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The kinetics of the solidification of highly supersaturated solutions of palmitic acid in oleic acid: a comparison between two models

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The crystallization of fatty acids is very important in industrial applications and biological systems. A comparison between theoretical models and experimental data helps in clarifying mechanistic aspects of these systems. In this contribution, we compare the performance of two models in fitting data from the crystallization of supersaturated solutions of palmitic acid in oleic acid. One of the models was developed by Avrami and the other is based on considering diffusion as limiting (the D-model). The D-model fitted the data better than the Avrami model in all cases. The D-model has a low value of the regression coefficient (r^2, lower than 0.9) in only three cases. For these points, the thermodynamic force was smaller. Differences in the parameter n (an index of dimensionality) were observed; these differences indicate that clusters were present previous to the crystallization process. Furthermore, there appears to be a difference in the mechanism of crystallization of pure solutions of palmitic acid and solutions with a small fraction of oleic acid. Thus, one is lead to the conclusion that the rate of crystallization of fatty acids at high concentrations is limited by diffusion.

Key words: palmitic acid, nucleation, Avrami, diffusion, non-linear regression, models.

Crystallization of chemical compounds from melts and solutions is an important separation-purification process with increasing industrial applicaton, especially in the organic and biochemical industries.[1] Despite the progress made in recent years, fundamental knowledge concerning the mechanistic aspects of the kinetics of crystallization are still lacking. This has prevented the development of applications that require the production of crystals of controlled purity and shape.[2]

Palmitic acid is one of the most widely used materials in the cosmetic and soap industry. A number of investigations have been published over the last 30 years focusing on the presence of polymorphism, the kinetics of single crystal growth of fatty acids[3] and on the effect of parameters, *i.e.*, the solvent.[4]

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Experimental investigation of crystallization kinetics and comparison of the data with theoretical values calculated using various models of crystallization helps to understand the laws of nucleation and crystals growth.[5] In this contribution we applied this approach for the crystallization of palmitic acid in oleic acid at high concentrations.

Kolmogorov, in 1937, proposed a model (tke K-model) and derived an equation that described the kinetics for the non-crystallized volume fraction during crystallization (see Ref. 5 for a detailed description).

After the paper by Kolmogorov, additional models were proposed. In 1939 Johnson and Mehl applied an original statistical method for the calculation of the liquid fraction ($q(t)$), considering that the nucleation and growth rates were constant and the crystals were spheres.[6] This is a special version of the K-model. However, computer simulations has shown that the Johnson-Mehl model cannot describe the crystal volume distribution even qualitatively.[7]

Avrami, in the 1940's, proposed the application of the Johnson-Mehl method to models different than the K-model.[8–10] As a result of such an application, the so-called Avrami equation was obtained:

$$q(t) = \exp(-kt^n) \tag{1}$$

where n is the Avrami exponent. In some cases, this exponent cannot be uniquely determined for a broad range of experimental conditions. In these cases, one can resort to other approaches.

Among these alternatives, the so-called D-model,[5] has shown itself to be particularly successful in describing the kinetics of crystallization for a broad range of systems. In order to understand the formulation of this model, let us assume that the radius of a spherical crystal, R, grow by a diffusional law (note that the assumption of spherical crystals remains for this model), that is: $R(t',t) = \sqrt{g}\,(t-t')$ where t' and t are the times of nucleation and observation, respectively, and g is a constant. Using the D-model, in the absence of exact descriptions, Shepilov in 1992 obtained detailed analytical estimates of the upper and lower bounds of $q(t)$[11] (for more details see Ref. 11). In cases with a constant nucleation rate, these estimates are in agreement with the results of computer simulations[5] and show that the D-model is reduced to:

$$q(t) = t^n - \exp(-8\pi\alpha g^{3/2}/15) \tag{2}$$

where α is the nucleation rate, t the time and n the Avrami exponent.

In this contribution, we have applied this model to describe the kinetics of crystallization of palmitic acid. These results are compared with the ones given by the Avrami model for the crystallization of palmitic acid in oleic acid at high concentrations (*i.e.*, melt crystallization).

EXPERIMENTAL

Palmitic acid (99% pure) and oleic acid (99%) were obtained from Sigma Chemicals Co. (St. Louis, MO), and used without additional purification.

Solutions of palmitic acid in oleic acid were prepared at four different concentrations (0.55, 0.7, 0.85 and 1 in the mole fraction of palmitic acid in oleic acid).

DSC scans were performed using a Perkin-Elmer Model DSC-7. A piece of indium (6 mg) was sealed in an aluminum sample pan and used as the reference. Samples of the solutions (8 mg) were also sealed in sample pans and held at 353 K for 30 min to destroy the crystal nuclei before each DSC scan[12] then they were cooled at 5 °C/min down to the transition temperature. The temperature was then increased by 10 °C for the crystallization of all the samples.

These thermograms were analyzed for the determination of the transition point of the samples, and then the isothermal analysis was performed. For each concentration, three temperatures were used for these analyses, two replicates were obtained in each case. Samples (8 mg) of each solution were sealed in sample pans and held at 353 K for 30 min to destroy the crystal nuclei before each DSC scan, and then cooled at 5 °C/min up to the desired temperature for isothermal analysis. The samples were held for 60 min at this temperature.

The area enclosed by the base line and the exothermic peak in the DSC scans corresponds to the heat of crystallization ΔH. The fraction of liquid in the system ($q(t)$) at a given time (t) was approximated by the ratio of the integration of the exothermic rate to the total area.[13]

The Eq. (1) was used and the parameters k and n were obtained from Eq. (1) by a non-linear regression procedure, following the approach suggested by Bates and Watts in 1988 for the interpretation of non-linear regression. A similar procedure was used to obtain α, g and n from Eq. (2).

The comparison of two models was made according to the following steps:[14]

1. Determination of the behavior of the samples (normal distribution of residuals).

2. Evaluation of the amount of variance explicate for the non-lineal regression (in terms of the regression coefficient r^2, similar to a linear regression).

3. Analysis of residuals.

These three steps were followed for each sample and condition evaluated.

RESULTS AND DISCUSSION

The transition temperature is a linear function of mass, with higher masses the transition temperatures are higher, and *vice versa*. The dependence of the transition temperature (crystallization temperature) with respect to the amount of palmitic acid is shown in Fig. 1. A linear regression analysis gives a correlation coefficient $r^2 = 0.96$. Similar results were obtained when using a partial correlation (values not shown). The distribution of the residuals was normal. An extrapolation of the data presented in Fig. 1 to 0 mole fraction of palmitic acid gives the crystalllization temperature of oleic acid, for which the estimation of the standard error is lower that 0.052 °C.

The behavior observed in Fig. 1 indicates that the palmitic acid is the only one undergoing a phase change in the system. There are no differences in the thermograms obtained in the heating and cooling mode, indicating that only one polymorphic form was present. The type of polymorphism was not determined.

Next, the kinetic models of crystallization were tested. For the Avrami model, seven different concentrations of palmitic acid were used at three different temperatures. These seven different concentrations were grouped into four sets for replicate reasons (evaluation of experimental error). The experimental error associated with

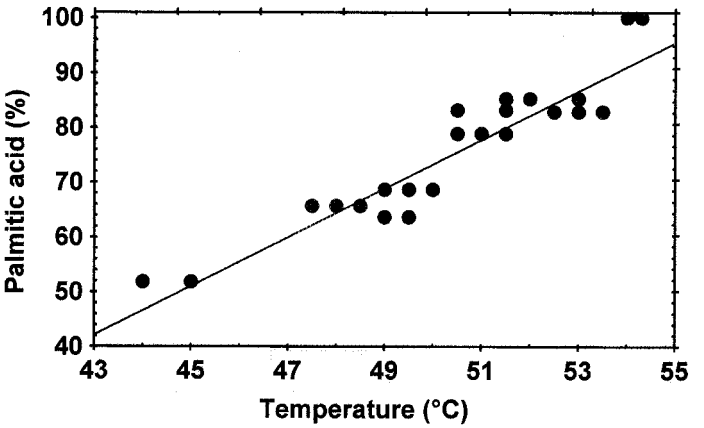

Fig. 1. Influence of the amount of palmitic acid over the crystallization temperature in mixtures of palmitic acid-oleic acid.

the different mole fraction was estimated to be less than 0.01 (in mole fraction). Equipment limitations limited the range of concentrations that could be used. Hence, only solutions with mole fractions of palmitic acid above 0.5 were probed. Experiments with pure oleic acid were performed for each experimental conditions. In all cases, the solvent (oleic acid) did not show a phase transition.

Firstly, the Avrami model (Eq. (1)) was applied. The fraction of liquids instead of the amount of solids, was used as the reference. In this manner, smaller deviations related to the rescaling are obtained.[15–17] Avrami, in 1940 had remarked that his model was appropriate for liquid fractions in the range 0.25–0.75, because a linear dependence is observed only in this range. The results for this model are given Table I.

TABLE I. Values of the parameters for the Avrami model

Conc. of palmitic acid mole fraction	Temperature/°C	k	n	r^2 x100
0.55	45	0.00016	2	84.83
0.55	45.5	0.000278	2	84.83
0.70	49	0.004078	2	77.01
0.70	49.5	0.000285	2	77.01
0.70	50	0.000251	1	77.01
0.85	50.5	0.000596	2	79.09
0.85	51.5	0.000132	1	79.09
0.85	53	0.0002475	2	79.09
1.00	54	0.007198	2	99.1
1.00	54.3	0.00042	2	99.1

As can be seen from Table I, a regression coefficient above 0.9 is obtained only for one concentration. Thus, the Avrami model is not a good model for describing the experimental data. From this, it can be concluded that nucleation does not occur simultaneously, even in the range of validity of the equation, as suggested by Avrami.

In addition, deviations were also found for concentrations outside this range. At higher concentrations, the deviations are attributed to the presence of a lower amount of solids, while for the lower concentrations, these deviations indicate a higher amount of solids present. These deviations suggest the formation of clusters.[18] In conclusion, it can be stated that the poor estimation by the Avrami model of the amount of solids at the start of the process of crystallization is one of its main drawbacks.

Next the D-model (Eq. (2)) is probed. The results are summarized in Table II.

TABLE II. Values of the parameters for the D-model

Conc. of palmitic acid mole fraction	Temperature °C	g	α	n	r^2 x100
0.55	45	0.017825	0.006893	3.5	99.75
0.55	45.5	0.08235	0.03595	3	99.35
0.70	49	0.086	0.08896	2	99.8
0.70	49.5	0.05068	0.002424	4	96.5
0.70	50	0.00794	0.002055	4.5	95.7
0.85	50.5	0.17347	0.07803	2	99.45
0.85	51.5	0.23438	0.076879	4.5	99.61
0.85	53	0.0289	0.003102	4.5	95.01
1.00	54	0.2919	0.1196	2	99.602
1.00	54.3	0.111272	0.04681	3	99.912

For this model, the regression coefficients obtained were very good (above 0.95) for all four concentrations used. Furthermore, for twenty-three cases out of twenty-six the fitting was excellent. For the other cases, the poor fitting can be attributed to lower supercooling, indicating that the application of the D-model is limited by the thermodynamic force used.

A comparison between the Avrami model and the D-model is presented in Fig. 2.

The figure shows the case for which both models fit the data well (pure palmitic acid). Note that, in the recommended range of application of the Avrami model, the D-model exhibits better results. The regression coefficient for the D-model was above 0.99 in this zone. In addition, an analysis of residuals showed no significant tendency. Thus, for pure palmitic acid the D-model can be considered as the K-model and, in this case, there are no significant differences with the Avrami model; both models are special cases of Kolmogorov's method and give the same result for pure substances.

A case for which the Avrami model exhibits poor fittingss (0.7 mole fraction of palmitic acid), while the D-model is once again successful is shown in Fig. 3. Here, the problems of the Avrami model in adjusting our experimental observations are evident. Note that the Avrami model underestimated $q(t)$ at the start of the crystallization. This can be explained in terms of the Kolmogorov method as being

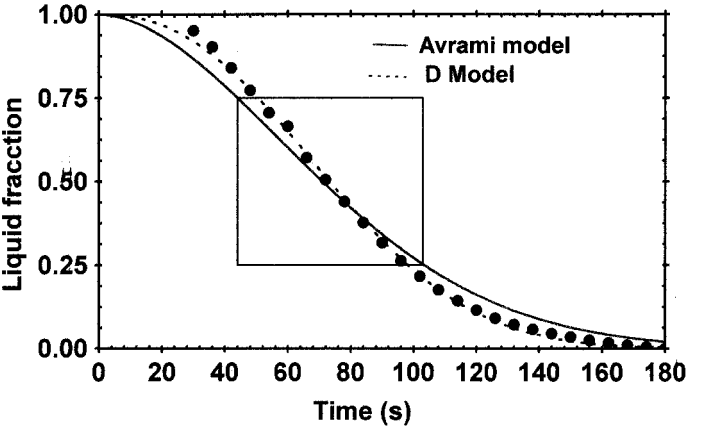

Fig. 2. Comparison between the Avrami model and the D-model. A case where both models give good fittings. (Pure palmitic acid, 54 °C).

due to the presence of "non-aggresors" (molecular cluster, nuclei that do not adsorb into the surface) with high molecular order which can penetrate into the non-crystallized region lowering the conditional probability of nucleation as calculated by Avrami's method, thus the underestimation of $q(t)$. The D-model does not take into account such a probability, but involves diffusion laws. From this, it can be concluded that the crystal growth involves a diffusion mechanism, *i.e.*, the medium limits the crystallization growth rate.[19] Furthermore, the Avrami model assumes that nucelation is simultaneous while the D-model assumes that nucleation is continuous. Thus, these results suggests that the crystal growth is diffusion limited, their form is spherical and that nucleation is continuous for mixtures of palmitic acid in oleic acid.

Figure 4 comprises a case for which both models exhibit poor fittings (0.85 mole fraction of palmitic acid). As mentioned before, the poor fitting of the D-model

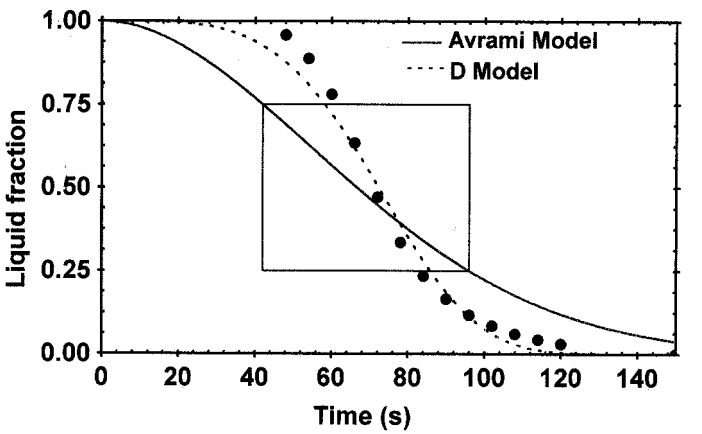

Fig. 3. Comparison between the Avrami model and the D-model. A case where the Avrami model gives poor fitting (0.7 mole fraction of palmitic acid, 49 °C).

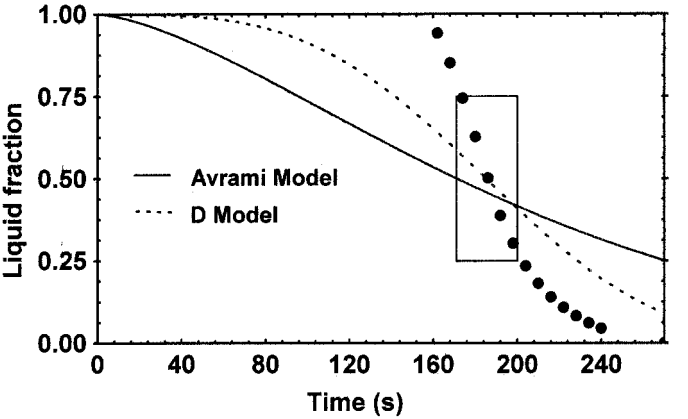

Fig. 4. Comparison between the Avrami model and the D-model. A case where both models gives poor fittings (0.85 mole fraction of palmitic acid, 51.5 °C).

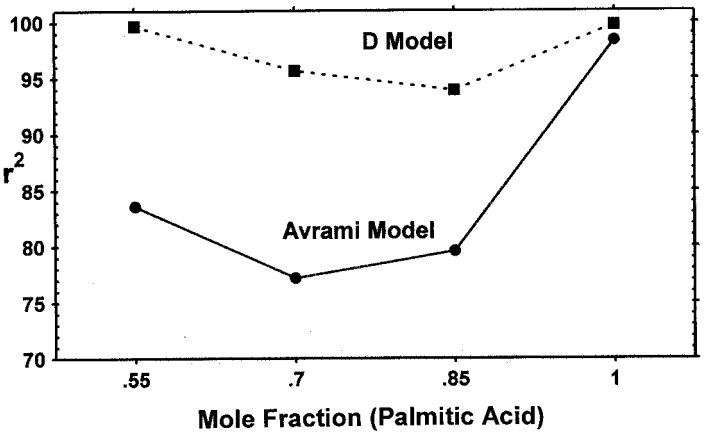

Fig. 5. Regression coefficients for the two models.

can be attributed to the lower supercooling used. The supercooling term was derived from the equation: $\phi = \Delta H_f(T_f - T)/T_f$, where ϕ is the chemical affinity, ΔH_f is the enthalpy change, T_f is the melting (or freezing) point and T is the temperature of the solution.[20] This is an approximation based on the chemical potential difference being the thermodynamic driving force. Thus the supercooling is given by ($T_f - T$).[21] T_f was obtained from DSC thermograms. When the driving force is low (*i.e.*, low supercooling) only a few nuclei are obtained and the growth is limited (low chemical potential). This observation suggests that the crystallization processes have a large energy barrier to overcome, and that there are fewer nuclei for the formation of crystals.[22] These considerations are not incorporated into either of the models employed, thus the poor fitting of the D-model. For the Avrami model, the reasons discussed for Fig. 3 hold once again in this case.

Additional comparison of the regression coefficients for the two models were

performed through a MANOVA (Multiple Analysis of Variance) analysis. These results (Fig. 5) indicate that the Avrami model is statistically different from the D-model.

From this figure, it is clear that our experimental data is better described by the D-model for all concentrations used; thus, it can be concluded that, for highly concentrated solutions of palmitic acid, the D-model should be used instead of the Avrami model, providing that there is a sufficient amount of supercooling. However, for crystallization from the melt (*i.e.*, pure palmitic acid), the Avrami model and the D-model are equivalent. These conclusions seem to indicate that the oleic acid forms group of molecules in liquid state with some order, similar behavior has been reported in lipids.[23] These "clusters" act as seeds for the nucleation of the palmitic acid.

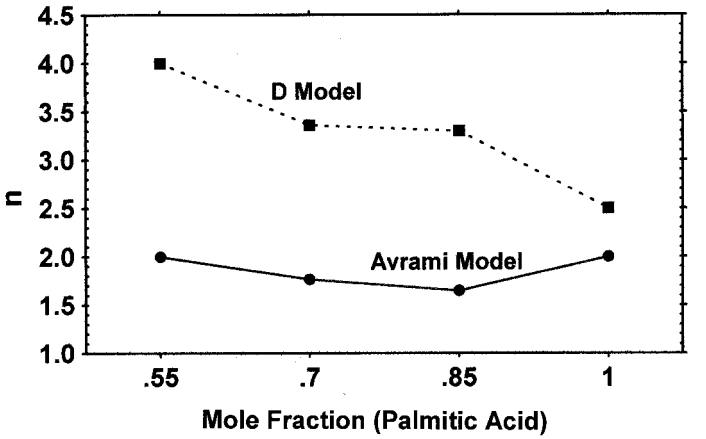

Fig. 6. Avrami index (n) for the two models.

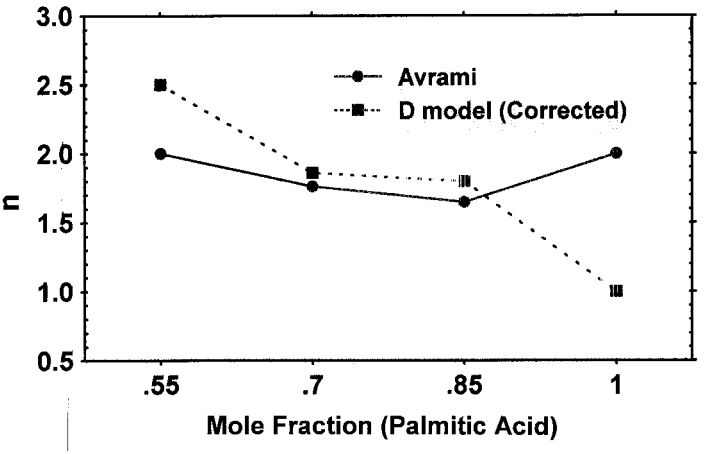

Fig. 7. Avrami index (n from the Avrami model) and n corrected for the D-model.

Not only the regression coefficients, but also the statistical significance of the parameters of the fitted models were tested by MANOVA analysis.

The parameter n, also known as the Avrami index, is closely related to the dimensionality of the crystallization process (D = 1 for stripe-like domains, D = 2 for circular domains, D = 3 for spherical domains).[24]

The values of n for both models are shown in Fig. 6. Note that these values are different in some cases (particularly for the sets for which the Avrami model exhibits poor fittings). This figure, together with Fig. 7, seems to support the interpretation that nucleation in the system does not occur simultaneously but is, instead, a continuous process, and that the nuclei have finite initial size because non-integer n values are obtained. If all nucleation starts from latent nuclei, and there is no further nucleation after the growth of the domains begins, the effective dimensionality of the problem is $n = D$; whereas, if nucleation continues to occur at a constant rate during the time over which the domains are growing, the effective dimensionality is $n = D+1$. Non-integer n values will be obtained when the activated nuclei have a finite initial size (*i.e.*, clusters), then $n = D+1.5(0.4,0.3,0.2)$. In Fig. 7, n was corrected by subtracting 1.5 from the value obtained from the regression procedure.

It is interesting to note that the differences in the values of n for the highest concentration is only 0.5, whereas larger differences were observed for the lower concentrations (above 1.5). In other words, the differences between the two models are not statistically significant for pure palmitic acid. However, for highly supersaturated solutions there are very important differences. With highly supersaturated solutions, or even almost pure palmitic acid with some contaminants, the solubility plays a very important role. Under these conditions, the medium imposes a barrier for crystal growth. Furthermore, at the start of crystallization some nuclei are generated, but as the process progresses, additional nuclei continue to be formed. Finally, it appears that clusters are also formed, the crystals present at least a non-random coordination and are likely to be sufficiently closely packed to be regarded as such.[25] These clusters forms sites for the generation of new nuclei, but this fact does not necessarily imply that the nucleation process is heterogeneous.

The parameter k in the Avrami model is a composite rate constant incorporating nucleation and growth rate characteristics.[13] If we examine only those values for which good fittings were obtained, it becomes clear that k depends on the degree of supercooling, the amount of palmitic acid, and the dimensionality of the system.

For the D-model, α is shown to be a function of the amount of palmitic acid, which suggests that crystallization takes place in solution, and not in the melt, because in the melt the rate of nucleation depends on the degree of supercooling.[21]

An additional interesting feature is the dependence of g on the dimensionality. This observation suggests that g is closely related to the rate of crystallization for highly supersaturated systems.

CONCLUSIONS

In highly supersaturated solutions of palmitic acid in oleic acid, the D-model is more effective in adjusting the experimental data than the Avrami model. The D-model is not effective when the magnitude of supercooling is low. During this process, the dimensionality is different to n, because the nucleation is continuous, not simultaneous. Furthermore, our results appear to indicate the presence of clusters that act like nuclei for crystallization. This latter fact prevents the Avrami model from achieving good fittings, but does not hinder the applicability of the D-model because the clusters growth is diffusion dependent.

The constant g of the D-model is a function of the degree of supercooling and the dimensionality of the process. Thus, g is closely related to the growth rate of the crystals.

The values of the parameter n, found using both models, are statistically different, suggesting that there is a different mechanism of nucleation.

И З В О Д

КИНЕТИКА ОЧВРШЋАВАЊА ВРЛО ПРЕСИЋЕНИХ РАСТВОРА ПАЛМИТИНСКЕ КИСЕЛИНЕ У ОЛЕИНСКОЈ КИСЕЛИНИ: ПОРЕЂЕЊЕ ДВА МОДЕЛА

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Кристализација масних киселина од велике је важности у индустријској примени и биолошким системима. Поређење теоријских модела и експерименталних података помаже у разјашњавању механистичких аспеката овог процеса. У овом раду упоређено је слагање два модела са експерименталним подацима за кристализацију пресићених раствора палмитинске киселине у олеинској киселини. Један модел је предложен од Аврамија, а други је заснован на разматрању дифузије као спорог ступња (D-модел). У свим случајевима D-модел боље прати експерименталне податке од Аврамијевог. Само у три случаја је D-модел показивао нижу вредност регресионог коефицијента (r^2, нижи од 0.9). За три тачке термодинамичка сила је била мања. Запажене су разлике у параметру n (индекс димензионалности). Ове разлике указују да се пре кристализације образују кластери. Затим, показује се да постоје разлике у механизмима кристализације чистих раствора палмитинске киселине и раствора са малим уделом олеинске киселине. Стога све наводи на закључак да је кристализација масних киселина при високим концентрацијама контролисана дифузијом.

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