Ordered structure in Room Temperature Molten Salts Containing Aliphatic Quaternary Ammonium Ions

Mizuhata, Minoru
Maekawa, Masanori
Deki, Shigehito

(Citation)
ECS Transactions,3(35):89-95

(Issue Date)
2007

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90005887

ECS Transactions, 3 (35) 89-95 (2007)
10.1149/1.2798650, copyright The Electrochemical Society

Ordered structure in Room Temperature Molten Salts Containing Aliphatic Quaternary Ammonium Ions

Minoru Mizuhata, Masanori Maekawa, and Shigehito Deki

Department of Chemical Science and Engineering,
Faculty of Engineering, Kobe University,
1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan

The small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) is measured for RTMS containing aliphatic quaternary ammonium cation; $[RNMe_3]^+$ (where R= n-C_nH_{2n+1}; n=3-16 which are denoted as "N111*n*") and bis(trifluoromethyl sulfonyl) imide anion. It is shown that a new peak at low q-value is confirmed above n=5. It is suggested that this new peak is of the local ordering structure formed by van der Waals force between alkyl chains of ammonium cations. From DSC result, the local ordering structure forms in [N111*n*]TFSI above n=8. This behavior is due to the thermal mobility of the alkyl chains of which local ordering structure has a good thermal stability. The other room temperature molten salts such as "[N*nnnn*]+(*n*-5-6), $[N1123]^+$, *N*-methyl-*n*-propyl piperidium cation $[PP13]^+$ and *N*-methyl-*n*-propyl pyrrolidinium cation $[P13]^+$ having the same anion; $TFSI^-$ were also used. The layer spacing (d) of this ordering structure is decrease with increase of the temperature. In the [N*nnnn*]TFSI (n=5-6) systems, the peak of the local ordering structure is sharply confirmed around q=5 nm^{-1} and this peak does not shift with increase of the temperature. From SAXS results of RTMSs ([N*nnnn*]TFSI (n=5-6), [N1123]TFSI, [PP13]TFSI and [P13]TFSI), the peak around q=7 nm^{-1} is assigned to the form factor of the electron density around N atom of aliphatic quaternary ammonium cation or the structure factor between the electron density around N atom of aliphatic quaternary ammonium cations.

1. Introduction

Room temperature molten salts (RTMSs) (so-called Ionic Liquids) have become an expanding topic of chemical research focusing their properties such as a negligible vapor pressure, non-flammability, and good ability to dissolve organic and inorganic compounds, and polymeric materials. Using these unusual properties, ionic liquids are expected as superior media or solvents for a various kinds of utilizations, for example, as environmentally friendly solvents for chemical synthesis, biocatalysis, separation technologies, and nanomaterial preparations. Also RTMSs which have good ionic conductivity are also suitable as solvent-free electrolytes in electrochemical devices and processes, such as rechargeable lithium batteries, fuel cells, electrochemical capacitors, and the electrodeposition [1-3]. The ionic species in RTMSs have complicated structure and symmetry. Especially aliphatic quaternary ammonium and asymmetric imidazolium ionic species having long alkylchain was expected to show the intensive "intermolecular interaction" and form the assembling structure in liquid media [4]. Recently, there is considerable interest in the structural features of RTMSs, for example, as oriented solvents which can impart selectivity in reactions by ordering reactants, as templates for the synthesis of mesoporous and zeolitic materials and in the formation of ordered thin films. In some kinds of ionic liquids, ordering structures have been suggested by SAXS and Xray scattering measurement [5].

We have been studied the effect of solid phase on the structural, conduction, and thermal properties of RTMSs coexisting with inorganic porous materials [6]. In such studies, conduction phenomenon was influenced by the solid phase and, in some case, an enhancement of the conductivity was found. Since ionic species in RTMS's has a significant intramolecule structure, the intermolecule interaction, was observed besides electrostatic ones between solid surface and ionic species. As well as this case, the molecular assembling and structural forming are expected in RTMS's caused by intermolecular interaction such as van dar Waals force between ionic species in single phase of RTMS's.

In this study, the small angle x-ray scattering and wide angle x-ray scattering is measured for containing aliphatic quaternary ammonium cation; $[\mathrm{RNMe_3}]^+$ (where R= n-$\mathrm{C}_n\mathrm{H}_{2n+1}$; n=3-16 which are denoted as "N111n") and bis(trifluoromethyl sulfonyl) imide anion; [N111n]TFSI (n=3-16) and the other room temperature molten salts shown in Table 1 and having the same anion; TFSI^-. The local ordering structure of AQA cations was found using AQA RTMS which has a long alkylchain length. We discussed the structural change of the molten salts with the chain length and dependence on the thermal and conductive properties.

2. Experimental

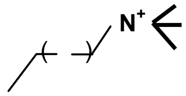
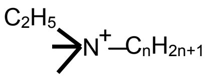
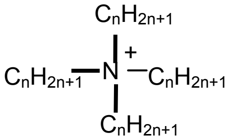
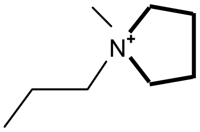
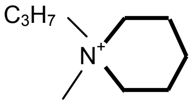
2.1 Samples

Various kinds of quaternary ammonium bis(trifluoromethyl sulfonyl) imide were used. For the samples containing aliphatic quaternary ammonium (AQA) cation, each aqueous AQA's iodide solution and LiTFSI (Fulka) solution was stoichiometrically mixed. From separated organic phase, each RTMS was extracted with $\mathrm{CH_2Cl_2}$, evaporated, and refined using distilled water until no residual byproduct was detected with the use of $\mathrm{AgNO_3}$. The resulting RTMSs were dried under vacuum (130ºC) for 24 hours. Used cations were shown in Table 1. The conductivity of each sample was measured by four probe method. The potential between electrodes was measured during electrolysis with changing electric current and I-E plots were obtained.

2.2 Small X-ray angle scattering (SAXS)

Small X-ray angle scattering (SAXS) and wide X-ray angle scattering (WAXS) of RTMSs was measured by Anton-paar SAXS system "SAXSess", as shown in Figure 1. The small angle and wide angle x-ray scattering instrument from Anton Paar GmbH was used in slit collimation configuration with PW3830 laboratory x-ray generator (40 kV, 50 mA) with long fine-focus sealed-glass x-ray tube (CuK_α, wavelength: λ=0.1542 nm). Each sample was loaded into quartz capillaries by a syringe. The temperature range of SAXS and WAXS measurements was from 10 to 70 ºC. X-ray accumulation of each

Table 1. Used room temperature molten salts and the range of their melting points.

Symbols	Cation	Anion	Melting point
N111*n* [TFSI] (*n*=3-16)		[TFSI$^-$]	**284.1 – 343.2 K**
N1123 [TFSI]			–
N*nnnn* [TFSI] (*n*=5, 6)			**298.4 K (n=5)** **266.4 K (n=6)**
P13 [TFSI] N-methyl-n-propyl pyrrolidinium cation			**285.2 K**
PP13 [TFSI] N-methyl-n-propyl piperidium cation			**285.2 K**

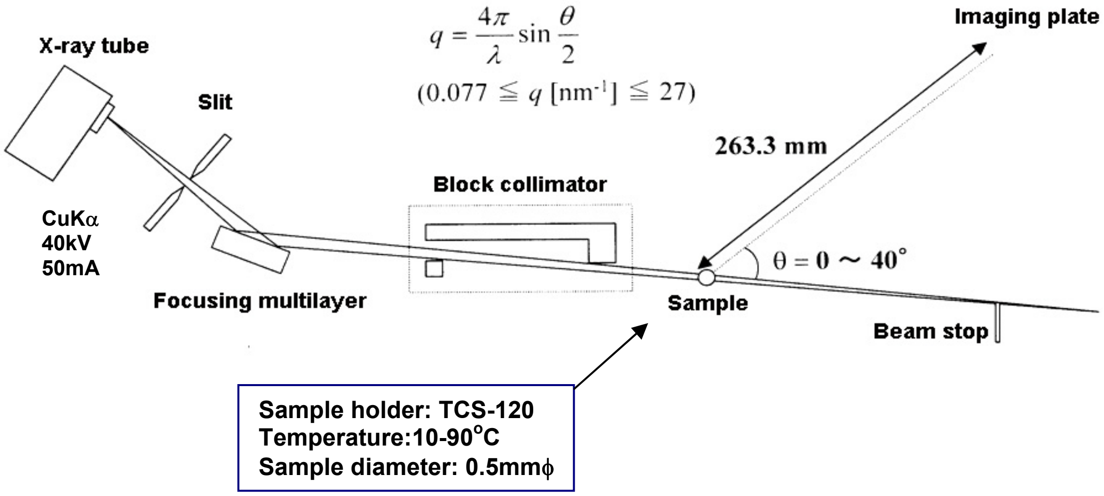


Figure 1. Schematic drawing of SAXS and WAXS measurement apparatus.

measurement was executed for 10 minutes. The detection of scattered X-ray was performed with the 2D imaging-plate reader Cyclone® by Perkin Elmer. From obtained scattering pattern, the scattering vector; *q*, was calculated from the following equation;

$$q = (4\pi/\lambda)\sin(\theta/2) \qquad [1]$$

where θ is scattering angle. We focused the scattering region at $q \geq 0.2$ nm^{-1}.

2.3 DSC measurement

The phase transition temperature of ionic liquids was determined by DSC measurement. DSC measurement was carried out using a Thermo Plus DSC 8230L (Rigaku Denki Co.) by sealing ca. 10 mg of the sample in an aluminum pan. Heating and cooling rates of 10ºC mim^{-1} were employed. At first, the sample was cooled to -100ºC and heated to 100 ºC. The cooling and heating processes are repeated three times after the sample obtained stabilization condition. Sample was kept in a dry nitrogen gas flowing.

Each decomposition temperature of ionic liquids was measured by Thermo plus TG 8120 (Rigaku Denki Co.). Samples were weakly covered by aluminum thin plate in Al pan. The weight of the sample was adjusted around 10 mg. Heating rates of 10^{o}C mim^{-1} were employed. Sample was kept in a dry nitrogen gas flowing. At the melting point, the exothermic peak which corresponded to an enthalpy of fusion was observed for each sample. The molar enthalpy of fusion, ΔH_m, was calculated from the area of exothermic peak. Additionally, we calculated the molar entropy of fusion, ΔS_m in order to discuss the relationship between the ionic structure and thermophysical properties of the AQA cations. The entropy of fusion, ΔS_m at the melting point was calculated from the following equation;

$$\Delta S_\mathrm{m} = \Delta H_\mathrm{m} / T_\mathrm{m} \qquad [2]$$

3. Results and discussion

3.1 SAXS spectra of AQA-TFSI samples

SAXS spectra was obtained from the measurement for the systems cotaining [N111n]TFSI with WAXS as shown in Fig.2. There are scattering peaks are observed at WAXS region of q = ca. 9 and ca.13 for all samples. On the other hands, it is shown that a new peak at low q-value is confirmed above n=5. The intensity of the peaks increased and shifted towards low q values with the alkylchain length of [N111n]$^{+}$ cations. It is suggested that this new peak is of the local ordering structure formed by van der

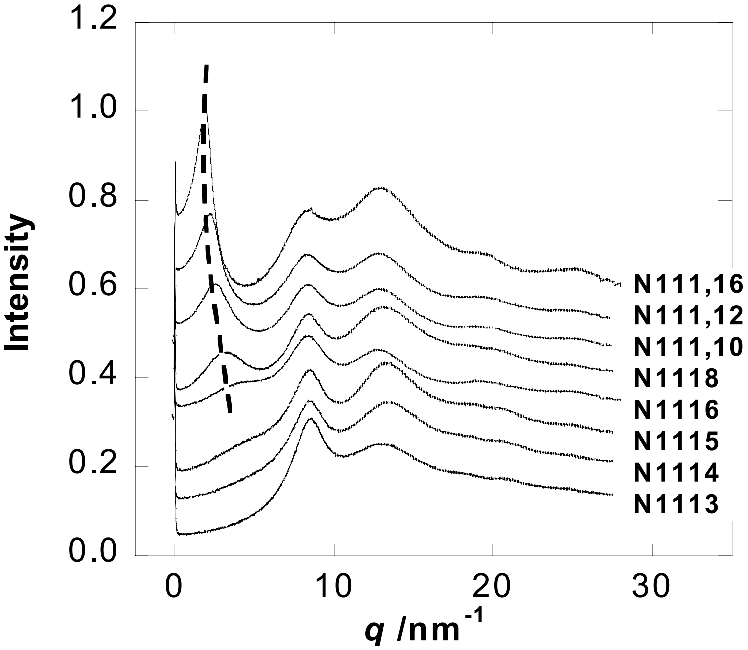


Figure 2 SAXS spectra of trimethyl aliphatic quaternary ammonium bis(trifluoromethyl sulfonyl) imide [N111n]TFSI at 30ºC.

Waals force between alkyl chains of ammonium cations. In shch case, bragg's d-space values are corresponded to ordering structural distance of the contained cations in the following equations;

$$d = 2\pi/q \qquad [3]$$

The layer spacing (*d*) of this ordering structure is decrease with increase of the temperature. This behavior is due to the thermal mobility of the alkyl chains. From DSC result, the local ordering structure forms in N111*n*[TFSI] above *n*=8.

Here, the relationship between the layer spacing and alkylchain length which was calculated from MOPAC PM3 method are shown in Figure 3. The linear relationship are observed from *n* =5 to 16. In this case, d values are less than twice of alkylchain length of each RTMS which means that the structure containing facing cation molecular with slant angle or each molecular was overlapped in micelle-like structure. If the cation was stacked without overlapping, the slant angle was ca 40º. The *d*-value shifted

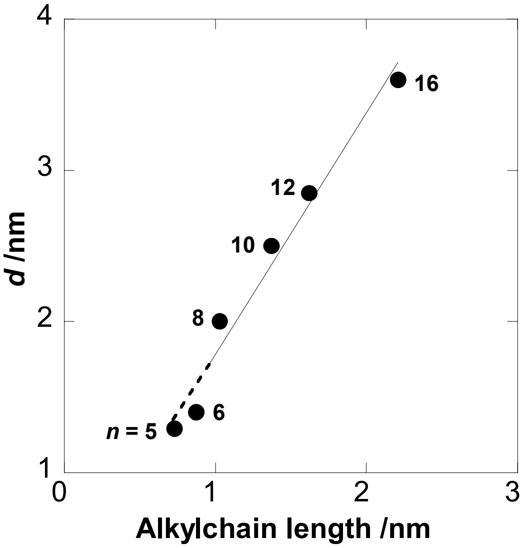


Figure 3. The relationship between the layer spacing and alkylchain length in [N111*n*]TFSI at 30 ºC.

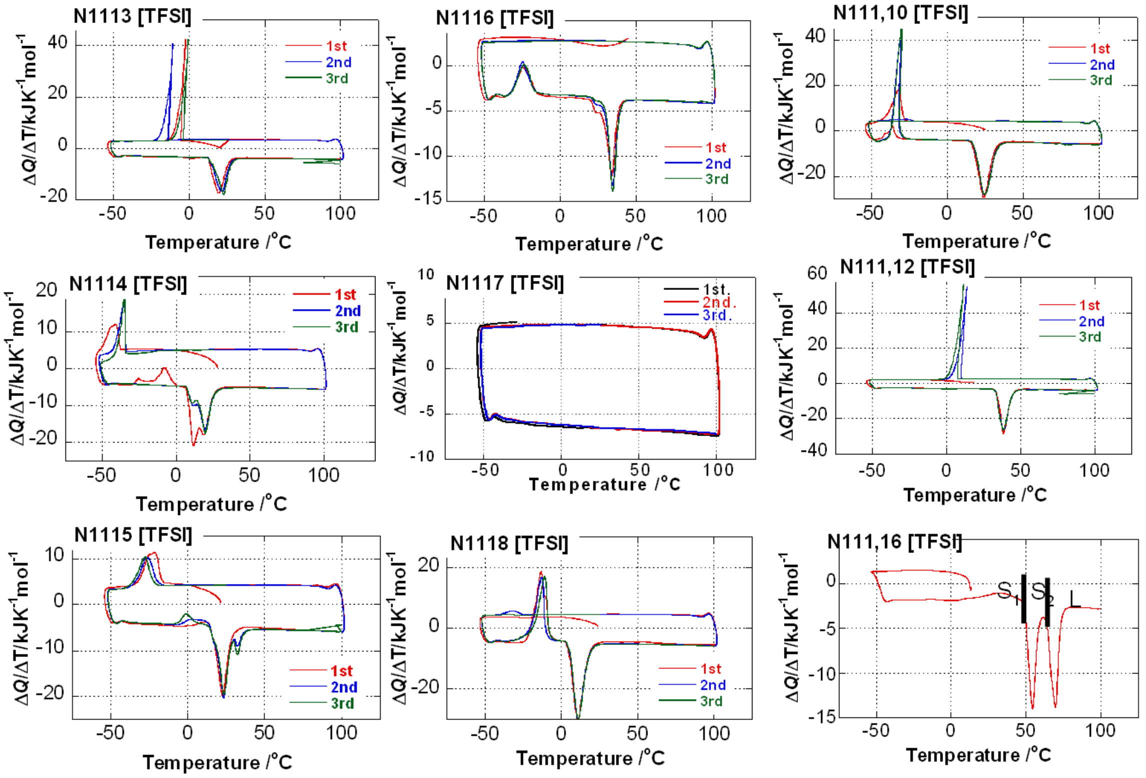


Figure 4. DSC curves of [N111n]TFSI Scan rate: 10 K/min.

to lower values with the temperature, however, relationship are not changed. Also, reproducibility of the distance calculated from *d* values was kept after temperature change, the structural change of ordering structure does not occurred in this systems.

3.2 Relationship between melting behavior and structural properties for [N111*n*]TFSI

The obtained SAXS spectra of [N111n]TFSI suggested that ordering structure exists in RTMSs, especially containing long alkylchain length. Such difference indicates the thermophysical properties of AQA-TFSI molten salts in DSC measurements. The DSC curves of cooling-heating cycle for the system containing N111*n*TFSI melts are shown in Figure 4. The endothermic peaks indicating melting behavior are observed in each system except N1117TFSI system. In this system, we repeated cooling-heating cycle with various scanning rates; however, there is no melting point during the DSC operations. It is suggested that the structure rearrangement are difficult in due to transition energy of phase transition and the RTMS changed to glassy structure in the lower temperature range. Such sign was observed the freezing behavior in N1116 and N1119 systems; i. e., these sample were frozen during heating process, whereas the other samples were frozen via supercooled phase during cooling process. It is suggested that the certain ordering structure is formed in liquid phase for the [N111*n*]TFSI systems.

The melting and transition point of these samples and their entropy of fusion, ΔS_m obtained from each DSC curve are shown in Figure 5. For N1117TFSI, the melting point was obtained using the sample frozen by slow scanning operation down to -140ºC. The melting points rose from ca 290K to 310K for [N1113]TFSI – [N1117]TFSI and discontinuously rose from ca 280K to 340K for [N1118]TFSI – [N111, 16]TFSI having the resemble ΔS_m value. Generally, the ΔS_m corresponding to the structural change is observed at the phase transition point such as melting and glass transition. Therefore the large molecular has a large ΔS_m. In such cases, the alkyl chain has an ordered structure, the increase of entropy might be caused by anion species and so on. At n=8, an abrupt change of the melting points and entropy are observed at which the first peak appeared at lower q values in SAXS spectra. It is suggested that the ordering structure was caused by the intermolecular interaction of the cation species in the RTMSs which reduced the entropy of fusion at the melting points. Such tendency agreed with the normal alkyl alcohol system.

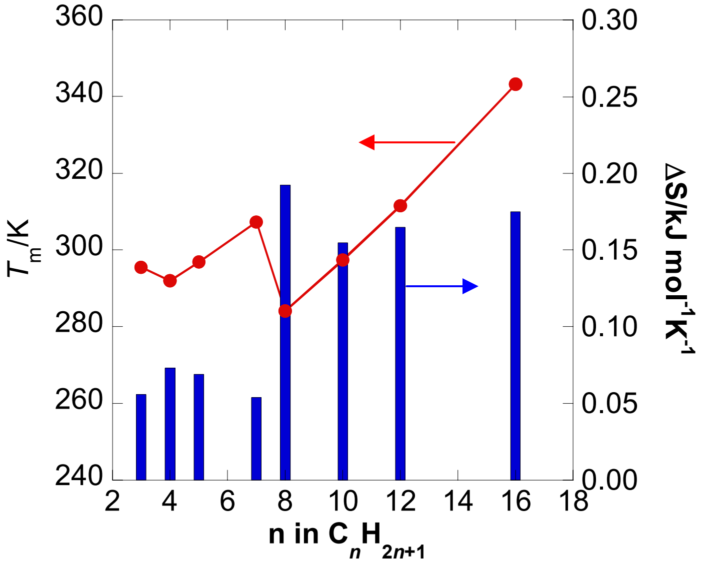


Figure 5. Melting points and the entropy of fusion of the [N111*n*]TFSI (n=2-16).

3.3 SAXS profiles of various AQATFSI

As reference systems, the small angle x-ray scattering and wide angle x-ray scattering is measured for [N*nnnn*]TFSI (*n*=5-6), [N1123]TFSI, [P13]TFSI and [PP13]TFSI as shown in Figure 6.

In the [N*nnnn*]TFSI (*n*=5-6) systems, the peak of the local ordering structure is sharply confirmed around q=5 nm^{-1} and this peak does not shift with increase of the temperature. As a result, this local ordering structure has a good thermal stability. From SAXS results of RTMSs ([N*nnnn*]TFSI (*n*=5-6), [N1123]TFSI, [P13]TFSI and [PP13]TFSI), the peak around q=7 nm^{-1} is assigned to the form factor of the electron density around N atom of aliphatic quaternary ammonium cation or the structure factor between the electron density around N atom of aliphatic quaternary ammonium cations. For all systems including [N111*n*]TFSI, certain peak is observed at q = 13 nm^{-1} assigned to the anion species. It is suggested that quaternary normal alkyl ammonium cation has an ordered structure in room temperature molten salts which depends on the cationic structure.

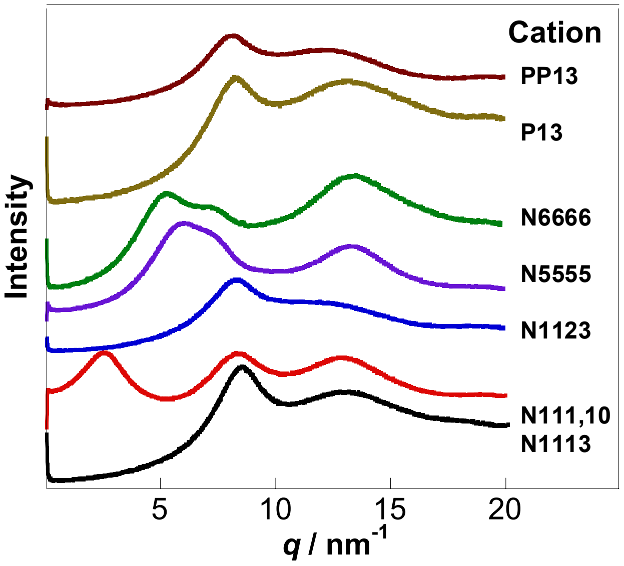


Figure 6. SAXS spectra of various aliphatic quaternary ammonium bis(trifluoromethyl sulfonyl) imide at 30°C.

Acknowledgments

Original salts including PP13, P13 and N5555, N6666 cations are provided from Dr. H. Matsumoto of AIST Kansai, Japan. A part of this work was supported by Grant-in-Aid for Scientific Research “Science of Ionic Liquids” from MEXT of Japan.

References

1. N. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, and Y. Aihara, *J. Electrochem. Soc.*, **150**, A695 (2003).
2. Z-B. Zhou, H. Matsumoto, and K. Tatsumi, *Chemistry – A. Euro. J.*, **12**, 2196 (2006).
3. A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K Hayamizu, and M. Watanabe, *J. Phys. Chem. B*, **107**, 4024 (2003).
4. M. Yoshio, T. Kagata, K. Hoshino, T. Mukai, Hi. Ohno, and Takashi Kato, *J. Am. Chem. Soc.*, **128**, 5570 (2006).
5. A. E. Bradley, C. Hardacre, J. D. Holbrey, *Chem Mater.*, **14**, 629-635 (2002).
6. M. Mizuhata, K. Yaso, Y. Ito, S. Deki, *Electrochemistry*, **73**, 606 (2005).