Modelling of essential oils kinetics release from encapsulation matrix

JOSÉ DANIEL WICOCHEA-RODRÍGUEZ[1], Thierry Ruiz[2], Emmanuelle Gastaldi[1] and Pascale Chalier[1]

[1] *UMR IATE, Univ. Montpellier, INRAE, Agro Institute, Montpellier, France, danielwicochear@gmail.com*
[2] *UMR Qualisud, Univ. Montpellier, CIRAD, Montpellier, France*

Abstract

Essential oils (EO) contain active agents (AA) possessing repellent, antimicrobial and insecticidal properties. Encapsulation is a way to control their release and increasing the AA activity. The release kinetic from the matrix in a controlled environment can be interpolated by the solution of a zero-, half- or first-order differential equation. Even if in practical the release rate might be more complicated, their parameters provide pertinent information about the processes. Several models exist to fit the experimental data and also to describe the release mechanisms such as Avrami, Korsmeyer-Peppas or Higuchi. In the field of controlled release, the Avrami's equation was generally used to describe the dissolution of a drug in a liquid. Indeed, Avrami's equation considers several phenomena that may occur simultaneous such as the diffusion of the penetrant into the matrix, the potential swelling of matrix and the release of drug. The objective of this study was to use these three different models to evaluate the release in atmosphere of two different essential oils from an organic matrix. The two essential oils: spearmint and sweet orange, are characterised by varied properties, the former being less volatile, more polar and more viscous than the latter. Moreover, limonene was present in both oils but in higher concentration in one of them. As expected, Avrami's model leads to the best fit of the experimental kinetic data. The identification of the exponent of Avrami's model: n, varying between 0.40 and 0.75, indicates that the prevailing release mechanism is diffusional for both essential oils. The usefulness and relevance of the other models will be discussed taking into account the essential oil nature and the envisaged practical applications.

Keywords: release, EO, encapsulation, model

Introduction

Aroma compounds are efficient active agents for a broad range of applications (flavouring, antimicrobial, anti-oxidant, repellent, insecticide…). Their high volatility and reactivity provoke their losses or transformation during processing and storage. Their encapsulation in a protective matrix is a way to prevent these losses. Moreover, by the optimal choice of the matrix, the release of the aroma compound can be controlled depending on the initial concentration but also the environmental conditions like open or closed system, the nature of solutions, the temperature, the relative humidity …etc. In an idealised system, the release of the active agent from the matrix can follow a zero-, half- or first-order kinetic. In practical, the release rate of the active agent might be more complicated and dependent on the physicochemical and thermodynamical properties of the systems [1]. Moreover, the initial active agent concentration in the matrix is generally considered as uniform which is not always the case [2]. Several models exist to fit the experimental data and to propose an interpretation of the release mechanisms such as Higuchi (square root law) Korsmeyer-Peppas (power law) and Avrami (stretched exponential law) [2, 3]. These models allow to describe the apparent drug release in a liquid for different shape materials (film, tablet, and cylinder). The Avrami's equation was first used to the crystallisation phenomena, however, its usage in the field of the controlled release for various application such as encapsulated aroma compound has been developed with success [1]. Indeed, Avrami's equation considers several phenomena that may occur simultaneously such as the diffusion of the penetrant into the matrix, the potential swelling of matrix and the release of drug. The objective of this study was to use the above-mentioned three different models to evaluate the release of two different essential oils from an encapsulating organic matrix. The two essential oils: spearmint and sweet orange, are characterised by varied properties, the former being less volatile, more polar and more viscous than the latter. Moreover, limonene was present in both oils but in higher concentration in one of them.

Experimental

Materials

Spearmint (Mentha spicata) essential oil from India, and sweet orange (Citrus sinensis (L) Persoon CH essential oil from Mexico were purchased from Golgemma (Esperza, France). The major components of spearmint EO was *(R)*-Carvone (49%) and *(R)*-Limonene (25%) followed by menthol, β-myrcene, β-

DOI: 10.5281/zenodo.5913061

caryophyllene, β-bourbonene, β-phellandrene. The major components of sweet Orange EO were *(R)*-limonene (96.8%) and β-myrcene (2.8%).

Methods

The encapsulating system is a porous matrix shaping with a cylinder form and obtained from a specific process**.** The release experiments were carried out in controlled environmental conditions (70% RH and T =25°C°). At selected times, the EO from the matrix was extracted by liquid–liquid extraction using hexane as solvent and quantified by GG-FID using 2-heptanol as internal standard. The dimensionless release rate: $\frac{M_t}{M_0}$ of the whole components (above-mentioned) was estimated with M_o, the initial amount in the matrix and M_t, the amount released at time t. M_t was deducted from the residual amount in the matrix. The kinetic release was made in duplicate and the reported data are the average of the two experiments.

Models

For all models, "n" indicates the nature of the mechanism of release and "k" is linked to the apparent release rate constant.

The Higuchi model is based on a fixed value of n equals to 0.5:

$$\frac{M_t}{M_0} = kt^{0.5} \qquad \text{Equation 1}$$

The Korsmeyer-Peppas describes the kinetic by a power law where n needs to be adjusted:

$$\frac{M_t}{M_0} = kt^n \qquad \text{Equation 2}$$

For a cylinder when n = 0.45, the mechanism of release is considered as diffusive.

The Avrami model is based on a Weibull distribution:

$$\frac{M_t}{M_0} = 1 - (exp^{-kt^n}) \qquad \text{Equation 3}$$

By taking a double logarithm of both sides of Eq. (3) that yields to Eq. (4) allowing to determine n and k by a simple linear regression to adjust the best fit:

$$\ln\left[-\ln\left(1-\frac{M_t}{M_0}\right)\right] = \ln k + n \ln t \qquad \text{Equation 4}$$

Results and discussion

In table 1 the values of n and k are reported. The values of k are presented with the unit imposed by their respective equation: h^{-n}. We have also reduced them to: h^{-1} in order to be able to compare them. In each case, they were determined considering the entire set of data. As the nature and the texture of the matrix is identical for both EOs, the variations of n and k are only dependent on the EOs properties and on their affinity with the matrix. Whatever the model, the values of release rate constant expressed in h^{-1} were always higher for sweet orange EO than for spearmint EO. The former is more volatile, less viscous and more apolar than the latter. This means that EO can be less retained by the matrix in relation to weak affinity and/or more easily driven in liquid and gaseous phases in the porous matrix. Clearly, the physicochemical properties of EO influence the release but it was not possible to conclude about the discriminant parameter.

The simplest model is those of Higuchi, as n is fixed, only one parameter, k, can vary with EO. For this model k is described depending on the diffusion coefficient and the area of specific surface of the matrix. As the surface area of matrices is unchanged for both EO, the determinant parameter was the diffusion coefficient which would be higher for Sweet Orange oil compared to Spearmint EO. The R^2 was higher than 0.9 but was the lowest of the three models. The comparison between experimental data and fitting for Spearmint EO showed clearly that this model allows to predict only the first part of the kinetic data (Figure 1). After 70% of release, a strong deviation was observed. This bad fitting at the end of kinetic release is also observed for both Kersmayer-Peppas models reflecting the fact that a power law model cannot describe a saturating phenomenon. The values of n were close to 0.4 and imposing n=0.45 increased the R^2 indicating that the prevailing mechanism is Fickian diffusion for the two EOs.

Table 1: The parameters and R2 of the fitting by the three models (after linearization) to the release of Spearmint EO and sweet Orange EO from encapsulating matrix.

Model and parameters	Spearmint EO				Sweet Orange EO			
	k (h^{-n})	**n**	***k* (h^{-1})**	R^2	k (h^{-n})	**n**	*k* (h^{-1})	R^2
Higuchi	0.0785	**0.50**	***0.280***	*0.92*	0.197	**0.5**	*0.443*	0.93
Korsmeyer-Peppas	0.147 0.099	**0.36** **0.45†**	***0.499*** ***0.353***	*0.94* *0.95*	0.264 0.227	**0.39** **0.45†**	*0.594* *0.513*	0.94 0.96
Avrami	0.113	**0.56**	***0.293***	*0.97*	0.232	**0.73**	*0.344*	0.97

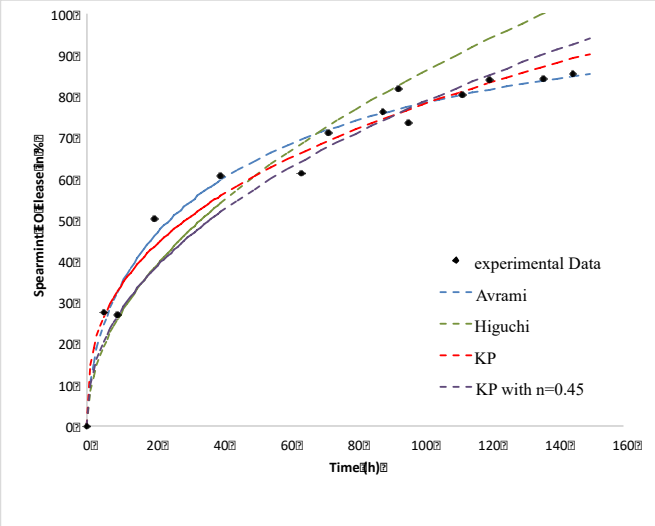

Figure 1*: Release kinetic of spearmint EO under controlled conditions (T=25°C and RH 70%): Experimental data and fitting by the different mode.*

Avrami's model leads to the best fit of the entire dataset for both EOs. The sigmoidal shape of the stretched exponential function being, a priori, able to describe a saturating phenomenon which is initiated by a latent phase. The model well characterised the entire set of data compared to the others as already described in literature [3]. The values of k reflected always the fast release of sweet orange compared to spearmint EO. However, due to the more accentuated difference between n values, the release rate constants were closer than for the other models.

A value of 0.73 was identified to characterise the release for sweet orange oil and corresponds to a diffusion mechanism for a cylinder as previously described [3, 4]. For a cylinder form system, the release is considered as a Fickian diffusion if *n* lies in the range of 0.69-0.75. When *n* was between 0.39 and 0.69, the diffusion mechanism is considered to take place in a fractal or disordered substrate different from percolation cluster [3, 4]. It is important to highlight that the models were always established for the release of monomolecular liquid.

For Spearmint EO, the value of n is lower than 0.69 and could be indicative of different behaviours of the EO molecules. Indeed, the global kinetic corresponded to the release of 7 molecules together ((*R*)-carvone, *(R)*-limonene, menthol, β-myrcene, β-caryophyllene, β-bourbonene and β-phellandrene). By comparison, the data used to follow the Sweet Orange oil release corresponded only to 2 molecules *(R)*-limonene and β-Myrcene with one major. The values of n and k considering only *(R)*-limonene were not significantly different from those

found for sweet orange EO. For the spearmint, the values of k and n calculated for *(R)*-carvone were slightly different from those found for the global (n=0.567 and k = 0.257 h^{-1}) but varied values were observed for the other compounds which influenced the final values.

It was also demonstrated a correlation between the n values found both Avrami and KP models: when n=0.45 which indicates pure diffusion for the KP model, n is in a range of 0.69-0.75 for Avrami [3]. This correlation is not clearly evidenced because we considered the entire set of data. If we only considered spearmint EO, the 60% first release for the KP model, the R^2 was increased but the n remained unchanged. For sweet orange oil, the R^2 increased and n was approaching 0.45. This report confirmed that the characterization of EO transfer with numerous molecules is more complicated than for EO with a major component.

Conclusion

All models allow to differentiate the behaviour of each EOs: the values of k indicating that the release being slower for Spearmint EO which is less volatile, more polar and more viscous than sweet Orange EO. Avrami model allows to fit the entire set of data while the other model gives a good correlation only for the first kinetic data. Diffusion is clearly the main mechanism for Sweet Orange EO which is characterised by a major component. For Spearmint EO, the presence of numerous components seems to induce a more complex mechanism. The release of aroma compounds is complex and several mechanisms of mass transfer but also the interactions between matrix and aroma compounds or between aroma compounds into the matrix can occur limiting the completely understanding of a mixture of aroma compounds such as essential oils behaviour.

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