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Determination of melting temperatures in hydrocarbon mixtures by Differential Scanning Calorimetry

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Abstract

There is a lack of consistency in the literature about how to determine the melting (liquidus) temperature in a hydrocarbon mixture from thermograms recorded by differential scanning calorimetry (DSC). This paper establishes a robust technique for determining *liquidus* temperatures by DSC by testing the two methods detailed in the literature and assessing the potential for de-mixing to preclude repeatable measurements. Liquidus temperatures determined via the end set scanning method were found to be consistent with literature measurements of the same mixture obtained visually, and with a *liquidus* temperature measured for a fresh sample using the step method. In contrast, use of the thermogram's peak temperature produced inconsistent results that often could not be reasonably extrapolated to zero scan rate. The impact of any sample de-mixing that may have occurred over multiple freezemelt cycles was negligible, as demonstrated by the consistency of the thermograms repeated at the same scan rate, and the consistency of *liquidus* temperatures obtained with different sample loadings into the DSC. New (solid + liquid) equilibrium results are reported for {heptane + hexadecane (C_{16}) } and (hexane + hexadecane) binaries as well as a (hexane + para-xylene + hexadecane) ternary over a temperature range from (260.80 to 279.17) K at atmospheric pressure. Comparisons of the binary measurements against both literature data and the calculations with a property package implemented in commercial software showed deviations of less than 1 K for mixtures with C_{16} solute mole fractions around 0.3, and -3 K for the mixture with a C_{16} solute mole fraction around 0.1, due to the increasing sensitivity of the *liquidus* temperature on composition as the solute fraction decreases. The ternary mixture, with a C₁₆ solute mole fraction of around 0.1, showed a deviation of -5 K, suggesting the

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