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Isothermal and non-isothermal melting of the binary solution inside an emulsion

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Abstract

The aim of the present paper is to study the melting process inside an emulsion using the non-equilibrium model of microscopic heat transfer between the emulsifying medium and the dispersed droplet of binary solution (DSC). DSC experiments are used to validate the numerical results. The effects of the heating rate, mass fraction of the dispersed saline binary solution, initial mass fraction of the solute and the sample mass on the kinetics of the melting process are examined.
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1. Introduction

Emulsions are the subject of several studies in the recent literature. Much of this work is concentrated upon the caracterizing of the emulsion morphology and the effects of some parameters on it [1,2].

Our research group worked for a long time on the heat transfer during crystallization or melting within an emulsion. We have presented some models concerning the heat transfer in the case of a phase change of binary solutions dispersed within emulsions or micro-emulsions (see Refs. [3–6]).

To obtain more information about the kinetics of the eutectic and progressive melting of the crystallized droplets dispersed inside emulsion, we have developed a non-equilibrium model taking into account the interphase heat transfer between the emulsifying medium and the dispersed droplet. The effects of the heating rate, mass fraction of the dispersed saline binary solution, initial mass fraction of the solute and the sample mass on the kinetics of the melting process are investigated.

2. Equilibrium phase diagram of binary system

Fig. 1 shows the equilibrium phase diagram for the NH$_4$Cl–H$_2$O system. The symbols L, S and L+S denote the

liquid phase, the solid phase and the solid–liquid two-phase, respectively.

The lowest temperature possible for liquid salt solution is $-15.7\,^{\circ}$C. At that temperature, the salt begins to crystallize out of solution, along with the ice, until the solution completely freezes. The frozen solution is a mixture of separate solute crystals and ice crystals. This mixture is called a eutectic mixture. If the ice, salt and the saltwater are present in the binary mixture, and their amounts are not changing over time we must be at the eutectic point ($T_E = -15.7\,^{\circ}$C and $X_E = 0.195$).

In our application, the over-eutectic part is not of interest. If the solute mass fraction X_a is lower than X_E the ice mass fraction X_{ic} can be calculated from the liquidus temperature of the binary mixture solution, which is a function of X_a.

$$T = T(X_a) \tag{1}$$

Once the initial mass fraction of solute in the binary mixture solution before freezing $X_{a,i}$ and temperature are known, the equilibrium ice mass fraction is calculated with:

$$X_{ic}(T) = 1 - \frac{X_{a,i}}{X_a(T)} \tag{2}$$

in which $X_a(T)$ is found from the liquid curve, the inverse of Eq. (1).

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Nomenclature

c	specific heat $(\mathrm{J\,kg^{-1}\,K^{-1}})$
h	exchange coefficient for the droplet $(\mathrm{W\,m^{-2}\,K^{-1}})$
h_1, h_2	external exchange coefficient for the cell $(\mathrm{W\,m^{-2}\,K^{-1}})$
k	thermal conductivity $(\mathrm{W\,m^{-1}\,K^{-1}})$
L_D	heat of dissolution of salt in the solution $(\mathrm{J\,kg^{-1}})$
L_F	latent heat of melting of the ice $(\mathrm{J\,kg^{-1}})$
P	mass fraction of the dispersed solution
ΔS	area $(\mathrm{m^2})$
t	time (s)
T	temperature (K)
X_E	eutectic concentration
X_{ic}	ice mass fraction
X_g	ice mass fraction which is melted

Greek symbols

β	heating rate $(\mathrm{K\,min^{-1}})$
ρ	mass density $(\mathrm{kg\,m^{-3}})$
ε	porosity
Φ	specific heat flow rate $(\mathrm{W\,kg^{-1}})$

Subscripts

a	antifreeze
em	emulsion
f	emulsifying medium
i	initial
ic	ice
s	solution

3. Formulations

Thermal analysis was carried out using a PYRIS DIAMOND DSC of Perkin-Elmer. The temperature scale of the instrument was calibrated by the melting point of pure ice (273.15 K or 0 °C) and mercury (234.32 K or −38.82 °C). The principle of the power-compensation used in dispersed droplet of binary solution (DSC) is widely detailed in Refs. ([7,8]).
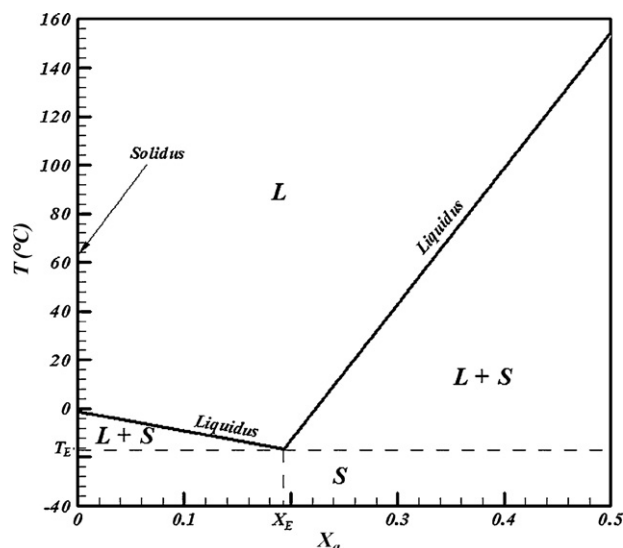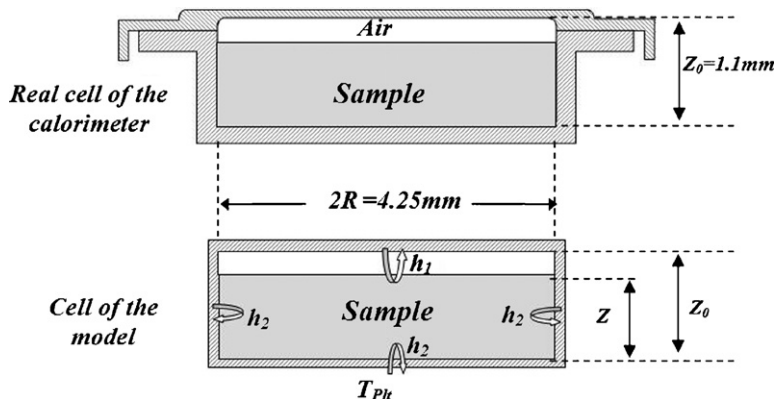

Fig. 1. Phase diagram for a binary solution (NH_4Cl–H_2O).

In Fig. 2, we have drawn the real cell and the simplified scheme used in our model. The emulsion fills a cylindrical cell of height $Z_0 = 1.1$ mm and radius $R = 2.125$ mm.

To study the melting process inside an emulsion, we assume that the emulsifying medium and the droplets are not in local thermodynamic equilibrium and, therefore, a two-temperature model of microscopic heat transfer applies. The governing equations for the emulsifying medium and the solution temperatures are:

$$\varepsilon(\rho c)_f \frac{\partial T_f}{\partial t} = \varepsilon k_f \nabla^2 T_f + h(T_s - T_f) \tag{3}$$

$$(1 - \varepsilon)(\rho c)_s \frac{\partial T_s}{\partial t} = h(T_f - T_s) \tag{4}$$

where T is the temperature, ρ the mass density, c the specific heat, k the thermal conductivity, h the overall constant heat transfer coefficient, f and s subscripts denote the emulsifying medium and solution phases, respectively, and ε is the porosity defined by the following relation:

$$\varepsilon = 1 - P\frac{\rho_{em}}{\rho_s} \tag{5}$$

Fig. 2. Experimental cell and scheme for the model.