

Determining the thermodynamic parameters of dispersed systems by variable temperature multiple light scattering

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Abstract – Nanocapsule suspensions and nanoemulsions of octyl methoxycinnamate were analyzed by variable temperature multiple light scattering (23°C-56°C). Using van't Hoff equation, the thermodynamic parameters such as standard-enthalpy and standard-entropy of flocculation or agglomeration were determined. Those values were higher for the nanoemulsion indicating that the polymeric wall of the nanocapsules exerts a significant effect on the physical stability of the colloid.

Nanocapsules (NC) and nanoemulsion (NE) formulations of octyl methoxycinnamate (OMC) were prepared by the interfacial deposition of preformed polymer and by spontaneous emulsification, respectively [1,2]. The formulations were called NC_{OMC/CCT} and NE_{OMC/CCT}. The variable temperature multiple light scattering was carried out to predict the physical stability of the systems, as an innovative method to determine the thermodynamic variables of colloidal systems. The backscattering signals (BS) were determined under a temperature gradient from 23°C to 56°C, using a rate of 3 °C/5 min.

The colloidal systems presented unimodal and narrow size distribution (polydispersity index below 0.2) with mean diameters close to 220 nm for NC and 180 nm for NE. The formulations showed zeta potential values of -10 mV due to the steric effect of polysorbate 80 as coating material. The multiple light scattering experiments (using Turbiscan[®] equipment) proceeded for 10 h under a fixed temperature (25 °C) showed a slight tendency to particle migration (Fig 1.) For NC, the sedimentation showed that the particles have density higher than 1, while for NE a tendency for both top and bottom is due to their density near 1. The variable temperature analysis showed a reduction of the BS with the increase in the temperature for both formulations (NC_{OMC/CCT} and NE_{OMC/CCT}). Those correlations were linear ($R > 0.99$). The reduction of the BS was related to changes in the particle/droplet mean diameter. Considering the equilibrium agglomeration-redispersion as a consequence of the thermodynamic process and type and concentration of surfactant in the colloidal systems, BS_{T_x} and BS_{T_i} are the final and the initial state of a tendency to agglomeration with the increase in the temperature. So, the equilibrium constants for the phenomena would be given by $K = BS_{T_x}/BS_{T_i}$.

The ΔH° and ΔS° values were obtained using a van't Hoff plot based on the equation: $\ln K = -\Delta H^\circ/R \cdot 1/T + \Delta S^\circ/R$, where $R = 8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and T in Kelvin. Fig. 2 shows the comparison between formulations. ΔH° and ΔS° were higher for the NE system ($P = 0.002$, $\alpha = 0.05$). The negative of ΔH° and ΔS° indicated that the agglomeration-redispersion process is enthalpically governed. Comparing those values was possible to determine quantitatively that the polymer increases the final physical stability of NC. In conclusion, the new method is able to demonstrate the relative stability among colloidal systems in shorter space of time (<1h) than any other existing method, with the advantages of furnishing quantitative values to compare those stabilities, as well as with no need of sample treatment before analysis.

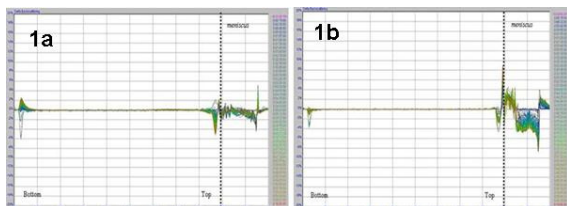


Figure 1: Backscattering versus time profiles (reference mode) of a) NC_{OMC/CCT} and b) NE_{OMC/CCT} obtained from the fixed temperature analysis.

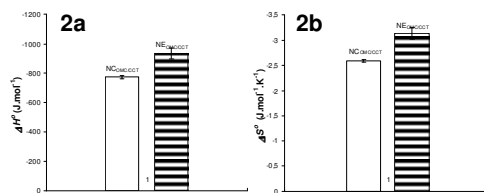


Figure 2: Comparison between the values of a) standard-enthalpy ($\text{J} \cdot \text{mol}^{-1}$) and b) standard-entropy ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) of the flocculation process of NC_{OMC/CCT} and agglomeration process of NE_{OMC/CCT} formulations.

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[2] V. Weiss-Angeli, F.S. Poletto, L.R. Zancan, F. Baldasso, A.R. Pohlmann, S.S. Guterres. J. Biomed. Nanotechnol. 4 (2008) 80–89.