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Phase Transition of [bmim][PF_6] under High Pressure

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Compression of both liquid and solid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was measured at temperatures 293-323 K and pressures up to 400 MPa and melting curve was estimated.

To measure the compression of the solute, a piston-cylinder type pressure vessel (9 mm inner diameter, 50 mm outer diameter, and 80 mm height of the cylinder made of 17-4PH stainless steel) was designed. It was pressed using an oil press and the position of the piston was measured by using a micrometer. Temperature of the cylinder was regulated by attaching a water- circulating jacket around it. Pressure was monitored by a load cell calibrated by a Heise pressure gauge. Piston was pressed at intervals of 10 minutes by 0.5 mm each and the position and pressure were measured at each step up to 400 MPa at a constant temperature, and then the pressure was released in a similar manner. Volume (V) of the solute in the cylinder at each pressure was estimated by the position of the piston and both V-p compression and depression curves were drawn. Phase transition (solid to liquid) of the solute was clearly observed in depression curve though the large hysteresis over 100 MPa was observed in compression curve suggesting a metastable liquid state.

Depression curves show the phase-transition pressure; 48 MPa at 293.2 K, 74 MPa at 298.2 K, 96 MPa 303.2 K, 119 MPa at 308.2 K, 179 MPa at 318.2 K, and 206 M at 323.2 K. From these values, melting point of the solute at 0.10 MPa can be extrapolated to be 284 K, and the slope of p-T transition curve were estimated to be (dp/dT =) 5.6±0.2 MPa/K at 200 MPa and 5.0±0.2 MPa/K at 0.10 MPa. On the other hand, the volume change of phase transition was estimated to be 13.5±0.3 cm^3 mol^{-1} from the V-p depression curve and the enthalpy of the phase transition was separately measured to be 20±1 kJ mol^{-1} from DSC at atmospheric pressure. Then similar value of dp/dT = 5.0±0.3 MPa/K is obtained from Clapeyron's equation. These values for the phase transition of [bmim][PF_6] coincide with those up to 90 MPa estimated by de Azevedo *et al.* [1] by measuring sound velocity. Present work expands the transition curve up to 200 MPa.

[1] R. G. de Azevedo, *et al.*, *J. Chem. Eng. Data*, **50**, 997 (2005).