

Solubility and Stability of Superoxide Radical Anions in Room-Temperature Ionic Liquids

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Superoxide anion O_2^- is obtained by one electron reduction reaction of the oxygen molecule ($O_2 + e \rightarrow O_2^-$) [1]. It was reported that O_2^- generates in the lithium air cell [2]. Since O_2^- has one unpaired electron it is also used for the radical polymerization initiator for organic synthesis [3]. Generally O_2^- is dissolved in aprotic solvents because O_2^- decomposes in the presence of H_2O or protic solvents (e.g. $2O_2^- + H_2O \rightarrow O_2 + HO_2^- + OH^-$ and $2HO_2^- \rightarrow O_2 + 2OH^-$). However, it is known that KO_2 has little solubility even in acetonitrile, a highly polar aprotic organic solvent, although the solubility increases dramatically by adding 18-crown-6-ether. Additionally, organic solvents have high volatility and flammability. By contrast, ionic liquids (ILs) possess inflammability, nonvolatility, high ion conductivity, and so on. Therefore, it would be attractive if we could use IL as an electrolyte or a radical polymerization initiator. In this study, we investigated solubility and stability of superoxide anion in ILs.

Potassium superoxide (KO_2), a yellow solid at room temperature, was chosen as an O_2^- source and its solubility in three kinds of ILs was tested: trihexyl-tetradecylphosphonium chloride ($P_{14,6,6,6}Cl$), 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]amide (EMI-TFSA) and trimethyl-*n*-hexylammonium bis[(trifluoromethyl)sulfonyl]amide (TMHA-TFSA). KO_2 and the solvents were stirred at 300 rpm and heated at 100 °C in a glove box of Ar atmosphere ($H_2O, O_2 < 1$ ppm). The solubility was visually judged from the color of solution and the existence of precipitation. The presence of O_2^- was also checked with UV-vis spectra (Hitachi U-3500).

Table 1 shows the solubility of KO_2 to three kinds of ILs and CH_3CN . As a result, KO_2 hardly dissolves in TMHA-TFSA, EMI-TFSA and CH_3CN while dissolves in $P_{14,6,6,6}Cl$ to some extent (20 mM). Note that all ILs decomposed when heated for longer than 24 h. Such difference in the solubility between an IL $P_{14,6,6,6}Cl$ and a neutral molecule solvent CH_3CN may be related to their different solvation mechanism as schematically illustrated in Figs. 1a and b.

It was also found that larger amount of KO_2 was dissolved in $P_{14,6,6,6}Cl$ by adding 18-crown-6-ether, probably due to the decrease in charge density of cation where K^+ cation is coordinated by 18-crown-6-ether ($[18\text{-crown-6K}]^+$) (see Fig. 1. (c)). Since large cations of $P_{14,6,6,6}^+$ and $[18\text{-crown-6K}]^+$, and small anions of Cl^- and O_2^- are similar in size, we speculate that the improved solubility can be attributed to the combination of the big cations and the small anions.

Figure 2 demonstrates the UV-vis absorbance spectra for (a) neat $P_{14,6,6,6}Cl$ and (b) $[18\text{-crown-6K}]^+O_2^-$ solution. For the latter case we attained a broad absorbance peak centered at around 280 nm, which should be attributed to O_2^- absorbance [4]. This strongly suggests that O_2^- stably exists in $P_{14,6,6,6}Cl$ without decomposition.

[3] R. A. Greenwald, "Electrochemical Generation of Superoxide Ion and Other Oxy Radicals". In Handbook of Methods for Oxy Radicals Research; CRC Press: Cleveland, OH 1984.

[4] M. Hayyan, *et al.*, *J. Electroanalytical Chem.*, **664**, 26 (2012).

Table 1. Solubility of KO_2 in the three ionic liquids and acetonitrile (CH_3CN) with reaction time of 3 h, 24 h, and 48 h. The reaction temperature was 100 °C and agitating speed was 300 rpm.

	3 h	24 h	48 h
TMHA-TFSA	poorly soluble	poorly soluble	decomposed
EMI-TFSA	poorly soluble	decomposed	—
$P_{14,6,6,6}Cl$	soluble (20 mM)	decomposed	—
CH_3CN	poorly soluble	—	—

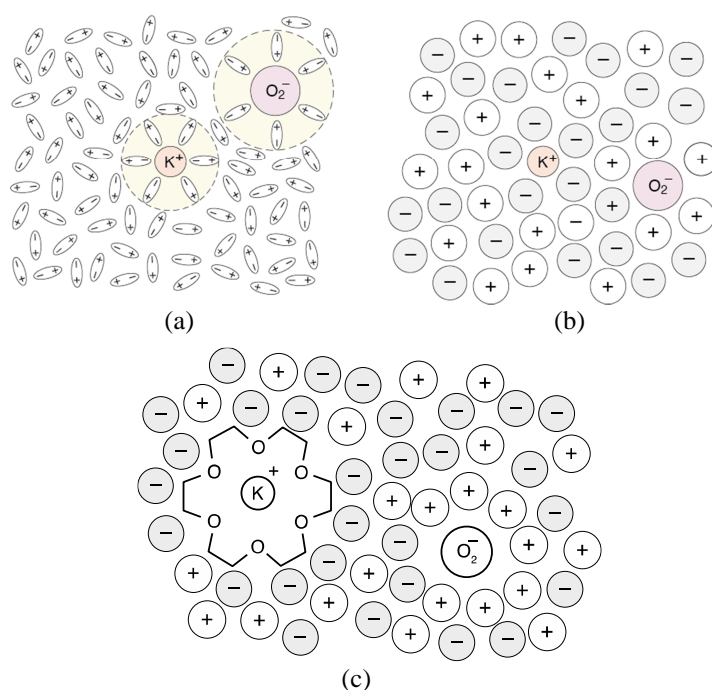


Figure 1. Solvation behavior of (a) K^+ and O_2^- in a neutral molecule solvent, (b) K^+ and O_2^- in an ionic liquid, and (c) $[18\text{-crown-6K}]^+$ and O_2^- in ionic liquid.

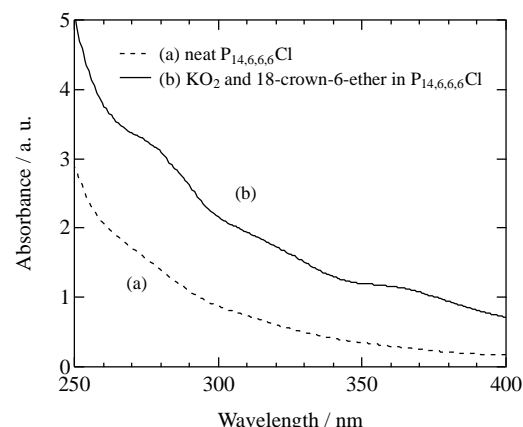


Figure 2. UV-vis spectra for (a) neat $P_{14,6,6,6}Cl$ and (b) $P_{14,6,6,6}Cl$ dissolving KO_2 and 18-crown-6-ether.

[1] M. Merritt *et al.*, *J. Org. Chem.*, **35**, 2157 (1970).

[2] V. S. Bryantsev *et al.*, *J. Phys. Chem.*, **115**, 12399 (2011).