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ScienceDirect
Food Chemistry 101 (2007) 1714–1718
Food Chemistry
www.elsevier.com/locate/foodchem

Partition coefficient of migrants in food simulants/polymers systems

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Received 14 February 2005; accepted 29 March 2006

Abstract

Partition coefficients of six migrants (ethyl acetate, acetaldehyde, acetonitrile, methyl ethyl ketone, isopropyl acetate and butyraldehyde) were determined between four food simulants (water, 10% ethanol, 3% acetic acid and 95% ethanol) and two polymers (polyamide and polyethylene terephthalate). The results showed that partition coefficient is highly dependent on the nature of the migrant, polymer and food simulant. Of the six migrants, acetonitrile and ethyl acetate had the highest affinity for polar food simulants such as water, 10% ethanol and 3% acetic acid. Partition values for systems containing 95% ethanol as a food simulant were higher for non-polar migrants and lower for polar migrants.

Keywords: Migration; Food simulant; Physico-chemical property; Phase ratio variation

1. Introduction

The increasing use of plastics in food packaging has led to the need for more information about the interactions between plastic packaging materials and foods (Halek, 1988). Studies have been published about migration from packaging materials, as well as chemical reactions between food components and packaging materials (Charara, Williams, Schmidtt, & Marshall, 1992; Konczal, Harte, Hoojjat, & Giacin, 1992; Letinski & Halek, 1992). Printing solvents can migrate from plastic packaging to food. Solvents consist of low molecular weight compounds, such as hydrocarbons, alcohols, ketones and esters (Kumai et al., 1983), which can migrate to the food. Several studies have presented partition coefficient of printing solvents between food and air (Halek & Hatzidimitriu, 1988; Heydanek, Woolford, & Baugh, 1979) and found factors that affected the partitioning behaviour (An & Halek, 1995; Halek & Levinson, 1988, 1989; Halek & Chan, 1994). Additional data are needed on food ingredients, and polymers, as well as solvent chemical structures and their properties in relation to partitioning behaviour.

In general, partition coefficient is defined as the ratio of the migrant equilibrium concentration in the food simulant C_s or in the polymer C_p, to its equilibrium concentration in the gas phase C_g:

$$K_{sg} = \frac{C_s}{C_g} \quad K_{pg} = \frac{C_p}{C_g}$$

Using these coefficients (K_{sg} and K_{pg}), we can determine the partition coefficient for a food simulant/polymer system.

$$K_{sp} = \frac{C_s}{C_p}$$

The phase ratio variation method (PRV) (Ettre, Welter, & Kolb, 1993) can be used to establish the partition coefficient of a compound in a gas–liquid system, using headspace extraction with gas chromatography. This method is based on the relationship between the partition coefficient and the phase ratio.

The objective of this study was to determine partition coefficients in food simulant/polymer systems, using the PRV method.

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doi:10.1016/j.foodchem.2006.03.058

2. Material and method

2.1. Instrumentation

The measurements were made using a Perichrom Sarl PR 2100 automatic headspace sampler and a gas chromatograph with flame ionization detection.

A fused silica capillary column (Varian, Canada) was employed (30 m × 0.25 mm, coated with: CP Wax 52CB; film thickness: 0.25 μm). The gas chromatograph oven was maintained at 100 °C. The carrier gas was nitrogen at a flow rate of 229 ml/min.

Detector and injector temperature were 260 °C and 250 °C, respectively. Carrier injector 100/100, split 40/40.

2.2. Sample preparation

Model solutions (distilled water, 3% acetic acid, 10% ethanol, 95% ethanol) were prepared as food simulants with 10 μl pure migrant (acetaldehyde, acetonitrile, butyraldehyde, ethyl acetate, methyl ethyl ketone, isopropyl acetate) in 100 ml of each model solution. Some properties of these solvents are shown in table. Increasing volumes (1, 2, 3, 4 and 5 ml) of these solutions were placed into headspace (11 ml) and sealed with magnetic septa (Perichrom). Thus, each vial represented a gas/liquid phase ratio (β) of 10, 4.5, 2.67, 1.75 and 1.2, respectively, calculated according to Eq. (3). Equilibrium times for each solvent at 20 °C were determined by plotting percentage differences between controls and sample headspace values until they did not change. After storing each vial for 1 day, a 1 ml sample of headspace (for all volume ratios) was injected into the GC by gas-tight syringe. The withdrawal of gas phase samples constituted up to 15% of the total volume.

Solvents	Purity (%)	Company
Acetonitrile	>99	Carlo Erba (France)
Acetaldehyde	99% Min	Merck (Germany)
Ethanol	95%	Prolabo (France)
Acetic acid	99.5%	Merck (Germany)
Butyraldehyde	99%	Prolabo (France)
Methyl ethyl ketone	>99%	Fisher Scientific (UK)
Ethyl acetate	99.7	Merck (Germany)
Isopropyl acetate	⩾99	Merck (Germany)

2.3. Plastic films

Two polymeric films were used in this study: PET (polyethylene terephthalate; Danisco Flexible, Barbezieux (France)), and PA (polyamide; Danisco Flexible, Barbezieux (France)). The respective thicknesses of the films were 12 μm and 15 μm.

A film piece (= 5 cm × 5 cm) was placed in an 11 ml vial with different volumes (1, 2, 3, 4 and 5 ml) of each solution (100 ml liquid + 10 μl solvent). The film piece was fully covered with liquid.

2.4. Method

2.4.1. Phase ratio variation (PRV method)

The original sample solution is defined by V_S, m_S and C_{in}.

V_S = volume of the original sample solution introduced into the sample vial, m_S = the miss of the volatile compound in the original sample and C_{in} = the initial concentration of the volatile compound in the original sample, expressed as mass per volume:

$$C_{in} = \frac{m_S}{V_S}. \tag{1}$$

The phase ratio (β) of the vial is the ratio of the volumes of the headspace (V_G) the sample solution (V_s):

$$\beta = \frac{V_G}{V_S}. \tag{2}$$

The volume of the gas phase (headspace) is taken as the difference between the volumes of the sample vial (V_V) and the sample solution (V_S):

$$V_G = V_V - V_S. \tag{3}$$

The partition coefficient is defined as the ratio of migrant (volatile compound or solvent) equilibrium concentration in the solution material, C_S^*, to its equilibrium concentration, in the gas phase, C_G^*. K is defined as:

$$K = \frac{C_S^*}{C_G^*}. \tag{4}$$

Defining the two concentration as:

$$C_S^* = \frac{m_S^*}{V_S^*}, \tag{5}$$

$$C_G^* = \frac{m_G^*}{V_G}. \tag{6}$$

The partition coefficient can be expressed as:

$$K = \frac{C_S^*}{C_G^*} = \frac{m_S^*}{m_G^*} \cdot \frac{V_G}{V_S} = \frac{m_S^*}{m_G^*} \cdot \beta, \tag{7}$$

m_S is defined as:

$$m_S = m_S^* + m_G^*, \tag{8}$$

$$\frac{m_S}{V_S} = \frac{m_S^*}{V_S} + \frac{m_G^*}{V_S}, \tag{9}$$

but $V_S = \frac{V_G}{\beta}$. Therefore,

$$\frac{m_S}{V_S} = \frac{m_S^*}{V_S} + \frac{m_G^*}{V_G} \cdot \beta, \tag{10}$$

$$C_{in} = C_S^* + C_G^* \cdot \beta, \tag{11}$$

$$C_S^* = K \cdot C_G^*. \tag{12}$$

Therefore,

$$C_{in} = K \cdot C_G^* + C_G^* \cdot \beta = C_G^*[K + \beta], \tag{13}$$

and thus,

$$C_G^* = \frac{C_{in}}{K+\beta}. \quad (14)$$

Taking reciprocals of both sides of Eq. (14) we obtain:

$$\frac{1}{C_G^*} = \frac{K}{C_{in}} + \frac{1}{C_{in}} \cdot \beta. \quad (15)$$

However, in headspace analysis, the chromatographic peak area (A) is proportional to the equilibrium concentration in the headspace of the vials:

$$A = f_i \cdot C_G^*, \quad (16)$$

$$C_G^* = \frac{A}{f_i}. \quad (17)$$

Therefore, in order to establish the value of C_G^*, one would need the value of f_i, which is a proportion factor, depending on the particular system and the analytical conditions.

However, there is an easy way to overcome this problem. Substituting A/f_i for C_G^* in Eq. (15):

$$\frac{f_i}{A} = \frac{K}{C_{in}} + \frac{1}{C_{in}} \cdot \beta, \quad (18)$$

$$\frac{1}{A} = \frac{K}{f_i} \cdot \frac{1}{C_{in}} + \frac{1}{f_i} \cdot \frac{1}{C_{in}} \cdot \beta, \quad (19)$$

$$\frac{1}{A} = a + b \cdot \beta, \quad (20)$$

where

$$a = \frac{K}{f_i \cdot C_{in}}, \quad (21)$$

$$b = \frac{1}{f_i \cdot C_{in}} \quad (22)$$

and

$$K = \frac{a}{b}. \quad (23)$$

In another words, we can plot $1/A$ against β and carry out regression analysis of this plot, establishing its slope (b) and intercept (a).

To calculate of partition coefficient in a food simulant/packaging system, we used equations from a food simulant/air system. The initial concentration of migrant in solution was 0.1 μl/ml.

$$\frac{f_i}{A} = \frac{K}{C_{in}} + \frac{1}{C_{in}} \cdot \beta, \quad (18)$$

$$f_i = \frac{A(K+\beta)}{C_{in}} \quad (24)$$

and

$$f_i = \left(\frac{A}{0.1} \times (K+\beta)\right), \quad (25)$$

where f_i is the proportion factory, A is the peak area of migrant in the headspace in the food/air system, C_{in} is the initial concentration of migrant in each ml of solution, $K_{solution/polymer}$ is the partition coefficient of migrant in the food simulant/air system and β is the phase ratio.

The concentration of migrant in the gas phase at equilibrium can be expressed as:

$$C_{g1} = \frac{A}{f_i}. \quad (26)$$

Defining the concentration of migrant in the solution phase at equilibrium as:

$$C_{s1} = (C_{in} - (C_{g1} \times \beta)), \quad (27)$$

then:

$$K = \frac{C_{s1}}{C_{g1}}. \quad (28)$$

The partition coefficients of migrant between food and polymer were calculated by the following equations:

$$C_{g2} = \frac{A_2}{f_i}, \quad (29)$$

where C_{g2} is the concentration of the migrant in the gas phase at equilibrium in a food/polymer system and A_2 is the peak area of migrant in the headspace in a food/polymer system.

$$C_{s2} = C_{g2} \times K, \quad (30)$$

where C_{s2} is the concentration of migrant in the solution at equilibrium in a food/polymer system.

$$C_{p1} \cdot V_p = C_{in} V_s - (C_{g2} \times V_g + C_{s2} \times V_s), \quad (31)$$

where C_{p1} is the concentration of migrant in polymer phase, V_p is the volume of polymer, V_g is the volume of gas and V_s is the volume of solution (1–5 ml).

C_{p2} is the concentration of migrant in each cm^3 of polymer.

$$C_{p2} = \frac{C_{p1} \cdot V_p}{\text{surface area} \times \text{thickness}}. \quad (32)$$

Finally

$$K_{simulant/polymer} = \frac{C_{s2}}{C_{p2}}. \quad (33)$$

3. Results and discussion

3.1. Partition coefficients of ethyl acetate between food simulants and polymers

The equilibrium distribution of migrants or flavour compounds will depend on partitioning behaviour between the polymeric packaging and the food matrix. Table 1 shows the partition coefficient of ethyl acetate between two polymers (PA and PET) and four food simulants (water, 10% ethanol, 3% acetic acid and 95% ethanol).

Peak areas were the average (±standard deviation) of at least 12 assays on each volume for each sample. Partition coefficients (K) were the average (±standard deviation) of five concentrations (0.1–0.5 μl/ml).

Table 1
Partition coefficient of ethyl acetate between food simulants and polymer

Model system	Phase ratio (β)	Peak area without polymer (A)	PEAK area with PET (A)	Peak area with PA (A)	$K_{Food/air}$ value with PET	$K_{Food/air}$ value with PA
Water	10	53.1	46.9	47.0	0.15 ± 0.03	0.19 ± 0.06
	4.5	58.2	54.1	54.4		
	2.67	61.6	58.5	57.2		
	1.75	64.5	61.2	62.6		
	1.2	65.3	61.4	64.4		
Ethanol 10%	10	50.5	50	41.7	0.17 ± 0.01	0.11 ± 0.02
	4.5	56.7	52.5	48.6		
	2.67	59.2	56.4	52.6		
	1.75	60.8	60.2	56.1		
	1.2	61.7	61.0	60.8		
Acetic acid	10	46.0	41.3	42.2	0.14 ± 0.04	0.15 ± 0.02
	4.5	52.1	46.8	47.2		
	2.67	54.2	51.0	51.6		
	1.75	56.3	53.3	52.4		
	1.2	58.0	56.5	54.1		
Ethanol 95%	10	11.4	6.62	8.11	0.053 ± 0.005	0.064 ± 0.004
	4.5	11.7	9.24	9.13		
	2.67	11.20	9.94	9.97		
	1.75	12	10.7	10.3		
	1.2	12.1	11.3	11.0		

PET, polyethylene terephthalate; PA, polyamide.

Comparison between partition coefficients of ethyl acetate in food simulant/polymer system showed that PET absorbed ethyl acetate more than PA in three food simulants (water, 3% acetic acid and 95% ethanol). In the case of 10% ethanol, absorption of ethyl acetate by PA increased with increasing hydrophobic character of the solution. Polyamide and polyethylene terephthalate, polar polymers, absorb larger amounts of polar migrants (Gremli, 1996; Nielsen, Margaretha Jägerstad, Öste, & Wesslén, 1992; Quezada Gallo, Debeaufort, & Voilley, 1999). In addition, PA has a strong hydrogen-bonding character, contrary to PET. For 95% ethanol, partition coefficient of ethyl acetate was smaller than the other food simulants with the two polymers. The reason why ethyl acetate was not absorbed to a greater extent into this food simulant may be due to its hydrophobic character, which the other food simulants do not have. Therefore, ethyl acetate with its hydrophilic character was absorbed by the two polymers, relative to 95% ethanol.

3.2. Partition coefficients between food simulants and polymers of the other migrants

Table 2 gives the partition coefficients of acetaldehyde in food simulant/polymer systems. An understanding of absorption of the migrants in polymeric packaging materials requires knowledge of the chemical and physical structures of both the migrant and polymer. Knowledge of the binding behaviour of migrants to food simulants and their partitioning between different phases (food/air and air/polymer) is of great importance in estimating the rate of absorption of migrants by the polymer. The amount of acetaldehyde absorbed in PA was more than in PET. It was shown that there was a high relation between the binding behaviour and other physicochemical properties (such as $\log P$) of acetaldehyde and PA. Table 3 shows some properties of this migrant and the two polymers.

Table 2
Partition coefficient of five migrants between food simulants and polymers

Migrant	Food simulant	$K_{food\ simulant/PET}$	$K_{food\ simulant/PA}$
Acetaldehyde	Water	0.08 ± 0.01	0.048 ± 0.007
	10% Ethanol	0.075 ± 0.007	0.015 ± 0.003
	3% Acetic acid	0.017 ± 0.004	0.021 ± 0.003
Acetonitrile	Water	0.21 ± 0.06	0.436 ± 0.004
	10% Ethanol	0.038 ± 0.001	0.098 ± 0.006
	3% Acetic acid	0.14 ± 0.01	0.31 ± 0.06
Methyl ethyl ketone	Water	0.035 ± 0.004	0.047 ± 0.007
	10% Ethanol	0.056 ± 0.005	0.05 ± 0.01
	3% Acetic acid	0.042 ± 0.006	0.042 ± 0.005
	95% Ethanol	0.15 ± 0.05	0.12 ± 0.01
Isopropyl acetate	Water	0.051 ± 0.005	0.031 ± 0.004
	10% Ethanol	0.086 ± 0.005	0.129 ± 0.005
	3% Acetic acid	0.059 ± 0.005	0.049 ± 0.008
	95% Ethanol	0.15 ± 0.03	0.13 ± 0.02
Butyraldehyde	Water	0.021 ± 0.003	0.034 ± 0.003
	10% Ethanol	0.017 ± 0.003	0.042 ± 0.005
	3% Acetic acid	0.03 ± 0.01	0.042 ± 0.006
	95% Ethanol	0.021 ± 0.002	0.014 ± 0.001

As seen from Table 2 the two there were major differences between amounts of acetonitrile absorbed by the two polymers. The reason for this was mainly the polarity. Partitioning depends largely on the nature of the migrant, especially on its polarity and compatibility with food

Table 3
Physico-chemical properties of polymers and migrants

Polymer and migrant	log *P*[a]	Solubility[a]	Hydrogen bonding[a]	Polarity[a]
Acetonitrile	−0.39	24.4	6.08	18.0
Acetaldehyde	−0.22	20.2	11.3	8.00
Methyl ethyl ketone	0.26	19.0	5.13	9.01
Ethyl acetate	0.67	18.1	7.19	5.35
Butyraldehyde	0.83	17.1	7.03	5.27
Isopropyl acetate	1.20	17.5	6.73	4.14
Polyethylene terephthalate	2.38	21.8	3.00	9.65
Polyamide	−0.17	21.2	8.00	4.83

[a] Data from software of Molecular Modeling Pro (2002).

simulants and packaging material. Another factor that affected absorption is the energy of reaction, which is more important in food simulant/PET systems. Therefore, acetonitrile was absorbed in food simulants more than polyamide. The partition coefficient of acetonitrile in 10% ethanol/polymer system was lower than in water and 3% acetic acid, because the hydrophobic character of 10% ethanol was slightly higher than the water and 3% acetic acid. This might also explain why acetonitrile was absorbed to a greater extent into PET than PA.

Methyl ethyl ketone was absorbed in similar amounts in PET and PA (Table 3). According to Table 3, methyl ethyl ketone has a polarity parameter close to that of PET but log *P* value is close to that of PA. The amount of hydrogen bonding in methyl ethyl ketone is between that found for PET and PA. For 95% ethanol, this value increased up to 0.15 for PET and 0.12 for PA. Both 95% ethanol and methyl ethyl ketone had a high hydrophobic character, which explained why methyl ethyl ketone showed the highest affinity for 95% ethanol.

Isopropyl acetate has hydrophobic character. For this reason, the quantity of this migrant absorbed in polymers was more than absorbed by water and 3% acetic acid. For 10% ethanol, hydrophobic character slightly increased, leading to increased absorption of isopropyl acetate by 10% ethanol. It is clearly seen that the extent of uptake of isopropyl acetate into 95% ethanol increased significantly with increasing hydrophobicity of food simulant. Among the two polymers, isopropyl acetate was absorbed in PET more than PA, because its polarity parameter is very near to PET. The partition coefficient of butyraldehyde is higher in three food simulants (water, 10% ethanol and 3% acetic acid)/PA systems, because the energy of reaction between PET and butyraldehyde is higher than PA and butyraldehyde. The partition coefficients were low in relation to that of other migrants, because butyraldehyde showed the highest affinity for the polymers.

4. Conclusion

Partition coefficients were calculated using the phase ratio variation method, to determine the concentration of migrants in food/packaging systems. The amounts of migrants absorb different polymer packaging materials depend partly on the nature of the polymer and on the chemical features of the migrant. Factors that affected partition coefficient included polarity, solubility, hydrogen bonding, total energy, significant functional groups and log *P*(hydrophobicity) of polymers, food simulants and migrants.

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