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Research Article

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Study and modeling on saponification dynamics of the mixture of insect wax and oil-tea camellia seed oil

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ABSTRACT

The saponification reaction rate constant k and reaction order a of the mixture of insect wax and oil-tea camellia seed oil at 83、88、93 ℃ were derived out respectively by a series of experiments and MATLAB programming. And then according to the Arrhenius equation, the dynamics model was established as: $v=-\frac{dC}{dt}=6.8300\times10^{8}\exp\left(-\frac{9203.3}{T_S+273.15}\right)\cdot C^{a}$ *, which can reflect the saponification reaction process of the mixture of insect wax and oil-tea camellia seed oil and provide a theoretical foundation for saponification reaction of mixture of other waxes and olein and also can guide the existing laboratory study to select the most suitable operating conditions.*

Keywords: a mixture of insect wax and oil-tea camellia seed oil, saponification reaction, dynamics

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INTRODUCTION

As a unique product of resource insects in China, insect wax is an attractor among biological waxes. According to records of the Compendium of Materia Medica by Ya half stanza, insect wax could be able to beautify hair and promote the granulation, in addition, it is conducive to hemostasis and relieving pains. So, the insect wax has great value in medical health, cosmetics, industry and agriculture. While, the content of unsaturated fatty acid in oil-tea camellia seed oil is up to 90%[1] and it contains a good supply of vitamin E, which could protect skin from damage and aging and make the skin lustrous. Therefore, the potential of oil-tea camellia seed oil in cosmetics and health care is great. Based on the background above mentioned, different types of functional products could be developed by adding some auxiliary materials to the mixture of insect wax and oil-tea camellia seed oil. Then the first step is to prepare a mixed matrix of the mixture. While, the soluble matrix could be obtained via saponification reaction of the mixture of insect wax and oil-tea camellia seed oil due to a lot of monohydric alcohol esters and glycerol esters of higher aliphatic acid respectively existing in the insect wax and oil-tea camellia seed oil. And oil-tea camellia seed oil had priority over insect wax in saponification reaction, but the specific ratio of oil-tea camellia seed oil and insect wax which have reacted was not clear. And the chemical dynamics plays an important role in chemical reaction process development[2], so the study on saponification dynamics of the mixture of insect wax and oil-tea camellia seed oil is necessary. Currently, many studies on the saponification dynamics of oil have been reported[3-4], simultaneously, G. Chen[5] and H. Chen[6] respectively researched the saponification dynamics of sugarcane wax and bran-wax. So far, the studies on saponification dynamics of the mixture of insect wax and oil-tea camellia seed oil have not been reported. In this work, we studied saponification dynamics of the mixture of insect wax and oil-tea camellia seed oil at different reaction temperature and established the saponification dynamics model, which may provide a theoretical foundation for laboratory studies and realistic industrial production.

EXPERIMENTAL SECTION

Materials and instruments:
The main materials that used in this study were anhydrous alcohol (A.R.), petroleum ether (A.R.), phenolphthalein (A.R.), concentrated hydrochloric acid (A.R.), NaOH-85% alcohol (self made), oil-tea camellia seed oil (Golden Dragon Fish, food grade). And the refined insect waxes were purchased from Emei Insect Wax Institute. Some instruments such as digital constant temperature water bath (HH-8, Jintan Hongke Instrument Factory), electronic balance (LT1002, d=0.01g), analytical balance (METTLER TOLEDO AB204-S, d=0.0001g) were used.

Principles and methods:
Hypothesis and theory foundation of the modeling: In reference to relevant information[5-6], the saponification dynamic model of the mixture of insect wax and oil-tea camellia seed oil in this work was established based on the following hypothesis:

(1) The saponification of the mixture of insect wax and oil-tea camellia seed oil should be homogeneous reaction.
(2) Assuming there should be no temperature gradient among the reactants and the internal and external wall of reaction vessel. The saponification reaction would be completed at a constant temperature.
(3) The impact of the concentration of insect wax and oil-tea camellia seed oil on dynamic model parameters is not considered and could be included in the reaction rate constant k, because the amount of insect wax and oil-tea camellia seed oil far exceeds that of sodium hydroxide in this work.

The saponification reaction dynamic equation of the mixture of insect wax and oil-tea camellia seed oil was expressed as equation (1) based on the above hypothesis:

$$v = -\frac{dC}{dt} = kC^a \tag{1}$$

Where C is the real-time concentration of sodium hydroxide at the moment of t_s, k is the saponification reaction rate constant, and a is the reaction order.

Dynamic model parameters calculation:
In the study process on reaction dynamics, a simple pre-experiment should be organized before trying systematic experiment generally for a qualitative or semi-quantitative recognition on the reaction[7]. Assuming the reaction order a was equal to 1 and making integral on both sides of the Eq. (1), then:

$$t = \int_{C_0}^{C} -\frac{dC}{kC} = \frac{1}{k}\ln\frac{C_0}{C} \tag{2}$$

So: $$k = \frac{1}{t}\ln\left(\frac{C_0}{C}\right) \tag{3}$$

Where C_0 is the initial concentration of sodium hydroxide.
If the reaction rate constant k calculated according to Eq. (2) with the real-time concentrations of sodium hydroxide at different intervals was basically unchanged, then the saponification of the mixture of insect wax and oil-tea camellia seed oil would be the first order reaction. Conversely, the assumption did not hold, that is to say, a≠1, then Eq. (1) could be transformed into Eq. (4) by making integral on both sides of the equation.

$$t = \int_0^t dt = \int_{C_0}^{C} -\frac{dC}{kC^a} = \frac{1}{(a-1)k}\left(C^{1-a} - C_0^{\,1-a}\right) \tag{4}$$

So: $$C^{1-a} = (a-1)kt + C_0^{\,1-a} \tag{5}$$

There being three sets of data respectively corresponding to different experimental factors in this work, and then we assumed e_i (i=1,2,3) was the concentration error of alkali solution. Then, the optimization objective function could be showed as follows:

$$\min L\left(e_i,a,k\right)=\frac{1}{2}\sum_{i=1}^{3}e_i^{\,2} \qquad (6)$$

subject to:

$$C_i^{1-a}=\left(a-1\right)kt+C_{0,i}^{1-a}+e_i \qquad (7)$$

Let $$G_i\left(a,k\right)=C_i^{1-a}-\left(a-1\right)kt-C_{0,i}^{1-a}-e_i \qquad (8)$$

Then the objective function above mentioned could be converted to Eq. (9), according to the Wolfe duality theorem [8] and the Lagrange multiplier method[9].

$$\max L\left(e_i,a,k\right)=\frac{1}{2}\sum_{i=1}^{3}e_i^2-\sum_{i=1}^{3}\lambda_i*G_i\left(a,k\right) \qquad (9)$$

Where Lagrange multiplier $\lambda_i \geq 0$.
Then, from:

$$\begin{cases}\nabla_{ei}L\left(e_i,a,k\right)=e_i\\ \nabla_{ei}G_i\left(a,k\right)=-1\end{cases} \qquad (10)$$

We have:

$$e_i=-\lambda_i \qquad (11)$$

From:

$$\begin{cases}\nabla_a L\left(e_i,a,k\right)=0\\ \nabla_a G_i\left(a,k\right)=-C_i^{1-a}\ln C_i-kt+C_{0,i}^{1-a}\ln C_{0,i}\end{cases} \qquad (12)$$

Have:

$$\left(C_i^{1-a}\ln C_i+kt-C_{0,i}^{1-a}\ln C_{i,0}\right)\cdot\lambda_i=0 \qquad (13)$$

From:

$$\begin{cases}\nabla_k L\left(e_i,a,k\right)=0\\ \nabla_k G_i\left(a,k\right)=-\left(a-1\right)\cdot t\end{cases} \qquad (14)$$

Have:

$$\left(a-1\right)\cdot t\cdot\lambda_i=0 \qquad (15)$$

So, from Eq. (11), (13) and (15), the objective function could be given by:

$$\max L\left(\lambda_i,a\right)=\sum_{i=1}^{3}\left(-\frac{1}{2}\lambda_i^2-\lambda_i C_i^{1-a}+\lambda_i C_{0,i}^{1-a}\right) \qquad (16)$$

Subject to

$$\left(C_i^{1-a}\ln C_i+kt-C_{0,i}^{1-a}\ln C_{0,i}\right)\cdot\lambda_i=0 \qquad (17)$$

Where $C_{0,i}$ is the initial concentration of sodium hydroxide, C_i is the real-time concentration of sodium hydroxide at the moment of t_s.

Then the experiment data would be analyzed with Eq. (18) by the MATLAB programming in order to obtain the values of saponification reaction rate constant k and reaction order a at different reaction temperature.

$$\begin{cases} C_1^{1-a}\ln C_1 + kt_1 - C_{0,1}^{1-a}\ln C_{0,1} = 0 \\ C_2^{1-a}\ln C_2 + kt_2 - C_{0,2}^{1-a}\ln C_{0,2} = 0 \\ C_3^{1-a}\ln C_3 + kt_3 - C_{0,3}^{1-a}\ln C_{0,3} = 0 \end{cases} \tag{18}$$

Dynamic model establishing:
The selection of appropriate reaction temperature also affects the success or failure and costs of the reaction process. So the study on relationship between temperature and reaction rate is very important in practice and theory.

As is known, the Arrhenius equation is given: $k = k_0 \cdot e^{-\frac{E_a}{RT}}$

Then taking logarithm of both sides of the above equation, such that:

$$\ln k = -\frac{E_a}{R}\cdot\frac{1}{T} + \ln k_0 \tag{19}$$

Where E_a is the reaction activation energy, and k_0 is the pre-exponential factor.
According to Eq.(19), a straight line would be obtained by plotting lnk as a function of 1/T. And the values of E_a and k_0 would be calculated from the slope and intercept of the straight line, respectively.

Then, from the Arrhenius equation, Eq. (1) becomes

$$v = -\frac{dC}{dt} = kC^a = k_0 e^{(-E_a/RT_K)}\cdot C^a \tag{20}$$

Experimental method:
The oil-tea camellia seed oil (8.50g) was placed in a reaction vessel which was incubated in water bath at the setting temperature, then the insect wax (1.50g) was added into the oil-tea camellia seed oil. And then, 10.00 mL NaOH-85% alcohol solution was added into the vessel after the insect wax was dissolved. Accurate mass of reaction mixture which was taken out from the vessel in a certain interval during the reaction was dissolved in hot anhydrous alcohol/ petroleum ether (v/v, 1:3). Afterwards, we titrated the hot solution in the presence of phenolphthalein with 0.0250 M hydrochloric acid standard solution until the red colour just disappeared, and the volume of the consumed hydrochloric acid standard solution was recorded as V_1(mL). Then, the real-time concentration of sodium hydroxide was calculated according to Eq. (21).

$$C_{NaOH} = \frac{V_1 \times C_{HCl}}{V_{sample}} \tag{21}$$

Where V_{sample} is the volume of reaction mixture which was taken out from the vessel, C_{HCl} is the concentration of the hydrochloric acid standard solution.

RESULTS AND DISCUSSION

Dynamic model parameters calculation: As previously mentioned, we assumed the saponification of the mixture of insect wax and oil-tea camellia seed oil was the first order reaction on the concentration of sodium hydroxide. Then the reaction rate constant k calculated according to Eq. (3) with the real-time concentrations of sodium hydroxide at different intervals was given in table 1.

Table 1. The values of reaction rate constant k at different temperature

Reaction temperature (℃)	Saponification time (S)	Initial concentration of NaOH, C_0 (mol/L)	Real-time concentration of NaOH, C (mol/L)	k($\times10^{-3}$, S^{-1})
83	300	0.4081	0.03988	7.7521
83	420	0.5344	0.04529	5.8763
83	600	0.6664	0.02038	5.8122
88	180	0.4079	0.07501	9.4078
88	300	0.5340	0.41612	0.8314
88	420	0.6680	0.02228	8.0966
93	180	0.4084	0.06458	10.2463
93	120	0.6685	0.12388	14.0477
93	300	0.5335	0.01030	13.1577

As shown in table 1, the reaction rate constant k calculated with real-time concentrations of sodium hydroxide at different intervals fluctuated largely, which proved the saponification reaction of the mixture of insect wax and oil-tea camellia seed oil was not the first order reaction on the concentration of sodium hydroxide. Then, Eq. (18) was derived from Eq.(1).

Table 2. The initial and real-time concentrations of NaOH

Reaction temperature (℃)	Saponification time (S)	Initial concentration of NaOH, C_0 (mol/L)	Real-time concentration of NaOH, C (mol/L)
83	300	0.5344	0.07535
83	180	0.4081	0.05910
83	420	0.6664	0.07150
88	120	0.5340	0.12891
88	420	0.4079	0.01221
88	300	0.6680	0.07347
93	300	0.5335	0.01030
93	240	0.4084	0.04575
93	180	0.6685	0.10492

Table 2 provided the initial and real-time concentrations at the moment of t_s of sodium hydroxide at 83, 88, 93 ℃. Then analyzing all the data with Eq. (18), we had:

$$T=83\ ℃,\ \text{i}\ \begin{cases} 0.07535^{1-a}\ln 0.07535+300k-0.5344^{1-a}\ln 0.5344=0 \\ 0.05910^{1-a}\ln 0.05910+180k-0.4081^{1-a}\ln 0.4081=0 \\ 0.07150^{1-a}\ln 0.07150+420k-0.6664^{1-a}\ln 0.6664=0 \end{cases}$$

$$T=88\ ℃,\ \text{ii}\ \begin{cases} 0.12891^{1-a}\ln 0.12891+120k-0.5340^{1-a}\ln 0.5340=0 \\ 0.01221^{1-a}\ln 0.01221+420k-0.4079^{1-a}\ln 0.4079=0 \\ 0.07347^{1-a}\ln 0.07347+300k-0.6680^{1-a}\ln 0.6680=0 \end{cases}$$

$$T=93\ ℃,\ \text{iii}\ \begin{cases} 0.01030^{1-a}\ln 0.01030+300k-0.5335^{1-a}\ln 0.5335=0 \\ 0.04575^{1-a}\ln 0.04575+240k-0.4084^{1-a}\ln 0.4084=0 \\ 0.10492^{1-a}\ln 0.10492+180k-0.6685^{1-a}\ln 0.6685=0 \end{cases}$$

Then equations i , ii , iii were solved by the multivariable nonlinear optimization function under constrained conditions in MATLAB programming[10-11] to obtain the optimum values of reaction rate constant k and reaction order a of the saponification reaction of the mixture, as shown in table 3.

Table 3. The values of reaction rate constant k and reaction order aat different reaction temperature

Reaction temperature (℃)	reaction order a	reaction rate constant k ($\times10^{-3}$, $(mol/L)^{0.11}\ S^{-1}$)
83	0.8508778122	3.9588775691
88	0.9245024582	6.2516441504
93	0.9074416399	8.0107887929

As seen from table 3, the value of reaction order a was approximately 0.89 with some fluctuations at different reaction temperature. The different hydrolysis rates of ester groups in insect wax and oil-tea camellia seed oil under basic condition caused the polarity variance of the reaction system, which may lead to change in reaction order a[12]. Additionally, the different increase in viscosity of the reaction system may also lead to fluctuations in reaction order[13]. The saponification reaction rate constant k of the mixture of insect wax and oil-tea camellia seed oil was approximately $(3.96\sim8.01)\times10^{-3}\,(mol/L)^{0.11}\cdot S^{-1}$ under the temperature conditions in this work, and the values of reaction rate constant increased with increasing reaction temperature. That is to say, the higher the reaction temperature, the faster the saponification reaction rate.

Dynamic model establishing:
The values of lnk and $1/T_K$ were calculated by analyzing the data listed in table 3 for study on relationship between temperature and reaction rate, as shown in Table 4.

Table 4. The values of lnk and $1/T_K$

T_s (℃)	T_K (K)	$1/T_K$ (1/K)	lnk $(mol/L)^{0.11}\,S^{-1}$
83	356.15	0.0028078057	-5.5317947360
88	361.15	0.0027689326	-5.0749107858
93	366.15	0.0027311211	-4.8269660467

Then, as shown in Fig.1, a straight line was obtained by plotting lnk as a function of $1/T_K$ according to the data presented in table 4. And the values of E_a and k_0 were calculated from the slope and intercept of the straight line, respectively.

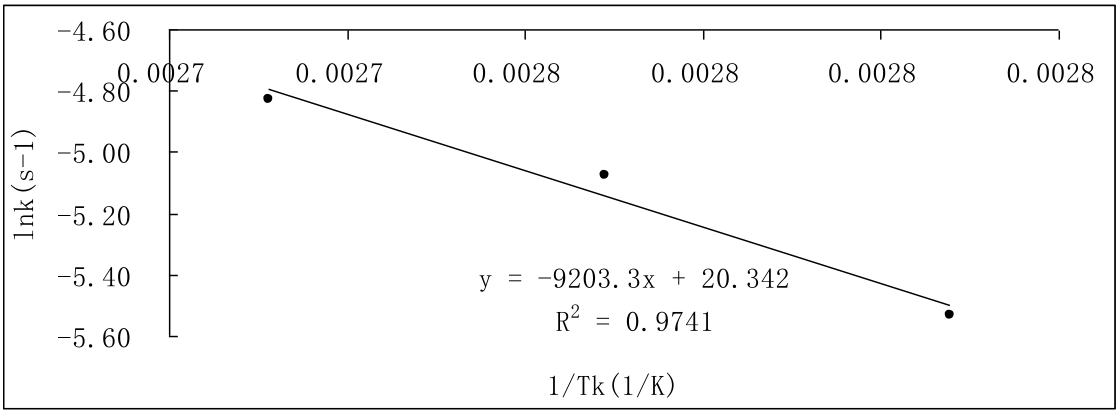

Fig.1. The relationship between lnk- $1/T_K$

The linear regression equation was showed as: $\ln k=-9203.3\times(1/T_K)+20.342$, and the correlation coefficient R=0.9870, which presented a good linear relationship between lnk and $1/T_K$. And from the linear regression equation, we could have:

$$\begin{cases} -E_a / R = -9203.3 \\ \ln k_0 = 20.342 \end{cases}$$

Then the values of E_a and k_0 were calculated to be 7.6516×10^4 J $\cdot mol^{-1}$ and $6.8300\times10^8\,(mol/L)^{0.11}\cdot S^{-1}$, respectively. So the saponification dynamics model of the mixture of insect wax and oil-tea camellia seed oil was established as:

$$v=-\frac{dC}{dt}=6.8300\times10^8\exp\left(-\frac{9203.3}{T_S+273.15}\right)\cdot C^a \qquad (22)$$

Eq. (22) reflected the relationship among reaction rate, time and temperature. In actual reactions, the saponification reaction rate at different reaction moment could be calculated at a certain reaction temperature, since the initial concentration of added alkaline solution was known. The study on saponification dynamics of the mixture of insect wax and oil-tea camellia seed oil could guide the selection of appropriate reaction conditions for lower production costs, higher saponification rate and better production quality, and also could provide a theoretical foundation for the realistic industrial optimal design and the control of the saponification reaction of the mixture. In addition, the established dynamic model which reflected relationship among reaction rate, time and temperature and the derivation process of the model could offer some fundamental theories and reference tactics to the saponification of mixture of other waxes and olein and the study on other reaction kinetics and thermodynamics.

CONCLUSION

The saponification reaction rate constant k of the mixture of insect wax and oil-tea camellia seed oil was calculated to be 3.9589、6.2516、8.0108×10^{-3} $(mol/L)^{0.11}$ • S^{-1} at 83、88、93℃, respectively. And the value of reaction order a was approximately 0.89.

The saponification dynamics model of the mixture of insect wax and oil-tea camellia seed oil which reflected relationship among reaction rate, time and temperature was established as:

$$v = -\frac{dC}{dt} = 6.8300 \times 10^{8} \exp\left(-\frac{9203.3}{T_S + 273.15} \right) \cdot C^{a}$$

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