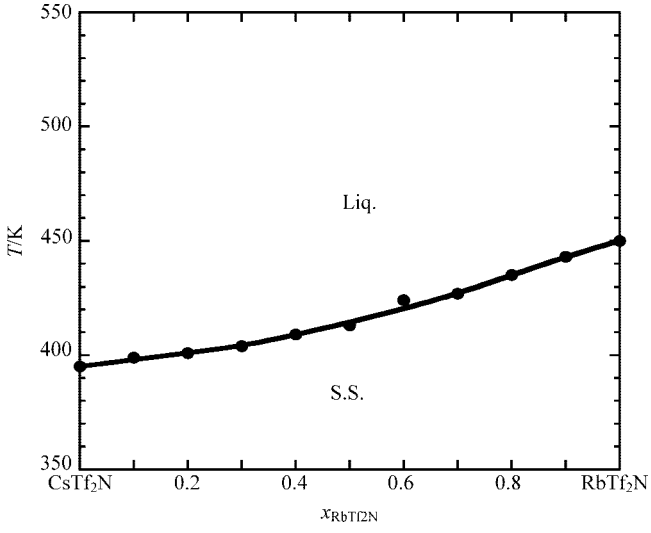

Figure 11. Phase diagram of $RbTf_2N + CsTf_2N$.

It is found that the melting points are not lowered in the case of $KTf_2N + RbTf_2N$, $KTf_2N + CsTf_2N$, and $RbTf_2N + CsTf_2N$ binary systems in which two of the three heaviest alkali metal salts are mixed. When the cation sizes are close (K, 1.51 Å; Rb, 1.61 Å; Cs, 1.81 Å), the binary salt system might behave as a pseudosingle phase, although the melting temperature shifts with the composition.

Conclusions

Thermal properties of the binary MTf_2N (M = Li, Na, K, Rb, Cs) salt mixtures were investigated. Ten binary phase diagrams have been constructed. In the cases of the seven binary salt mixtures, the melting points are lowered to intermediate temperatures (373 to 473) K by the mixing of two single MTf_2N salts. Thus, the mixing of the alkali metal Tf_2N salt is an effective way to lower the melting temperature of alkali metal Tf_2N salts except for a few combinations.

Supporting Information Available:

The tables of data for Figures 2 to 11 are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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