Micro-Calorimetric Study on the Structural Transition in Micellar Solution Phase

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The phase behavior of polyoxyethylene alkyl ether (C_mEO_n)/water system has been investigated by means of the ultrasensitive differential scanning calorimeter (VP-DSC). This VP-DSC is able to detect a few microcalorie of heat change accompanied by the very weak 1st order phase transition such as cloud point and Lα→L3. The calorimetric profile showed not only the cloud point but an as-yet-unknown micelle structure transition (pre-transition) below the cloud point. Regardless of the unit numbers of EO and alkyl chains, this pre-transition occurred at approximately 25˚C below the cloud point (Figure 1), where indeed the micelle suddenly initiated to grow up. In the L_1 region below this pre-transition temperature, the micelle size is almost independent on temperature as well as the EO chain length. On the other hand, the growth rate of micelle with temperature (dD/dT) depends on the EO and alkyl chain lengths in the L_1' region, and interestingly correlates with the transition enthalpy at the pre-transition temperature. In addition, our recent results demonstrated that additives such as inorganic salt can control the onset temperature of micelle growth and dD/dT, which may refer to Hofmeister series. In our presentation, we will further discuss significance of the pre-transition about practical solution properties such as solubilising oil, and Hofmeister series from the point of view of the thermodynamic parameters obtained from the VP-DSC measurement.

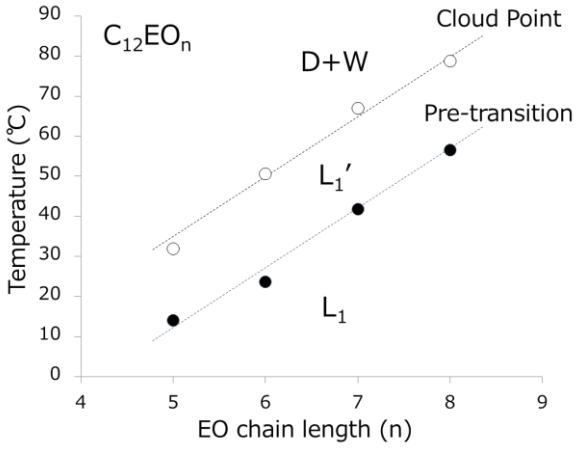

Figure. 1 Phase diagram of the $C_{12}EO_n$/water system as functions of temperature and EO chain length (n). The $C_{12}EO_n$ concentration is kept at 1 wt%. The micellar solution (L_1) turns to the two-phase (D+W) at the clouding temperature via another micellar solution phase (L_1') identified by VP-DSC.

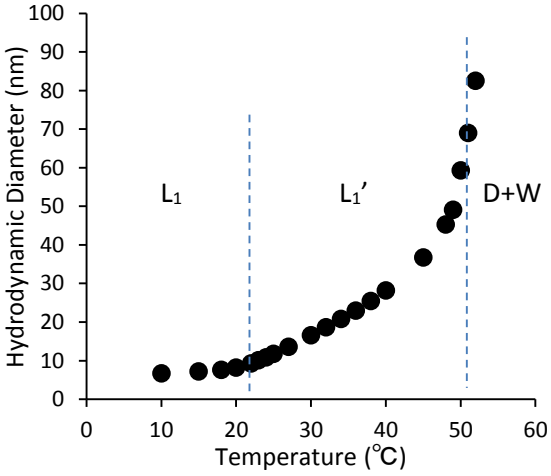

Figure. 2 Change in the hydrodynamic diameter of micelle with temperature in 1wt% $C_{12}EO_6$ aqueous solution. The dotted lines indicates each critical temperature, pre-transition (lower temperature) and cloud point (higher temperature), determined by VP-DSC measurement.