The Electrical Conductivity of the Molten Binary Systems $CO(NH_2)_2$-MNO_3 (M = Li, Na, NH_4)

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The electrical conductivity of molten $CO(NH_2)_2$-MNO_3 (M = Li, Na, NH_4) with various nitrate contents has been measured at 358 – 393 K. For Li and Na the conductivity increased with increasing concentration of urea [$CO(NH_2)_2$], whereas for NH_4 the conductivity decreased with increasing concentration of urea. The relationship between the conductivity and the temperature can be expressed by $\kappa = \kappa_0 \exp(-E_\kappa/RT)$. For the mole fractions 0.7, 0.8, and 0.9 of urea, the activation energies E_κ are 31.28, 25.91, and 22.96 kJ/mol for the $CO(NH_2)_2$-$LiNO_3$ system, and 32.64, 30.51, and 25.40 kJ/mol for the $CO(NH_2)_2$-$NaNO_3$ system, whereas for the mole fractions 0.5, 0.7, and 0.8 of urea the activation energies are 20.39, 19.73, and 18.95 kJ/mol for the $CO(NH_2)_2$-NH_4NO_3 system. The more stable the forming complex is, the lower is the conductivity. The conductivities are in the order $CO(NH_2)_2$-NH_4NO_3 > $CO(NH_2)_2$-$NaNO_3$ > $CO(NH_2)_2$-$LiNO_3$.

Key words: Electrical Conductivity; Activation Energies; Amide Molten Salts.

1. Introduction

Amide molten salts are fairly stable over a wide temperature range and exhibit a low vapor pressure, low viscosity, and high electrical conductivity. They have large dipole moments and dielectric constants, and a large variability of acid-base properties. They can be used as good solvents for both organic and inorganic species [1]. These properties offer a wide range of physicochemical characteristics that are desirable in various electrochemical processes [2].

From the viewpoint of energy conservation and corrosion problems, the low temperature amide melts have been explored for several applications, e. g., ammonium formate-formamide (m. p. 393 K) can act as electrodeposition electrolyte for metals [3]; urea-KCNO (m. p. 408 K) can be used as electrochemical reaction medium [4]; acetamide-KCl [5] (m. p. 353 ∼ 413 K), acetamide-urea-NH_4NO_3-$LiNO_3$ [6] (m. p. 298 K), and *N*-methylacetamide-NH_4NO_3 can be used as thermal battery electrolytes [1]; and $NaNO_3$-KNO_3-acetamide/urea [7] (m. p. 337 K) can be used as electrolyte for anodizing processes. The potential utility of amide molten salts is referred by Gale and Lovering [1]; however, to our knowledge there are no literature data on the conductivity of amide melts in a wide range of composition and temperature.

In the present study, the systems $CO(NH_2)_2$-$M(NO_3)$ (M = Li, Na, NH_4) were selected for measurement of the conductivities with a computerized D. C. method. The same method was used to collect a series of conductivities of molten salts at room temperature [8 – 13].

2. Experimental

$LiNO_3$, $NaNO_3$, and NH_4NO_3 were vacuum-dried overnight at 383 K, and urea was used as received. The conductivities were measured at 358 to 393 K when x_{urea}, the mole fraction of $CO(NH_2)_2$, was greater than 0.7 for $CO(NH_2)_2$-$LiNO_3$ and $CO(NH_2)_2$-$NaNO_3$. As for $CO(NH_2)_2$-NH_4NO_3, the temperature remained in the same range, but x_{urea} was greater than 0.5. The temperature was limited by the melting points of the melts and the thermal decomposition of urea.

Table 1. Parameters of the electrical conductivity equation of molten $CO(NH_2)_2$-$LiNO_3$.

$\kappa = a + bT + cT^2$					
$CO(NH_2)_2$ /mol%	$a/10^{-2}$S cm^{-1}	$b/10^{-4}$S cm^{-1}K^{-1}	$c/10^{-7}$S cm^{-1}K^{-2}	*R*-squared	Temp. range /K
70	26.27	−17.10	28.06	0.99999	358 – 393
80	−5.599	0.153	4.79	0.99983	358 – 393
90	4.254	−5.122	12.06	0.99999	358 – 393

Table 2. Parameters of the electrical conductivity equation of molten $CO(NH_2)_2$-$NaNO_3$.

$\kappa = a + bT + cT^2$					
$CO(NH_2)_2$ /mol%	$a/10^{-2}$S cm^{-1}	$b/10^{-4}$S cm^{-1}K^{-1}	$c/10^{-7}$S cm^{-1}K^{-2}	*R*-squared	Temp. range /K
70	38.52	−25.10	41.12	0.99998	358 – 393
80	27.27	−19.10	32.99	0.99996	358 – 393
90	−2.081	−2.345	9.264	0.99900	358 – 393

Table 3. Parameters of the electrical conductivity equation of molten $CO(NH_2)_2$-NH_4NO_3.

$\kappa = a + bT + cT^2$					
$CO(NH_2)_2$ /mol%	$a/10^{-2}$S cm^{-1}	$b/10^{-4}$S cm^{-1}K^{-1}	$c/10^{-7}$S cm^{-1}K^{-2}	*R*-squared	Temp. range /K
50	10.54	−17.69	46.64	0.99999	358 – 393
70	2.121	−9.654	29.53	0.99983	358 – 393
80	−0.133	−6.58	22.03	0.99999	358 – 393

Table 4. Activation energies from Arrhenius fits of the conductivity of $CO(NH_2)_2$-MNO_3 (M = Li, Na, NH_3).

Composition	$\kappa = \kappa_0 \exp(-E_\kappa/RT)$ E_κ/kJ mol^{-1}
70 – 30 mol% $CO(NH_2)_2$-$LiNO_3$	31.28
80 – 20 mol% $CO(NH_2)_2$-$LiNO_3$	25.91
90 – 10 mol% $CO(NH_2)_2$-$LiNO_3$	22.96
70 – 30 mol% $CO(NH_2)_2$-$NaNO_3$	32.64
80 – 20 mol% $CO(NH_2)_2$-$NaNO_3$	30.51
90 – 10 mol% $CO(NH_2)_2$-$NaNO_3$	25.40
50 – 50 mol% $CO(NH_2)_2$-NH_4NO_3	20.39
70 – 30 mol% $CO(NH_2)_2$-NH_4NO_3	19.73
80 – 20 mol% $CO(NH_2)_2$-NH_4NO_3	18.95

The molten salts were prepared in an atmosphere of flowing dried nitrogen gas. Each composition was prepared by heating $CO(NH_2)_2$ with $LiNO_3$, $NaNO_3$, or NH_4NO_3 in a silicone oil bath. The electrical conductivities were measured by a computerized system using the D. C. four-probe method described in [8].

3. Results and Discussion

The electrical conductivities of the binary molten salts are shown as functions of the temperature in Figs. 1, 2, and 3. The experimental data were least-squares fitted to $\kappa = a + bT + cT^2$, where T is the temperature in K. The obtained values of *a*, *b*, and *c* are given in Tables 1, 2, and 3. The conductivities were fitted by the Arrhenius equation $\kappa = \kappa_0 \exp(-E_\kappa/RT)$ as shown in Figs. 4, 5, and 6, and the activation energies (E_κ) are presented in Table 4.

The dependence of the conductivity on the amount of urea in $CO(NH_2)_2$-$NaNO_3$ and $CO(NH_2)_2$-$LiNO_3$ at three temperatures is shown in Figure 7. There is a maximum of the conductivity at $x = 0.8$, which is presumably due to the formation of the intermediate tetrahedral complex species $M^+[NH_2$-$C{=}O$-$NH^-]$ which would increase with increasing amount of MNO_3 (M = Na, Li). While Li^+ has a smaller ionic radius than Na^+, Li^+ is likely to form a stable complex compound. Thus $CO(NH_2)_2$-$LiNO_3$ tends to have a lower conductivity than $CO(NH_2)_2$-$NaNO_3$. In addition, the deviation of the conductivity would increase with increasing temperature. In an ionic (Li-Na)NO_3 mixture [14], the internal mobility of the larger Na^+ is always greater than that of the smaller Li^+ in the whole temperature and composition range. We have shown that the internal mobility is closely related to the self-exchange velocity of neighbouring unlike ions. A smaller cation is more capable of associating with an anion, which will reduced its mobility.

Gruthner [15] has reported that the conductivity of pure molten acetamide has the characteristics of self-ionization or auto-protolysis, which can also be found in water. The reaction is $2CH_3CONH_2 \rightleftarrows CH_3CONH_3{}^+ + CH_3CONH^-$. This ionization causes an amphiprotic acid-base character of acetamide. In the present study, a decrease of the conductivity with increasing the content of alkali nitrate has been confirmed. The form of the reaction is

$$NH_2\text{-}CO\text{-}NH_2 \rightleftarrows NH_2\text{-}CO\text{-}NH^- + H^+,$$

$$M^+X^- + NH_2\text{-}CO\text{-}NH^- \rightarrow M^+[NH_2\text{-}CO\text{-}NH^-] + X^-$$

$$(M = Li, Na, NH_4; X^- = NO_3{}^-).$$

The formation of complexes retards the transport properties. However the increase of $CO(NH_2)_2$ content increases not only the free space but also the mobility of the disassociated species. The conductivity of a compound depends on its structure and the nature of bonding within and between the complex species. Studies on the ionic conductivity of alkali nitrates are known [16 – 21]. In the present study it is assumed that the main current carriers are free species, i. e., NH_2-$C{=}O$-NH^-, H^+, $NO_3{}^-$. Thus, the decrease in the electrical conductivity is going from

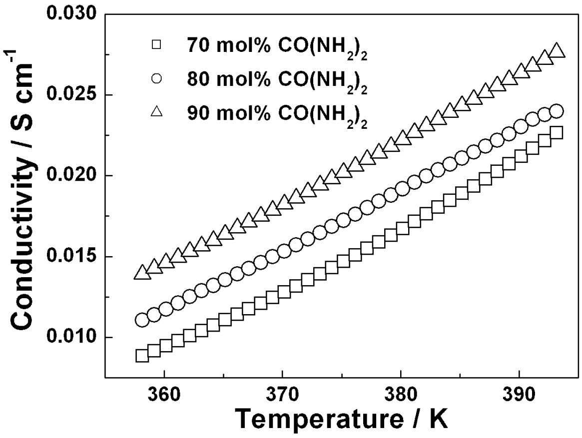

Fig. 1. The electrical conductivity of molten $CO(NH_2)_2$-$LiNO_3$ as a function of temperature.

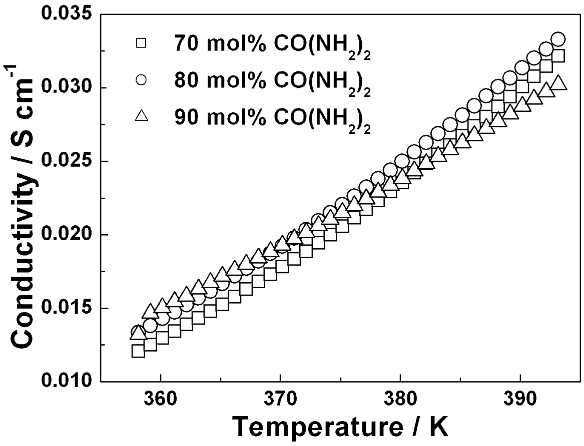

Fig. 2. The electrical conductivity of molten $CO(NH_2)_2$-$NaNO_3$ as a function of temperature.

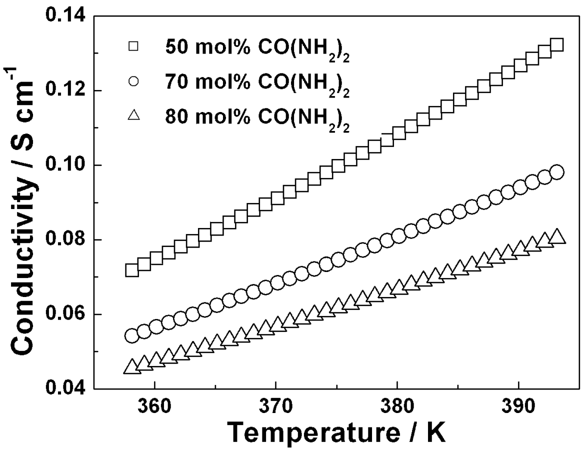

Fig. 3. The electrical conductivity of molten $CO(NH_2)_2$-NH_4NO_3 as a function of temperature.

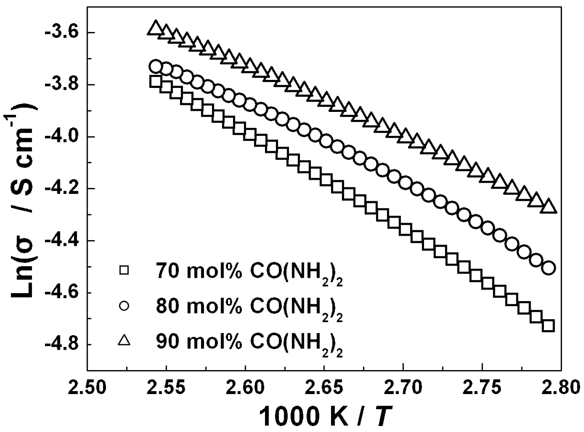

Fig. 4. Arrhenius plots of the electrical conductivity of molten $CO(NH_2)_2$-$LiNO_3$.

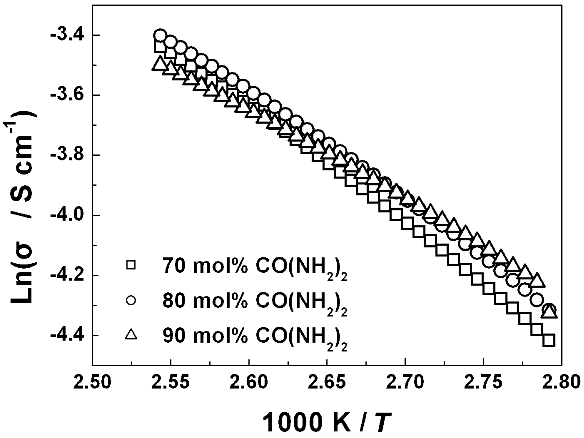

Fig. 5. Arrhenius plots of the electrical conductivity of molten $CO(NH_2)_2$-$NaNO_3$.

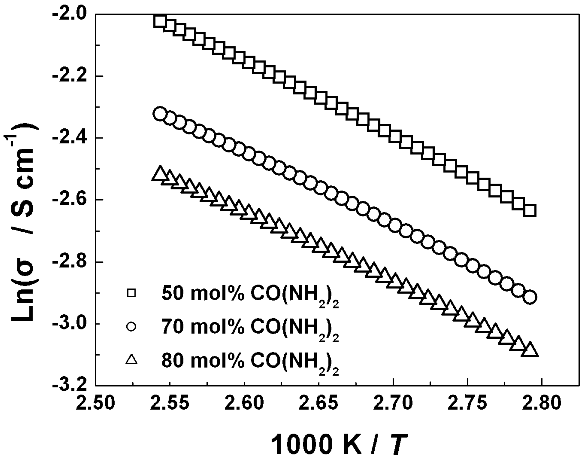

Fig. 6. Arrhenius plots of the electrical conductivity of molten $CO(NH_2)_2$-NH_4NO_3.

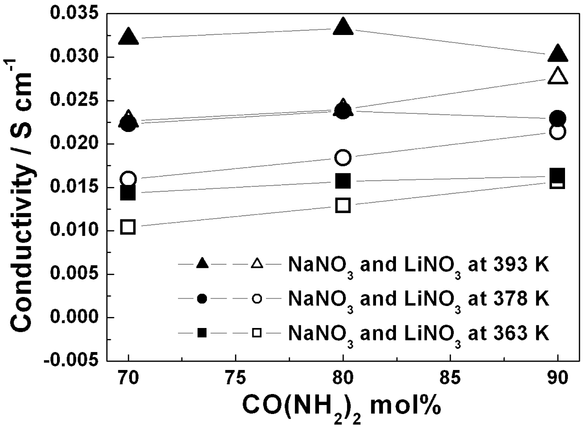

Fig. 7. Isotherms of the electrical conductivity as functions of $100x_{\mathrm{CO(NH_2)_2}}$ in the systems $CO(NH_2)_2$-$NaNO_3$ and $CO(NH_2)_2$-$LiNO_3$ at 363, 378 and 393 K.

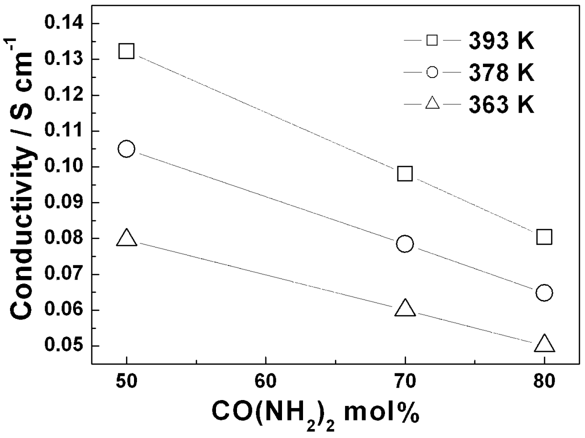

Fig. 8. Isotherms of the electrical conductivity as function of $100x_{\mathrm{CO(NH_2)_2}}$ in the system $CO(NH_2)_2$-NH_4NO_3 at 363, 378, and 393 K.

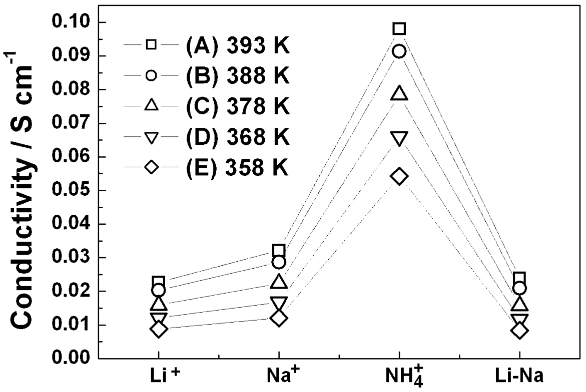

Fig. 9. The electrical conductivity of 70 mol% $CO(NH_2)_2$ and 30 mol% $LiNO_3$, $NaNO_3$, NH_4NO_3 and 15 mol% $LiNO_3$ + 15 mol% $NaNO_3$, respectively, at the indicated temperature.

pure amide melts to complex species of amide with alkali nitrate. The isotherm of the conductivity vs. mole fraction of urea in the systems $CO(NH_2)_2$-$LiNO_3$ and $CO(NH_2)_2$-$NaNO_3$ at different temperatures is shown in Figure 7. The study shows that the conductivity of $CO(NH_2)_2$-$NaNO_3$ decreases with increasing mole fraction of urea from 80 to 90 mol% at 378 – 393 K. This is quite similar to the molten binary systems (MCl-$AlCl_3$) (M = Li, Na, and K) [22, 23], in which the complicated and large structure of the polymeric anion affects the mobility of cations.

Furthermore, the study reveals that the electrical conductivity of the amide-alkali nitrate melts increases in the order $\kappa_{\mathrm{CO(NH_2)_2-LiNO_3}} < \kappa_{\mathrm{CO(NH_2)_2-NaNO_3}}$. Also for the binary chloroaluminate systems the equivalent conductivity increases in the order $\Lambda_{(\mathrm{Li-Al_{1/3})Cl}} < \Lambda_{(\mathrm{Na-Al_{1/3})Cl}}$. The higher the temperature, causing a larger molar volume of the mixture, the lower the distance between the smaller cations and anions, and therefore the smaller cation's mobility. Therefore, the complex species containing the larger cation, $Na^+[NH_2\text{-}C{=}O\text{-}NH^-]$, is more mobile than that containing the smaller one, $Li^+[NH_2\text{-}C{=}O\text{-}NH^-]$. Similar phenomenon are observed in molten (Li-Na)NO_3 [14] and (Li-Na)Cl [24].

The relationship between the conductivity and the content of urea in $CO(NH_2)_2$-NH_4NO_3 at various temperatures is shown in Figure 8. At the mole fraction 0.5 of urea there is a maximum of the conductivity at 363 to 393 K, and conductivity increases with increasing content of NH_4NO_3. This result differs from those found for the $CO(NH_2)_2$-$LiNO_3$ and $CO(NH_2)_2$-$NaNO_3$, where the conductivity decreases with increasing content of MNO_3 (M = Li and Na), as shown in Figure 7. This is presumably due to the low stability of the forming complex $NH_4{}^+[NH_2\text{-}C{=}O\text{-}NH^-]$. By the increasing mobility of such a complex the conductivity will increase. Because the interaction between the ion and the solvent is weaker for $NH_4{}^+$, the complex species containing the bigger cation, $NH_4{+}[NH_2CONH^-]$, is more mobile than those containing the smaller cation $Li^+[NH_2CONH^-]$ or $Na^+[NH_2CONH^-]$.

Isotherms of the electrical conductivity of various mixtures are shown in Figure 9. The electrical conductivity increases in the order $\kappa_{\mathrm{CO(NH_2)_2-LiNO_3}} < \kappa_{\mathrm{CO(NH_2)_2-NaNO_3}} < \kappa_{\mathrm{CO(NH_2)_2-NH_4NO_3}}$. When no specific interactions are involved, the solvation energy can be related directly to the molecular attraction and association [25], and the effects of the formation of complex species due to specific ion-solvent interactions could be taken into account. It has been reported in [26] that anions have a much greater solvation energy to the smaller alkali metal cations than to the ammonium cation, thus the solvation energy decreases in the order $Li^+ > Na^+ > NH_4^+$ in the present study. Consequently, the stability of $NH_4^+[NH_2CONH^-]$ is lower than that of $M^+[NH_2CONH^-]$ (M = Li, Na). This is the reason for NH_4^+ to show a noticeable increase in the electrical conductivity for the binary $CO(NH_2)_2$-MNO_3 system as shown in Figure 9.

The internal cation mobility in the molten binary systems $(M\text{-}NH_4)NO_3$ (M = Li, Na) [27, 28] have been measured by Okada et al., and the mobility of the larger NH_4^+ ion is greater than that of the smaller Li^+ and Na^+ ions. The general interpretation for this effect has already been explained, based on the assumption that the internal mobility is related to the separating motion of neighboring unlike ions. The conductivity of room temperature melts, e. g., $ZnCl_2$-$DMSO_2$ [29] and $FeCl_3$-$DMSO_2$ [30], that use $DMSO_2$ as organic solvent, have been determined, and the conductivities changed due to the formation of complex species.

The conductivities of the amide mixtures are in the order of $CO(NH_2)_2$-$NH_4NO_3 > CO(NH_2)_2$-$NaNO_3 > CO(NH_2)_2$-$LiNO_3$, and it is interpreted based on the assumption of complex formation with ion-solvent interaction. Therefore, the mobility of free species in the $CO(NH_2)_2$-NH_4NO_3 system is greater than that of $CO(NH_2)_2$-$NaNO_3$ and $CO(NH_2)_2$-$LiNO_3$, which is due to the weaker interaction between cation and solvent in the former system.

For the conclusion see the abstract.

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