

High-Resolution Adiabatic Scanning Calorimetric Study of Phase Transition Behavior of Some Piperidinium and Morpholinium Ionic Liquid Crystals

C. S. P. Tripathi^{C, S}, J. Leys, P. Losada-Pérez and C. Glorieux

K.U.Leuven, Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Leuven, Belgium

chandrashekharpatripathi@gmail.com

K. Lava and K. Binnemans

K.U.Leuven, Laboratorium voor Coördinatiechemie, Departement Chemie, Leuven, Belgium

J. Thoen

K.U.Leuven, Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, Leuven, Belgium

Ionic liquid crystals are a fascinating class of materials that combine the properties of both ionic liquids and liquid crystals [1]. Recently, piperidinium and morpholinium cations have been used for the design of ionic liquid crystals [2]. These cations were combined with several types of anions among which tetrafluoroborate and hexafluorophosphate. The compounds show a rich mesomorphic behavior. High-ordered smectic phases (crystal smectic E and T phases), smectic A phases were observed, depending on the type of cation and anion. In an effort to characterize the transitions between these phases and to extract the quantities associated with the transition, high resolution adiabatic scanning calorimetry (ASC) [3] measurements of enthalpy H and heat capacity C_p as a function of temperature have been carried out for the compounds [pipC₁₄][BF₄]⁻ (cation: piperidinium and anion: BF₄⁻), [morphC₁₄][BF₄]⁻ (cation: morpholinium and anion: BF₄⁻), [pip(C₁₄)₂][PF₆]⁻ (cation: piperidinium and anion: PF₆⁻) and [pip(C₁₄)₂][BF₄]⁻ (cation: piperidinium and anion: BF₄⁻). For [pipC₁₄][BF₄]⁻, the three transitions, Crystal 2 to Crystal 3, Crystal 3 to Crystal Smectic T and Crystal Smectic T to Isotropic phase were found to be first order with latent heats of 23±2 Jg⁻¹, 8±2 Jg⁻¹ and 10±1 Jg⁻¹ respectively and exhibited the usual pretransitional increase in the lower temperature phase. For [morphC₁₄][BF₄]⁻, a preliminary analysis shows that all the three transitions, Crystal to Smectic X (crystal smectic E or T phase), Smectic X to Smectic A and Smectic A to Isotropic phase are also first order. For the compounds with two alkyl chain, [pip(C₁₄)₂][BF₄]⁻ and [pip(C₁₄)₂][PF₆]⁻, the two transitions detected, Crystal to Smectic X and Smectic X to Isotropic phase, were also first order. Supercooling and superheating of the transitions were also observed.

[1] K. Binnemans, *Chem. Rev.*, **105**, 4148-4204 (2005).

[2] K. Lava et al., *J Phys. Chem. B*, **113**, 9506–9511 (2009).

[3] J. Thoen et al., *Liq. Cryst.*, **36**, 669-684 (2009).