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STUDY ON MIGRATION BEHAVIOR OF NANO-SELENIUM PARTICLES OF NANO-SELENIUM PACKAGING MATERIALS IN FOOD SIMULANTS

X. XIAO[a,b], X.ZHANG[a], S. YANG[a*], C. ZHAO[a*]
[a]*College of Chemical Engineering, Huaqiao University, Xiamen 361021, China.*
[b]*College of Ecological Environment and Urban Construction，Fujian University of Technology，Fuzhou 350118，China.*

This paper aims to investigate the migration behavior of nano-selenium particles of nano-selenium packaging materials in food simulants. Iodimetry was used to determine the migration volume of nano-selenium particles in food simulants. The effects of different temperature (20 ^{o}C, 30 ^{o}C, 40 ^{o}C, 50 ^{o}C) and different food simulants (distilled water, 4% acetic acid, N-hexane, 10% ethanol) on migration volume of nano-selenium particles were analyzed. The results showed that the migration volume of nano-selenium particles increased gradually with the increase of migration temperature and migration time until equilibrium. The migration volume of nano-selenium particles in food simulants was in the order of N-hexane > 4% acetic acid> 10% ethanol > distilled water. According to power law equation, the migration mechanism of nano-selenium particles accords with Fick's law of diffusion, and the diffusion coefficient of migration equation increases with the increasing migration temperature, while the distribution coefficient is opposite to the diffusion coefficient of migration equation. The results of this study can provide valuable references for the safety evaluation of nano-selenium particles in nano-selenium packaging materials.

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Keywords: Nano-selenium; Packaging material; Food simulants; Migration mathematical model; Migration

1. Introduction

With the continuous improvement of nanomaterials processing technology, nanomaterials are increasingly used in the field of food packaging due to their excellent characteristics. Nanomaterials have strong antioxidant activity and efficient antibacterial property, and also can improve barrier properties, mechanical strength, heat resistance, flame retardancy and oxidation stability of conventional packaging materials. Although it is generally accepted that nano-components in traditional packaging materials do not affect food safety, nanoparticles in traditional packaging materials have motivation and tendency to migrate to food [1]. Due to the small particle size and large surface area, nanoparticles have strong absorbability and diffusivity, high surface activity and catalytic activity. While brining certain properties to the packaging

*Corresponding author: yangsuping@hqu.edu.cn

material, these properties of nanoparticles may also pose a risk to food and biosecurity. Some scholars [2] used four kinds of food stimulants including oils, acids, alcohol and water to study migration of silver nanoparticles in nano-silver polyethylene food preservation kits. The results show that the migration volume of nano-silver increased with soaking time and soaking temperature, which was the largest in oil food simulants. Relevant data show that [3], the infiltration of nanoparticles through cell membrane may cause some inflammatory reactions and oxidative damage. Although there is limited scientific data on the migration of nanoparticles from packaging material to food, once nanomaterials are present in food packaging materials, more or less nanoparticles will migrate into the food and into the human body [4], which in turn may pose potential threats to human health. As a result, the migration of nano-ingredients in nano-packaging materials to food becomes a new source of security risk in the field of food safety. It is of extremely important significance for safety evaluation of nano-food packaging materials to actively carry out study on migration of nanoparticles in food packaging materials. At present, little has been reported on the law of the migration and variation of nano-selenium particles in nano-selenium packaging materials. With nano-selenium packaging materials as the study object, this study aims to investigate migration volume and migration law of nano-selenium nanoparticles in nano-selenium packaging materials under different temperatures (20 ^{o}C, 30 ^{o}C, 40 ^{o}C, 50 ^{o}C) and different food simulants (N-hexane, 4% acetic acid，10% ethanol, distilled water), so as to provide a reference for regulation and safety evaluation of nano-food packaging materials.

2. Experimental methods

2.1 Preparation of nano-selenium packaging materials

Nano-selenium was prepared by oxidoreduction of sodium selenite with anoxygenic photosynthetic bacteria (Rhodonacter sphaeroides YL75) separated and identified by Huaqiao University [5]. Nano-powder 30% (Nano-Selenium 35%, detitanium nanometer titania40%, attapulgite 25%), polyethylene plastic 56%, coupling agent 14% were subject to 1 h high-speed mixing before kneading, extrusion and 2 min cooling to obtain nano-masterbatch. Polyethylene plastic particles and nano-masterbatch (mass ratio of 77: 3) were mixed for 0.5 h and then film blown using a twin-screw extrusion molding machine to form nano- selenium packaging material with a thickness of 50 μm.

2.2 Selection of food simulants

China GB / T23296.1-2009 "Materials and articles in contact with foodstuffs-Plastics substances subject to limitation-Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants" and China GB / T31604.1- 2015 "National Food Safety Standard, General Principles of Food Contact Materials and Products Migration Test" specify the use of N-hexane as a lipid food simulant, 4% acetic acid as an acidic food simulant, 10% ethanol as alcoholic food simulant, and distilled water as an aqueous food simulant.

2.3 Migration test

With pure polyethylene film as the control group and nano-selenium packaging material as the test group, the control group and test group packaging materials were cut into 2.0 cm × 15.0 cm long strips, rolled in 100 ml volumetric flask as test unit. After adding food simulants, set the flask to a constant volume. Another set of samples were treated in the same way as a control. The volumetric flask was placed in an incubator at 20 ℃, 30 ℃, 40 ℃ and 50 ℃ (media and packaging materials were in double-sided contact). Nano-selenium content in food simulant solution was determined by sampling at 0d, 15d, 30d, 45d, 60d, 75d, 90d, 105 d, 120 d and 135 d.

2.4 Determination of migration volume

The 3.0 g sheared sample was weighed, placed in a porcelain crucible, carbonized to smokeless on an electric furnace, transferred to a muffle furnace and ashed at 500 ° C for 4 h. After cooling, the migration volume was measured by iodometry [6]: The dry ashed material obtained was transferred to a conical beaker, 15mL hydrochloric acid and 20 drops of nitric acid was added along the funnel wall, distilled water 100 mL, urea 5g was added before boiling for 5min on an electric hot plate. Afterwards, cool it to room temperature. Then, 5g • L^{-1} starch indicator 4mL and 2 drops of 10g • L^{-1} potassium iodide solution were added to the conical beaker. After shaking, titrate it with 0.2mol • L^{-1} sodium thiosulfate standard solution until blue color disappearance. Then, add 2 drops of potassium iodide solution, and then titrate until blue color disappearance. Perform repeated titrations until the solution is not blue after the addition of potassium iodide solution. The volume of sodium thiosulfate standard solution was recorded and blank test was performed at the same time.

Formula to calculate migration volume of nano-selenium particles in food simulants is:

$$m=(c\times V\times 78.93)/4 \quad (1)$$

In formula (1), c is the concentration of sodium thiosulfate standard titration solution, mol • L^{-1}; V is the volume of sodium thiosulfate standard solution consumed by titration, mL; 78.93 is the molar mass of selenium, g • mol^{-1}; m is the migration volume of nano-selenium particles, mg.

2.5 Migration mechanism

Migration diffusion type of nano-selenium particles of nano-selenium packaging materials in food simulants can be judged by the following formula:

$$\frac{M_{F,t}}{M_{F,e}} = kt^n \quad (2)$$

In formula (2): $M_{F,t}$ is the amount of nano-selenium particles migrating into food at time t, mg/cm^3; $M_{F,e}$ is the concentration of nano-selenium particles in food at equilibrium, mg/cm^3; k is macromolecule network characteristic constant; n is diffusion index. Diffusion type is Fick diffusion for 0 <n <0.5; diffusion rate is time dependent when n = 0.5; diffusion type is non-Fick diffusion for 0.5 <n <1.0; diffusion rate is proportional to time when n =1.0; diffusion type is super Fick law for n> 1.0[7-8].

2.6 Migration model establishment

The mathematical model for the migration of compounds in polymeric packaging materials is based on the migration behavior of Fick's diffusion law [9]. In this paper, based on the actual situation of migration, the second law of Fick is analyzed to study the migration behavior of nano-selenium particles in nano-selenium packaging materials. To simplify the analysis, only migration along thickness direction of the packaging material was considered and described with the econd-order partial differential equation below:

$$\frac{\partial C_{\chi,t}}{\partial t} = D\frac{\partial^2 C_{\chi,t}}{\partial \chi^2} \tag{3}$$

In formula (3): $C_{\chi,t}$ - concentration of migrant at time t at x location of the packaging material, mg/cm^3.

When only the migration along thickness direction of the packaging materials is considered, Fourier transform can be applied for the second-order partial differential equation describing the second law of Fick diffusion in Eq. (3). Meanwhile, considering the actual situation of packaging material migration, Piringer Model (formula (4)) can be derived [10]. There are many empirical or semi-empirical models for predicting material migration in packaging materials, of which, Piringer model is the most widely used. The migration and diffusion of nano-selenium particles in packaging materials may follow Piringer model.

$$\frac{M_{F,t}}{M_{F,e}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n{}^2} \exp(-D_p t \frac{q_n{}^2}{L^2}) \tag{4}$$

It can be known from the actual situation of migration that, $V_F >> V_P$, and formula (4) can be simplified into (5):

$$\frac{M_{F,t}}{M_{F,e}} = 1 - \frac{8}{\pi^2} exp\left(\frac{-\pi^2 D_P t}{L_P{}^2}\right) \tag{5}$$

2.7 Distribution coefficient and diffusion coefficient

The migration of chemicals is a diffusion process that follows thermodynamics and kinetics. The diffusion mathematical model of the process can be obtained using Fick's law and described in diffusion coefficient D_P and distribution coefficient $K_{P/F}$. The distribution coefficient $K_{P/F}$ is defined as the ratio of the concentration $C_{P,e}$ of the migrant in the polymer at equilibrium to the concentration $C_{F,e}$ in the food or food simulant, which can be expressed as follows:

$$K_{P/F} = \frac{C_{P,e}}{C_{F,e}} = \frac{M_{p,0} - M_{F,e}}{C_{F,e} V_p} \tag{6}$$

In formula (6), $C_{P,e}$ and $C_{F,e}$ are the equilibrium concentrations of nano-selenium particles in the material and food respectively, mg/cm^3; $M_{P,0}$ is the initial amount of nano-selenium particles in the material, mg; $M_{F,e}$ is the amount of nano-selenium particles in food at equilibrium, mg; V_P is the volume of the material, cm^3.

In this paper, the diffusion coefficient D_P is calculated according to curve of content variation of nano-selenium particles in food simulants. Based on the initial conditions and the boundary conditions of the experiment, $M_{F,e}<M_{P,0}$ during the experiment indicates distribution behavior in the migration. The diffusion coefficient can be accurately calculated by fitting of formula (7).

$$\left[\frac{1}{\pi}-\frac{1}{\alpha}\frac{M_{F,t}}{M_{p,0}}\right]^{0.5}=\frac{D_P{}^{0.5}}{\alpha}\frac{t^{0.5}}{L_P}+\frac{1}{\pi^{0.5}} \tag{7}$$

In formula (7): $M_{F,t}$ is the amount of nano-selenium particles migrating into food at time t, mg; $M_{F,e}$ is the concentration of nano-selenium particles in food at equilibrium, mg; L_p is the thickness of the packaging material, cm .

3. Results and discussion

3.1 Migration behavior of nano-selenium particles in food simulants

It can be seen from Figure 1 that in the food simulants, the migration volume of nano-selenium particles corresponding to different temperatures is non-linear with the migration time. At first, the migration volume of nano-selenium particles shows a rapid increase. After a certain time point, the increase of migration volume slows down and tends to an equilibrium value gradually. At the same time point, the higher the migration soaking temperature is, the higher the migration volume of nano-selenium particles is. The two show a positive correlation in variation.

In the same food simulant, the higher the migration temperature is, the greater the migration volume is. Some scholars [11] studied migration behavior of anti-bacterial agent thymol crystals of thymol crystal/ polylactic acid packaging materials in food simulants, and also found that the higher the temperature of food simulants is, the more migration volume of thymol crystals in packaging materials is, and the less time it takes to reach the equilibrium of migration. This may be because the increase of temperature enhances activity of solution molecules in food stimulant, so that nano-selenium particles gain extra free energy to overcome the interaction between nano-selenium particles and migrate out of the polymer, resulting in significant increase of nano-selenium particles in simulation liquid and shorter time to reach equilibrium of migration. It can be seen that temperature plays a decisive role in the process of migration kinetics, and the higher the temperature is, the easier it is to reach equilibrium.

From Figure 1, it can be seen that different types of food simulants cause different effects on the migration volume of nano-selenium particles in nano-selenium packaging materials. Under the same conditions, among the four food simulants, nano-selenium particles have the largest migration volume in N-hexane. In general, migration volume of nano-selenium particles in these four food simulants is in the order of: N-hexane> 4% acetic acid> 10% ethanol> distilled water. According to the principle of similarity and compatibility, N-hexane simulates oily food and has certain swelling effect on the packaging materials. The swollen packaging material can release nano-selenium particles more easily. Although 4% acetic acid exerts weaker swelling effect than N-hexane, the acidic environment is favorable for the dissolution of selenium, while

10% ethanol also has a swelling effect on the packaging material [12-13]. Thus, the food simulants affect the migration process through the interaction between the material matrix and the migrants, and different food simulators represent different food matrixes. The changes of food matrixes have a great influence on the compound migration.

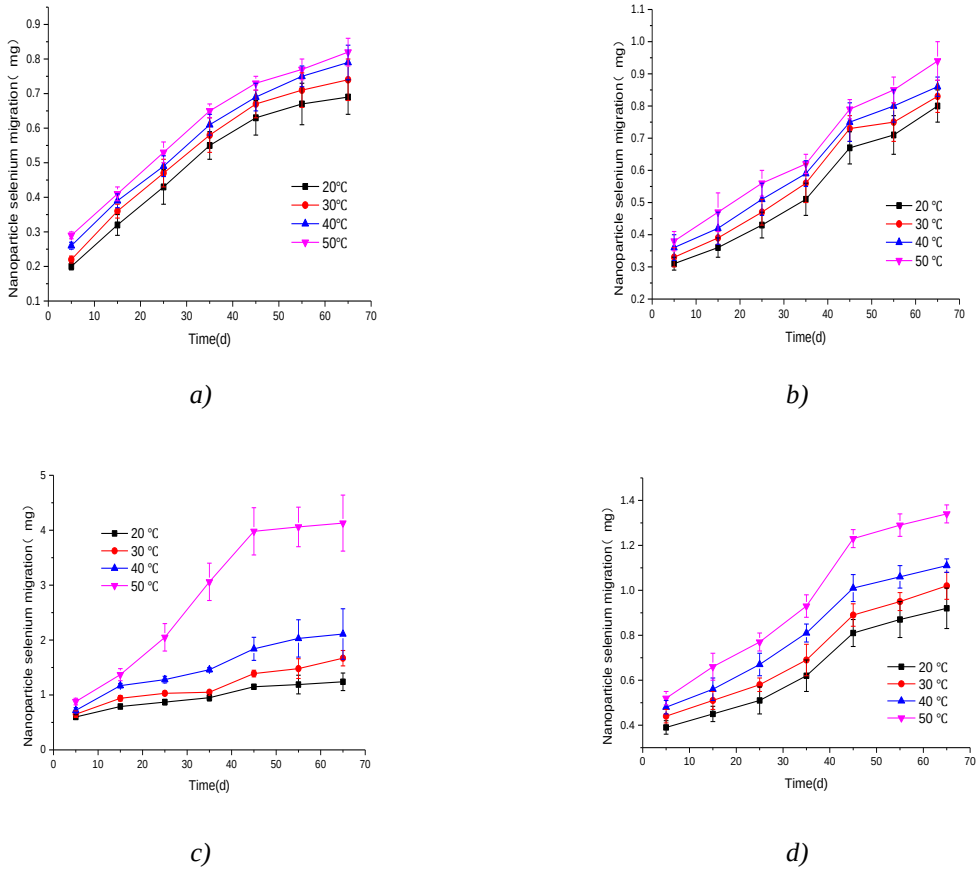

Fig. 1 Effect of temperature on the migration of nano-selenium particles in distilled water (a), 4% acetic acid (b), N-hexane (c) and 10% ethanol(d).

3.2 Migration type

The migration and diffusion mechanism of nano-selenium particles can be obtained by fitting the experimental data through formula (1). The relationship between $\ln(M_{F,t}/M_{F,e})$ and $\ln(t)$ is plotted as shown in Figure 2. According to the power law equation, the slope n and the intercept k of the linear formula can be obtained by fitting the data. The specific results are shown in Table 1. It can be seen from Table 1 that the correlation coefficient R^2 of each equation is high, indicating high fitting degree of the migration data. The migration index (b) of each linear equation of nano-selenium particles in four kinds of food simulants of distilled water, 4% acetic acid, N-hexane and 10% ethanol is between 0-0.5, indicating that the type of migration mechanism of nano-selenium particles in the four food simulants belongs to Fick diffusion within the experimentally set conditions.

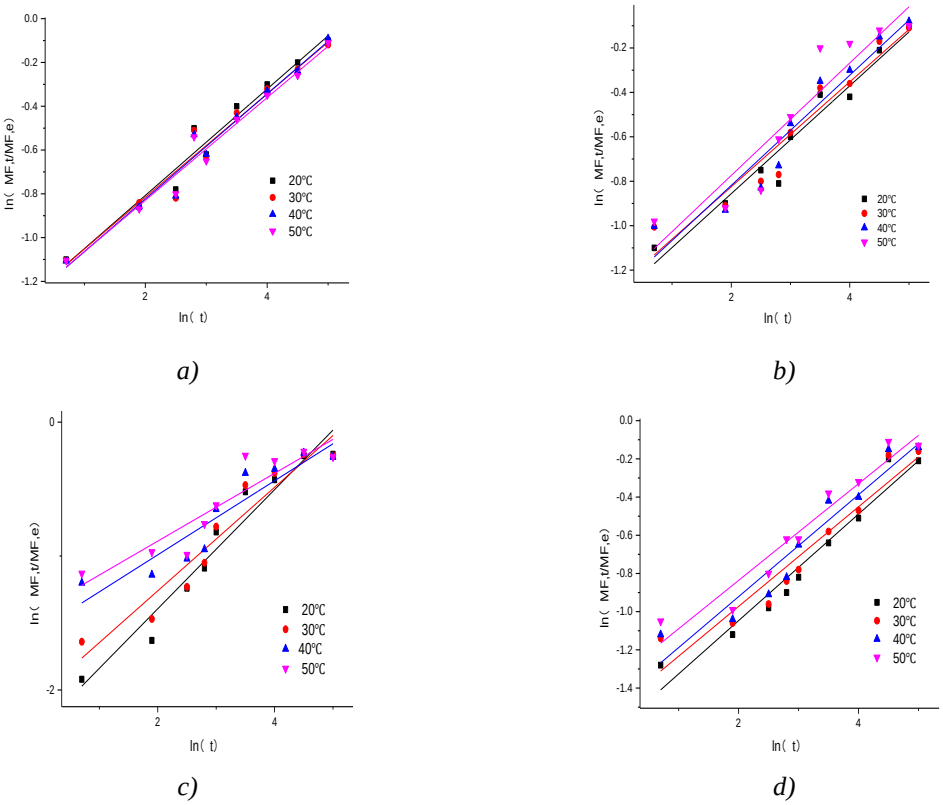

Fig. 2. Diffusion mechanism of nano-selenium particles in distilled water (a), 4% acetic acid (b), N-hexane (c) and 10% ethanol (d)

Table 1 Parameters of power law equation of nano-selenium particle migration

Food simulants	Temperature ℃	Slope (n)	Intercept (k)	Correlation coefficient (R^2)
Distilled water	20	0.2431	1.2936	0.9621
	30	0.2361	-1.2879	0.9539
	40	0.2403	-1.3045	0.9665
	50	0.2346	-1.2989	0.9670
4% acetic acid	20	0.2428	-1.3414	0.9487
	30	0.2361	-1.2970	0.9209
	40	0.2480	-1.3148	0.9151
	50	0.2531	-1.2802	0.8653
N-hexane	20	0.4448	-2.2833	0.9438
	30	0.3866	-2.0330	0.9150
	40	0.2766	-1.5440	0.8510
	50	0.2533	-1.3953	0.8271
10% ethanol	20	0.2790	-1.6049	0.9453
	30	0.2608	-1.4940	0.9140
	40	0.2668	-1.4550	0.9167
	50	0.2532	-1.3426	0.9326

3.3 Distribution coefficient and diffusion coefficient

3.3.1 Effect of temperature on distribution coefficient, diffusion coefficient

Distribution coefficient is an important parameter of the migration model. It mainly appears in the form of definition. By using the least square method to simulate the migration of nano-selenium particles, the migration equilibrium values of nano-selenium particles in the four food simulants can be obtained under different temperature (20 ℃, 30 ℃, 40 ℃, 50 ℃), and then the distribution coefficient of migration $K_{P/F}$ can be calculated.

Diffusion coefficient D_P was calculated according to Eq. (6). Origin 9.1 software was used to fit the migration test data of nano-selenium particles. By using the fitting data, diffusion coefficient D_P of nano-particles in distilled water, 4% acetic acid solution, N-hexane and 10% ethanol solution at different temperatures (20 ℃, 30 ℃, 40 ℃ and 50 ℃) was obtained. The relationship between distribution coefficient, diffusion coefficient of nano-selenium particles and temperature was investigated at different temperatures.

It can be seen from Fig. 3 that ambient temperature affects the distribution of nano-selenium particles in distilled water, 4% acetic acid, N-hexane and 10% ethanol. In N-hexane, the distribution coefficient of nano-selenium particles is the smallest under the same temperature and decreases fastest with increasing temperature, while the diffusion coefficient is the largest and rises rapidly with increasing temperature. Among the above four kinds of food simulants, with the increase of migration temperature, distribution coefficient of nano-selenium particles decreases and diffusion coefficient increases in varying degrees, indicating that the higher the temperature is, the bigger the amount of nano-selenium particles entering food simulants is. The reason for this phenomenon is that temperature can affect solubility of nano-selenium particles in food simulants. The higher the temperature is, the higher the solubility and the lower the distribution coefficient is. Diffusion coefficient describes the ability of migrants to search "free volume" for migration. As the temperature becomes higher, molecular thermal motion accelerates, so that free volume and diffusion rate are larger [14-15]. It suggests that the migration of compounds in the nano-selenium packaging material follows the rule that the smaller the distribution coefficient is, the bigger the diffusion coefficient is. At the same time, it further proves that the higher the temperature is, the larger the compound migration volume is. It also shows that temperature is the main factor affecting migration in the same type of food simulant. The conclusion of this study is consistent with what’s reported in literature [16].

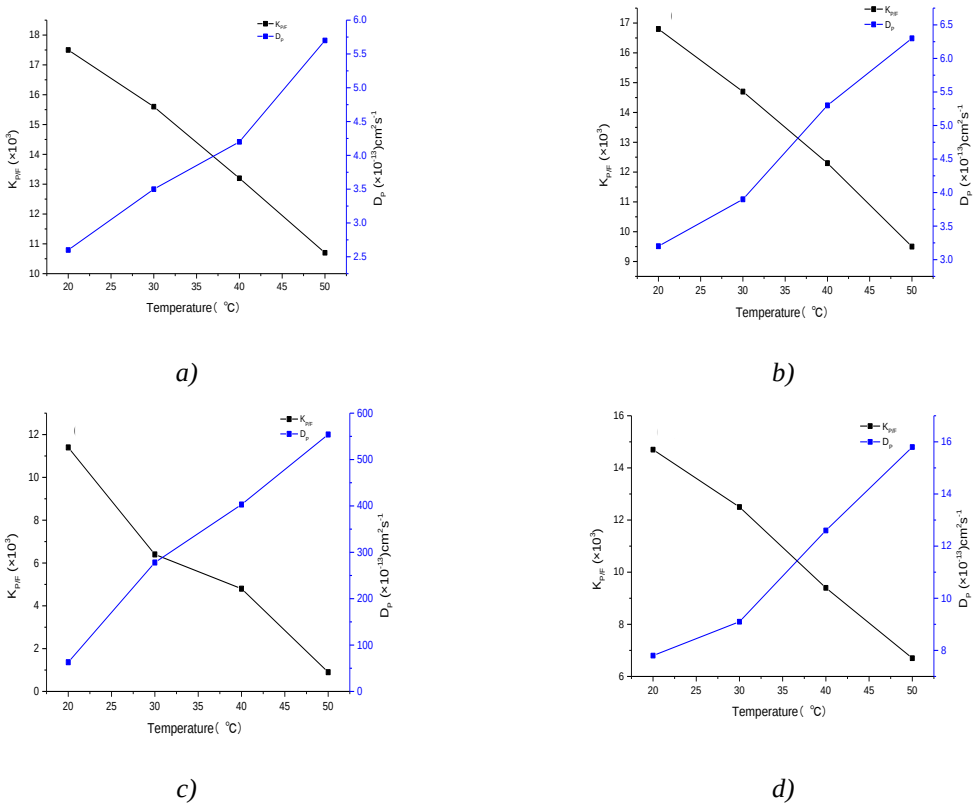

Figure 3 Effect of temperature on distribution coefficient and diffusion coefficient in distilled water (a), 4% acetic acid (b), N-hexane (c) and 10% ethanol (d)

3.3.2 Effect of food simulants on distribution coefficient, diffusion coefficient

Figure 4 shows the effect of distilled water, 4% acetic acid, N-hexane and 10% ethanol on distribution coefficients and diffusion coefficients of nano-selenium particles at 20 ℃ and 30 ℃. As can be seen from Figure 4, distribution coefficient of nano-selenium particles in N-hexane is smaller than that of the other food simulants, while the diffusion rate in N-hexane is obviously higher than that of the other food simulants, indicating that nano-selenium particles are most likely to migrate in N-hexane. This is because extraction effect of N-hexane on nano-selenium particles in nano-selenium packaging materials is stronger than that of the other three food simulants, which increases migration volume. Thus, relatively small distribution coefficient and high diffusion coefficient are shown in N-hexane.

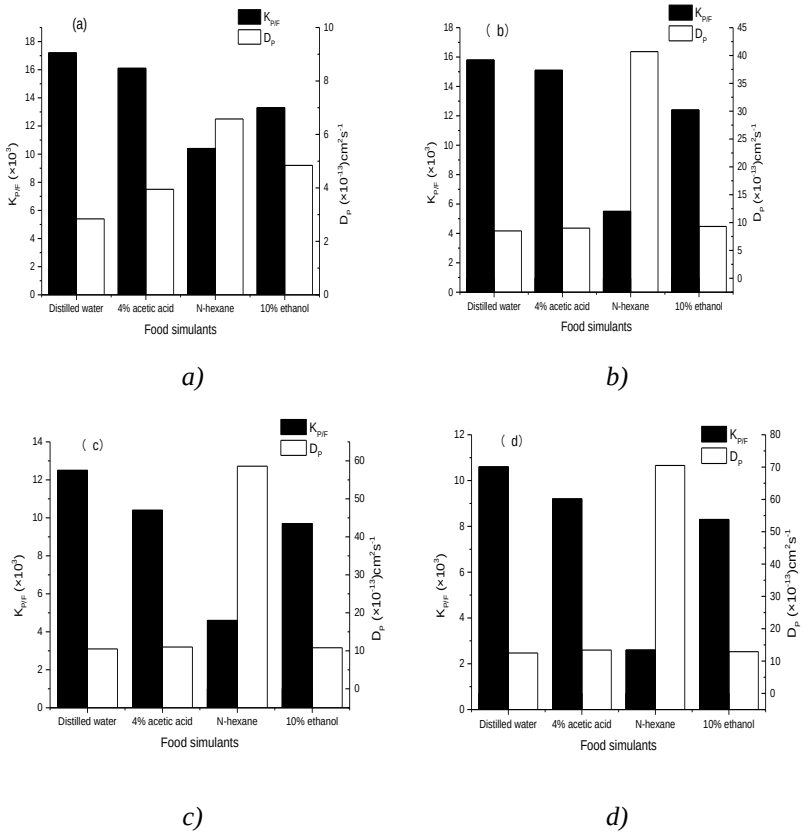

Fig. 4. Effect of food simulants on distribution coefficient and diffusion coefficient at 20 ℃ (a), 30 ℃ (b), 40 ℃ (c), 50 ℃ (d)

4. Conclusions

In this study, iodimetry was used to measure the migration variation of nano-selenium particles in nano packaging materials when in contact with food simulants. In the four food simulants of distilled water, 4% acetic acid, N-hexane and 10% ethanol, migration volume of nano-selenium particles tends to increase rapidly and then stabilize with the extension of migration time; in the same food simulant, the higher the migration soaking temperature is, the more migration volume of nano-selenium particles is for the same period of time. At the same migration temperature, the migration volume of nano-selenium particles in the four food simulants at the same time point is in the order of: N-hexane> 4% acetic acid> 10% ethanol> distilled water.

Thus, under the same conditions, the higher the moisture content of food simulants is, the less the migration volume of nano-selenium particles is. Within the experimentally set conditions, the migration mechanisms of nano-selenium particles in these four food simulants belong to Fick diffusion; the higher the temperature is, the smaller the distribution coefficient and the larger the diffusion coefficient of nano-selenium particles is. Among the four food simulants, nano-selenium particles have the largest diffusion coefficient and the smallest distribution coefficient in N-hexane. This study may provide a reference for the migration of compounds in similar packaging materials.

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