Raman Spectroscopic Study of a New Type of Room Temperature $ZnCl_2$-$DMSO_2$ Molten Salts

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In this study, Raman spectra of binary zinc chloride-dimethylsulfone ($ZnCl_2$-$DMSO_2$) melts have been measured. The intra-molecular vibrations of group and ionic species have been confirmed and discussed. From the Raman spectrum analysis and discussions, the equilibrium reaction equation about the complex ions forming in the $ZnCl_2$-$DMSO_2$ melt is submitted, such as

$$n\,ZnCl_2 + n(n-2)(CH_3)_2SO_2 \Leftrightarrow 2ZnCl_n{}^{2-n} + (n-2)\ Zn[(CH_3)_2SO_2]_n{}^{2+}, \quad (n \geqq 3).$$

However, the Raman spectra reveal that the $ZnCl_4{}^{2-}$ (375 cm^{-1}) and $ZnCl_3{}^{-}$ (290 cm^{-1}) complexes are the major ions for the 40 – 90 mol% $ZnCl_2$ melts; furthermore, as the $DMSO_2$ content is increased, the binary melt advantage the forming of $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ion and promote its transport characteristic.

Key words: Raman Spectra; $ZnCl_2$-$DMSO_2$; Complex Ion.

1. Introduction

Room temperature molten salt (RTMS) have drawn considerable attention [1, 2]. Best-known RTMS are melts containing $AlCl_3$. Hsu and Yang [3] have reported the conductivities of $AlCl_3$-BPC, $AlCl_3$-EMIC, and $AlCl_3$-BTEAC, measured by a computerized direct current method. $AlCl_3$ is a strong Lewis acid so that melts containing $AlCl_3$ are easily affected by the environment.

On the other hand, organic salt chlorides are good solvents for inorganic salts, but the preparation and conservation of organic salt chlorides are not so easy. Therefore, more stable and convenient RTMS are wanted. Electric conductivity and density of the binary melts have been investigated.

Some new melts have been prepared by adding inorganic salts to organic solvents, e. g. $AlCl_3$-$DMSO_2$ [4] and $ZnCl_2$-$DMSO_2$ [5]. It was shown that $DMSO_2$ is a good solvent, stable at high temperature and able to dissolve numerous metallic salts. A Raman study indicates that, when $AlCl_3$ is added to $DMSO_2$, peaks appear at 120, 179, and 347 cm^{-1}, which are assigned to $AlCl^-{}_4$ [4]. If a reaction occurs between $AlCl_3$ and $DMSO_2$, the coordination compound between Al^{3+} and $DMSO_2$ may be $[Al\text{-}(CH_3)_2SO_2]^{3+}$. Furthermore, the binary $ZnCl_2$-$DMSO_2$ melt was reported as a new type of room temperature molten salts by Shu et al. [5]. In the literature, the phase diagram, electric conductivity, and density of the binary melts have been obtained, but the Raman spectroscopy of $ZnCl_2$-$DMSO_2$ melts has never been reported. However, the ionic formation mechanism of the binary molten salt has not been understood well. In order to further understand the ionic formation mechanism, the Raman spectroscopic analysis will be carried out in this work, and the results will be discussed.

2. Experimental

$ZnCl_2$ (zinc chloride, Merck, anhydrous, 98%) and $DMSO_2$ (dimethylsulfone, Acros, 98%) were used under a nitrogen atmosphere in a dry glove box (Super) 1220/750, Mikrouna. The nitrogen had passed a drying column containing molecular sieves. The molten salts with different molar ratios were prepared by continuous stirring for 24 h at 70 ℃ on a hot plate with a silicone oil bath.

Table 1. Data of the bonding length l [Å] and bonding angle ϑ [°] for atoms of $DMSO_2$ and $ZnCl_2$.

Atoms	l [Å] or ϑ [°]	Atoms	l [Å] or ϑ [°]
S[1]-O[2]	1.45	S[1]-O[3]	1.45
O[2]-S[1]-O[3]	116.602	O[2]-S[1]-C[4]	107.704
O[3]-S[1]-C[8]	107.701	C[4]-S[1]-C[8]	109.29
S[1]-C[4]	1.784	S[1]-C[8]	1.784
O[2]-S[1]-C[8]	107.704	O[3]-S[1]-C[4]	107.697
ZN-Cl	2.24	Cl-Zn-Cl	109.47
		Zn-Cl-Zn	90

The liquid samples were put into the quartz test tubes for Raman measurements, carried out on a HORIBA Raman spectrometer and iHR330 detector at ambient temperature for various composition melts ($0 \sim 100$ mol% $ZnCl_2$). The wavelength of the laser was 633 nm. The frequency range was scanned from 200 to 550 cm^{-1} and 600 to 1500 cm^{-1}.

3. Results and Discussion

Raman spectroscopy is sensitive to the vibrations of ions in the molten salt mixtures, thus it is a powerful tool for probing the cation-anion interaction. The bonding mode can also often be determined from Raman spectra. Figure 1 shows the stable steric structure of $DMSO_2$, and Table 1 gives the bonding angles of O-S-O and C-S-C bonds, which are 116.602° and 109.29°, respectively. Moreover, it is clear that the O atom has a higher electronegativity than S and C atoms, resulting in that the O-S-O bond has a bigger bonding angle than the C-S-C bond. Therefore, it is supposed that the $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ion is formed through the interaction between $Zn^{\oplus}$ and $O^{\ominus}$ atom. However, the supposition will be confirmed with the analysis of the Raman spectrum for the binary ZnCl-$DMSO_2$ melt.

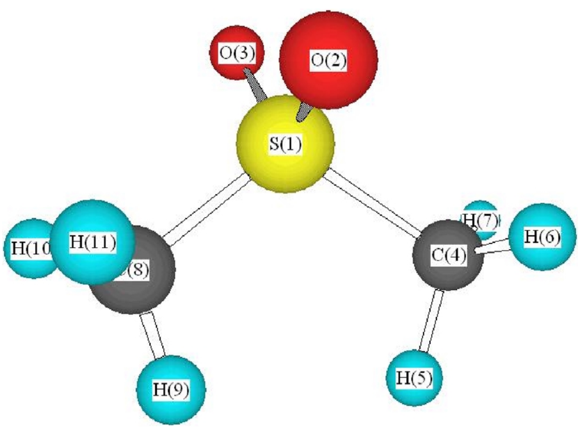

Fig. 1 (colour online). Stable steric structure of $DMSO_2$.

Figure 2a and b show the Raman spectra of the binary ZnCl-$DMSO_2$ RTMS with different molar ratios from 200 to 550 cm^{-1} and 600 to 1500 cm^{-1}, respectively. In Figure 2, we can see these Raman spectra data. The band at 324 and 391 cm^{-1} ($\omega\tau$ CH_3) are assigned to the CH_3 out-of-plane bending for wagging or twisting modes, the band at 1013 cm^{-1} (ρCH_3) is assigned to the CH_3 in-plane bending or rocking mode, the band at 1450 cm^{-1} (δ_s CH_3) is assigned to the CH_3 in-plane bending or scissoring mode, the band at 292 and 463 cm^{-1} (δ_s SC_2) are assigned to the SC_2 scissoring for bending modes, the band at 495 cm^{-1} (δ_s SO_2) is assigned to the SO_2 scissoring for bending mode, the band at 700 (ν_s SC_2) and 770 (ν_{as} SC_2) cm^{-1} are assigned to the SC_2 symmetric and asymmetric stretching modes, the band at 1119 (ν_s SO_2) and 1268 (ν_{as} SO_2) cm^{-1} are assigned to the SO_2 symmetric and asymmetric stretching modes, the band at 1403 cm^{-1}(ν_s SC_2) is assigned to the SC_2 stretching for overtone mode. These Raman spectra data are also shown in Table 2. However, Figure 2 shows that the bands at 495, 1119, and 1268 cm^{-1} to δ_s, ν_s, and ν_{as} SO_2, respectively, for the various composite $ZnCl_2$ melts ($40 \sim 90$ mol%) have blue-shifting as compared to the bands of pure $DMSO_2$. Moreover, Figure 2 also shows that Zn-O vibrations are observed at 545, 1148, and 1280 cm^{-1}. These bends have also blue-shifting phenomena as the $ZnCl_2$ content increases. The result is attributed to the increasing of Zn-O bonding energy, owing to the more Zn^{2+} and O=S=O groups existing in the melts as the $ZnCl_2$ content increases. Therefore, a coordination compound between Zn^{2+} ion and $DMSO_2$ is supposed to be generated in the $ZnCl_2$-$DMSO_2$ melts. On the other hand, the disappearance of the $\omega\tau$, ρ and δ_s CH_3 vibrations as the $ZnCl_2$ content increases above 70 mol% was observed, as well as lower wave number bands at 315, 1006, and 1424 cm^{-1} were found and assigned to Cl-H vibration. It can be explained by the coulombic force between H and Cl atom in the ZnCl-$DMSO_2$ melt formed as the $ZnCl_2$ content lies above 70 mol%; furthermore, the force increases with increasing the $ZnCl_2$ content, resulting in the CH_3 vibrations become weaker and disappear. Besides, the result also exhibits that the ν_s and ν_{as} SC_2 stretching are obvious different. It is assumed that the effect of interaction with the $ZnCl_2$ molecule is small owing to the SC_2 boding group amides the $DMSO_2$ molecule. However, the results of Figure 2

CH_3 bending	SC_2 stretching and bending	SO_2 stretching and bending	$ZnCl_n{}^{2-n}$	$(ZnCl_2)_n$
1450 cm^{-1} (δ_s)	1403 cm^{-1} (ν_s)	1268 cm^{-1} (asy.)	375 cm^{-1} (Td)	226 cm^{-1}
1013 cm^{-1} (ρ)	463 cm^{-1} (δ_s)	1119 cm^{-1} (sy.)	266 cm^{-1}	
391 and 324 cm^{-1} ($\omega\tau$)		495 cm^{-1} (δ_s)		

Table 2. Raman spectra data gotten from the analysis of Raman spectrum for $ZnCl_2$-$DMSO_2$ melt.

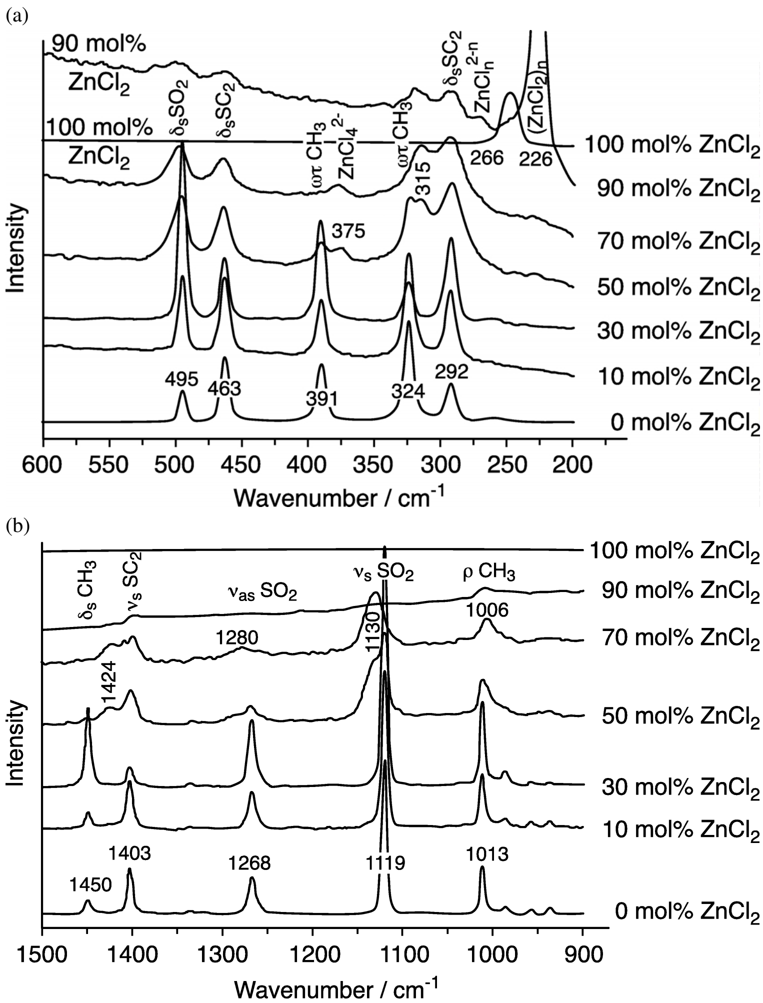

Fig. 2. Raman spectrum of a $ZnCl_2$-$DMSO_2$ melt at different compositions. The frequency range was scanned from 200 to 600 cm^{-1} (a); 900 to 1500 cm^{-1} (b).

reveal that the CH_3 vibrations have not disappeared completely and the Cl-H vibration is also observed in the 50 mol% $ZnCl_2$ melt; in the meanwhile, the blue-shifting phenomena of SO_2 stretching have also happened. Therefore, it is concluded that the equilibrium interaction between $ZnCl_2$ and $DMSO_2$ molecules has happened in the 50 mol% $ZnCl_2$ melt, and the interaction mechanism is illustrated in Figure 3. It exhibits that the coulombic force works between the Zn and Cl atoms in the $ZnCl_2$ molecules and the O and H atoms in the $DMSO_2$ molecules, respectively. The ZnO_5 hexahedra structure has been confirmed with Raman spectroscopy by R. W. Berg and N. Thorup [6]. However, the coulombic force improves the solvent effect of $DMSO_2$ in the $ZnCl_2$ molten salt, resulting in various complex ions and melt electrolytes formed. From the Raman spectrum analysis, the $ZnCl_n{}^{2-n}$ and $(ZnCl_2)_n$ complexes are observed in the binary $ZnCl_2$-$DMSO_2$ melts. Moreover, the Zn-O vibration in the $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ion increases with increasing the $ZnCl_2$ content. Based on above discussions, the equilibrium reaction equation about the com-

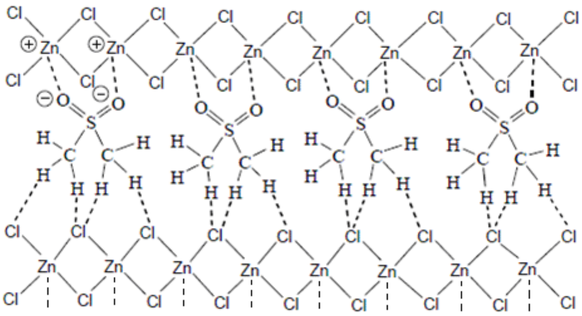
Fig. 3. Schematic of the interaction force in $ZnCl_2$-$DMSO_2$ molten salt systems.

plex ions forming in the $ZnCl_2$-$DMSO_2$ melt is submitted, such as

$$n\,ZnCl_2 + n(n-2)(CH_3)_2SO_2 \Leftrightarrow$$
$$2ZnCl_n{}^{2-n} + (n-2)\,Zn[(CH_3)_2SO_2]_n{}^{2+}, \quad n \geqq 3.$$

Therefore, the coordination complex between Zn^{2+} ion and $DMSO_2$ is supposed that the $ZnCl_4{}^{2-}$ (375 cm^{-1}) and the $ZnCl_3{}^{-}$ (290 cm^{-1}) complexes are the major ions in the 40 – 90 mol% $ZnCl_2$ melts, owing to their relatively stable bonding. The result exhibits that the transport characteristic can be attributed to the stable $ZnCl_4{}^{2-}$ complex ion, and the assumption is in accordance with the physical properties of the $ZnCl_2$-$DMSO_2$ melt as has been reported by Shu et al. [5]. Besides, the $Zn[(CH_3)_2SO_2]_n{}^{2+}$ (1148 cm^{-1}) complex ion formed via the interaction between Zn^{2+} ion and $DMSO_2$, and resulting in the molar volume and conductivity increase through the $DMSO_2$ being added to the $ZnCl_2$ melt. However, the interaction force also reduces the strength of the Zn^{+}-Cl^{-} bonding, the result induces the high melting point compound $ZnCl_2$ (mp = 318 °C) fusing at room temperature.

From above results, the interaction of the Zn^{2+} ion and $DMSO_2$ molecule results in the forming of binary $ZnCl_2$-$DMSO_2$ melt and the equilibrium reaction equation is obtained. Owing to the interaction, the redundant Cl^{-} ion is produced from the $ZnCl_2$ salt and the result promotes the $ZnCl_n{}^{2-n}$ complex ion forming in the binary melt. Besides, the different type complex ions $Zn_2Cl_{2n+1}{}^{3-2n}$ will also be produced through these reactions such as

$$ZnCl_2 + ZnCl_3{}^{-} \Leftrightarrow Zn_2Cl^{5-},$$
$$ZnCl_3{}^{-} + ZnCl_4{}^{2-} \Leftrightarrow Zn_2Cl_7{}^{3-}$$
$$ZnCl_n{}^{2-n} + ZnCl_{n+1}{}^{1-n} \Leftrightarrow Zn_2Cl_{2n+1}{}^{3-2n}, \quad n \geqq 2.$$

So, various type complex ions including $ZnCl_n{}^{2-n}$ and $Zn_2Cl_{2n+1}{}^{3-2n}$ are formed in the 40 – 90 mol% $ZnCl_2$ melts; meanwhile, it is observed that the vibration of $(ZnCl_2)_n$ (assigned to 226 cm^{-1}) increases significantly with increasing the $ZnCl_2$ content to 90 mol%, and the stable complex ions $ZnCl_4{}^{2-}$ and $ZnCl_3{}^{-}$ are consumed as the $ZnCl_2$ content increased. These results lead to the decreasing conductivity of binary $ZnCl_2$-$DMSO_2$ melt decrease with increasing the $ZnCl_2$ content. On the contrary, the bonding force of Zn-O and Cl-H will decrease with increasing the $DMSO_2$ content, the result will advantage the forming of $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ions and promote the transport characteristic of binary $ZnCl_2$-$DMSO_2$ melt. This also interprets that the increase of $DMSO_2$ will increase not only the molar volume but also the ionic mobility.

4. Conclusion

Raman spectra of binary $ZnCl_2$-$DMSO_2$ melts have been measured. The intra-molecular vibrations of group and ionic species have been confirmed and discussed. From the Raman spectrum analysis, the $ZnCl_n{}^{2-n}$ and $(ZnCl_2)_n$ complexes are observed in the binary $ZnCl_2$-$DMSO_2$ melts. Moreover, the Zn-O vibration in the $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ion increases with increasing the $ZnCl_2$ content. Based on these investigations, the equilibrium reaction equation about the complex ions forming is obtained. However, the Raman spectra reveal that the $ZnCl_4{}^{2-}$ (375 cm^{-1}) and $ZnCl_3{}^{-}$ (290 cm^{-1}) complexes are the major ions for the 40 – 90 mol% $ZnCl_2$ melts; furthermore, the various type complex ions including $ZnCl_n{}^{2-n}$ and $Zn_2Cl_{2n+1}{}^{3-2n}$ are also formed in the 40 – 90 mol% $ZnCl_2$ melts. As the $DMSO_2$ content increases, the binary melt will advantage the forming of the $Zn[(CH_3)_2SO_2]_n{}^{2+}$ complex ion and promote its transport characteristic.

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