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Determination and Prediction of Partition Coefficient Values (Kp) for Printing Ink Solvents on Cookie from the Kp of Each Cookie Ingredient

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Abstract

The partitioning behavior of five printing ink solvents was studied in cookie ingredients and cookies to examine migration behavior, and to determine if one could predict Kp of a cookie from summing the Kp of each ingredient multiplied by its weight factor in the cookie formula. Solvents were ethyl acetate, hexane, isopropanol, methyl ethyl ketone, and toluene. Gas chromatography was used to measure Kp values on each raw and baked (260°C for 10 min) cookie ingredients, and lab-made cookies. The baking process-decreases in water content in each sample generally affected Kp of polar solvents, but did not affect that of the non-polar solvents. Structural changes in cookie ingredients during the baking process also caused some change of migration behavior. While the prediction of Kp of lab-made cookies using the Kp of raw ingredients showed significant differences between calculated and experimentally found values, predictions with baked ingredients showed much smaller differences. This suggests that loss of water and changes of crystallinity in cookies and cookie ingredients due to the baking process are important and affect the Kp.

Key words: partitioning behavior, partition coefficient, printing ink solvents, cookie, cookie ingredient

INTRODUCTION

The widespread use of printing ink solvents on food package sometimes causes off-flavor in the food as a result of the migration of residual solvents, which consist of hydrocarbon, aromatic, alcohol, and ketone compounds (1,2). Migration of the residual solvents could generate off-flavor and deteriorate quality of the finished food, even causing safety problems in the contained food (3-7).

In highly consumer-oriented markets, the quality of the finished products is gaining more importance economically, so thorough study about ink solvent migration into food has become an important issue. Some studies have measured partition coefficient values between solvents and various food samples and have found factors that affected the partitioning behavior of solvent into the contained food in an effort to predict migration behavior (8-10). However, to enable prediction of partitioning, data are still needed on the relation of solvent chemical structure and properties to partitioning behavior, and on the partitioning behavior of various food ingredients and the total food compositions.

The objective of this research was to find out what was affecting the interactions of the solvents with the polar compounds (water and OH-rich compounds like flour and sugar) and to determine if Kp of a food could be predicted from summing the Kp of each ingredient multiplied by its weight factor in the cookie formula. To satisfy these objectives, this study determined the effect of the state of the individual ingredients on Kp by measuring the Kp values of selected printing ink solvents on each ingredient of cookie at each of two state (as it is and after being baked at 260°C for 10 min). Then, the relationship between the individual Kp values and that of the finished cookie was determined. Gas chromatography was used to measure ingredient sorption by equilibrating measured quantities of each sample and solute in sealed vials and control vials without sample in a system.

MATERIALS AND METHODS

Cookie ingredients

Flour (General Mills Co.), chocolate-chip (Keebler Co.), white and brown sugar (Domino Sugar Corp.) and dried whole egg powder (High-grade egg products Inc.) were tightly wrapped in aluminum foil and stored in a refrigerator at 3°C. Water and whey powder from Sigma Co. and vegetable shortening from Proctor and Gamble Co. were stored at room temperature with aluminum foil wrapping.

Solvents

Five printing ink solvents were used for determining

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partition coefficient value. Hexane, toluene, isopropanol, methyl ethyl ketone, and ethyl acetate which have 99.9% purity from Fisher Scientific Co. Hexane (99.9% purity) was obtained from Fisher Co. and was used for extraction of fat content.

Extraction of fat content in each cookie ingredient

Each of two cookie samples (5.0 g) was put into a cellulose extraction thimble (from Whatman Ltd. with 33 mm (ID) × 94 mm (length)), which was placed in a Soxhlet extraction apparatus (11). After pouring 150 mL hexane in the extraction flask (250 mL), the flask was fitted to the extraction apparatus and boiled at a such a rate that the hexane refluxed gently. After seven hours, the heating was stopped and the thimble was removed from the extraction apparatus. Hexane from the flask was evaporated by distilling into the extraction apparatus. After evaporating for 3 hr, the concentrated solution was transferred to a tared 100 mL flask. After evaporating most of the hexane for 4 more hr by distilling into the extraction apparatus, the flask was placed in a desiccator for overnight to remove trace amounts of hexane. After that, the flask was weighed for determining fat weight by subtracting original flask weight. These processes were repeated two times.

Measurement of water content

Moisture content was measured by using drying oven method (12). Triplicate samples (5.0 g) were put in a weighing dish and then placed in a preheated oven at 130°C for 1 hr. The heated sample was transferred to the desiccator and stored for 30 min, then weighed at room temperature for water weight.

Cookie formula and preparation of lab-made cookie

Cooking methods (baking at 260°C for 10 min) of commercial cookies were used for preparation of lab-made cookies. The baking conditions were selected based on previous work and commercial recipes. Based on compositions in commercial cookies, previously determined amounts of each of whey powder (0.3%), whole egg powder (0.6%), brown sugar (2.4%), white sugar (12.6%) and shortening (19.1%) were added in metal bowl (2000 mL). After mixing gently with an electric blender for 5 min, a determined amount of water (5.6%) based on the composition of each cookie was added and mixed for 2 min. Finally, chocolate chips (21.8%) and flour (37.0%) were added to make the dough, which was blended for 5 min. The dough was wrapped with aluminum foil and stored overnight at room temperature, and then the cookies were baked at 260°C for 10 min, in accordance with the cooking method of commercial cookies.

Determination of equilibrium day for each solvent on each cookie ingredients and lab-made cookie

5.0 g of each sample were placed into a 60 mL vial and sealed with rubber and a cap. Blank vials without sample also were prepared. After injection of 0.4 μL of each solvent into each blank vial and the vial with sample, the vials were stored at 25°C in a water bath. A 200 μL sample of headspace from each vial was injected into the gas chromatograph (G.C.) every other day. Equilibrium day was determined at the day of constant area difference between sample and blank vials. For determination of equilibrium day of baked sample, vials with baked samples (260°C for 10 min) were stored 25°C in the water bath, the procedure was the same as above and these processes were repeated three times.

Determination of partition coefficient values for each solvent on each cookie ingredient and lab-made cookie

Partition coefficient values were determined in a closed system based on the method of Biran et al. (13). 60 mL vials with each raw cookie ingredient sample (5.0 g) weighed to the nearest milligram and blank vials were prepared with sealing of septa and injected by 0.4 μL of each solvent. After storing each bottle for one day more than the determined equilibrium day at 25°C, a 200 μL sample of headspace from each vial was injected into the G.C. with a gas-tight syringe to find the area value. The amount of solvent absorbed by the sample was determined by the difference between the area of the headspace in the vials with sample and the area of headspace in the blank vials. These experiments were repeated three times. Partition coefficients of each solvent between each sample and headspace were calculated by the following equation (10):

Kp={(Wt. of solvent in headspace in blank)−(Wt. of solvent in headspace in bottle with sample)/ Weight of sample}/ {Weight of solvent in 1 mL headspace in bottle with sample/ Density of air}

Baked cookie ingredients and finished cookies samples were cooled down to 25°C after being baked at 260°C for 10 min. The procedures of determination of partition coefficient values for the baked cookie ingredients and the finished cookies followed the same method as those for raw cookie ingredients, and the partition coefficients values were also calculated by using above equation.

G.C. condition for determination of partition coefficient values

A Varian 3300 Gas Chromatograph with flame ionization detector and Supelco fused silica capillary column, DB-1 (0.25 mm×30 m) was used. Operating conditions included helium carrier gas at 1 cc/min and temperatures, injection port (230°C), column (70°C), and detector (230°C). A Varian 4270 recorder-integrator was used.

RESULTS AND DISCUSSION

Equilibrium day for each solvent on each raw, baked cookie ingredient and lab-made cookie

The time for equilibrium at 25°C of each solvent in each sample was measured by plotting % difference between control and sample headspace of initial headspace values until they did not change (Table 1). The point of constant value between control and sample of initial headspace was considered equilibrium day. With raw and baked ingredients and finished cookies, except for white, brown sugar and whey, isopropanol and methyl ethyl ketone have 1 day, ethyl acetate and hexane needed 2 days and toluene had 3 days for the equilibrium time. In case of raw and baked white and brown sugar, and whey sample, isopropanol, methyl ethyl ketone and ethyl acetate needed 2 days, and hexane and toluene have 3 days for equilibrium time. These results indicate that sorption of the polar solutes into the sample was faster than non-polar solutes and also that the sorption rate decreased with an increase in crystallinity of sugar and whey.

Determination of fat and water content of raw and baked cookie ingredients

The fat and water content of each raw and baked cookie ingredient was measured. Among the raw cookie ingredients, the decreasing order of fat content was as follows: shortening (93.2%)> egg powder (39.55%)> chocolate chips (25.6%)> flour (0.9%)> whey powder and brown and white sugar (0.0%). Water content diminished in the following order: flour (11.6%)> whey (9.3%)> egg powder (3.4%)> chocolate chips (1.8%)> brown sugar (0.3%)> white sugar (0.1%)> shortening (0.0%). Among the fat and water content of each baked cookie ingredient, the decreasing order of fat content was the same as that of raw ingredient: shortening (93.2%)> egg powder (41.7%)> chocolate chips (27.4%)> flour (1.1%)> whey powder and brown and white sugar (0.0%) and the fat content remained almost constant after the baking treatment (for 10 min at 260°C). Even though a lot of water content decreased after baking process, the order remained similar to that of the raw ingredients: flour (5.6%)> whey (4.1%)> egg powder (1.1%)> chocolate chips (0.9%)> brown sugar (0.5%)> white sugar (0.1%)> shortening (0.0%).

Comparison of partition coefficient values of solvent in cookie ingredients before and after baking

Partition coefficient values for each raw and baked cookie ingredient measured at 25°C are shown in Tables 2 and 3. The order of Kp value for each solvents in baked shortening, chocolate chips flour, white and brown sugar samples was the same as that of each raw sample. However, baked whole egg and whey powder have different order than that of each raw sample. The reasons appear to be a combination of polarity and crystallinity difference.

Ingredients with high fat (shortening, chocolate chips and egg powder): The shortening has almost constant

Table 1. Equilibrium day of each solvent on raw and baked cookie ingredients, and lab-made cookie

Sample		Ethyl acetate	Hexane	Isopropanol	Methyl ethyl ketone	Toluene
Shortening	Raw	1	2	1	1	3
	Baked	1	2	1	1	2
Whole egg	Raw	1	2	1	1	3
	Baked	1	2	1	1	3
Chocolate chips	Raw	1	2	1	1	3
	Baked	2	2	1	1	3
Flour	Raw	1	2	1	1	3
	Baked	1	2	1	1	2
Water	Raw	1	1	1	1	1
Whey powder	Raw	1	2	1	2	2
	Baked	2	2	1	2	2
White sugar	Raw	1	2	1	1	2
	Baked	2	1	1	1	2
Brown sugar	Raw	1	2	1	1	2
	Baked	1	2	1	1	2
Cookie	Baked	1	2	1	1	3

Table 2. Kp values1) of five printing ink solvents on each raw cookie ingredient

Sample	Toluene	Isopropanol	Methyl ethyl ketone	Ethyl acetate	Hexane
Shortening	0.432±0.0077	0.215±0.0006	0.266±0.0097	0.212±0.0078	0.178±0.0089
Whole egg	0.303±0.0077	0.3602±0.0084	0.312±0.0092	0.208±0.0092	0.094±0.0044
Chocolate chips	0.057±0.0077	0.0484±0.0018	0.042±0.0011	0.032±0.0013	0.018±0.0008
Flour	0.024±0.0077	0.490±0.0084	0.297±0.0064	0.180±0.0026	0.004±0.0002
Water	0.001±0.0077	0.318±0.0031	0.274±0.0061	0.136±0.0064	0.0001±0.0003
Whey powder	0.0004±0.0077	0.002±0.0001	0.0004±0.00003	0.0007±0.0006	0.0001±0.00002
White sugar	0.0005±0.0077	0.001±0.0001	0.001±0.0001	0.001±0.0006	0.0002±0.00003
Brown sugar	0.0004±0.0077	0.002±0.0001	0.001±0.0001	0.001±0.0004	0.0002±0.00003

1)Average±standard deviation.

Table 3. Kp values1) of five printing ink solvents on each baked cookie ingredient

Sample	Toluene	Isopropanol	Methyl ethyl ketone	Ethyl acetate	Hexane
Shortening	0.423±0.0077	0.177±0.0050	0.243±0.0040	0.170±0.0018	0.162±0.0022
Whole egg	0.340±0.0064	0.332±0.0114	0.312±0.0023	0.215±0.0066	0.105±0.0008
Chocolate chips	0.081±0.0024	0.054±0.0012	0.053±0.0017	0.041±0.0017	0.036±0.0014
Flour	0.022±0.0008	0.285±0.0097	0.145±0.0048	0.090±0.0021	0.004±0.0001
Whey powder	0.0003±0.00002	0.001±0.0001	0.0003±0.00002	0.001±0.0001	0.0001±0.00001
White sugar	0.0005±0.00005	0.001±0.0001	0.001±0.0001	0.001±0.0001	0.0002±0.00004
Brown sugar	0.001±0.0001	0.001±0.0001	0.001±0.0001	0.001±0.0001	0.0001±0.00001

1)Average±standard deviation.

fat and water content after the baking process and the Kp values in baked shortening for all five solvents were close to those of the raw shortening. In the case of baked chocolate chips, all five printing ink solvents, including polar solvents, showed higher Kp values than those of raw chocolate chips, even though the water content of baked chips was a little bit decreased. This behavior can be explained by two ways. First, structural change of fat in chocolate chips can make the migration process of solvent easier. Second, heat treatment of raw chocolate chips can interrupt or weaken the binding interaction between fat and carbohydrate, and the relatively free fat in chips can be more involved in migration behavior of five solvents. The Kp values in baked whole egg powder for the non-polar solvents like toluene and hexane increased and this behavior can be explained by increased amounts of interaction sites of fat in egg powder by weakening of interaction among fat and protein or carbohydrate. The polar solvents like isopropanol, methyl ethyl ketone and ethyl acetate, showed mixed results. After heat treatment, Kp values of ethyl acetate increased. The Kp for methyl ethyl ketone decreased slightly, but isopropanol's Kp decreased much more. This behavior can be explained by hydrogen bonding. Decreased water content in baked egg powder can sharply affect partitioning behavior of isopropanol among polar solvents because isopropanol has hydrogen bond donors and acceptors but others have only hydrogen bond acceptors.

Ingredients with high water (water and flour): In the water sample and flour sample (0.9% fat and 11.6% water content), the decreasing order of Kp was as follows: isopropanol> methyl ethyl ketone> ethyl acetate> toluene> hexane. This order can be explained by hydrogen bonding effects. The common major component in the sample is water, which can be hydrogen bonded with the polar solvents. Among the polar solvents, isopropanol's -OH group can act as both hydrogen bonding donor and acceptor with water. However, methyl ethyl ketone and ethyl acetate can act only as hydrogen bonding acceptors. Therefore, isopropanol has a stronger affinity on hydrogen bonding with water than methyl ethyl ketone and ethyl acetate. The Kp values in baked flour for the polar solvents were much lower than those of raw flour, while the Kp of non-polar solvents in baked flour are very close to those of original flour. This result can also be explained by hydrogen bonding. After the baking process, water content in baked flour was remarkably decreased, while fat content in the flour remain almost constant. Therefore, Kp values of the polar solvents that are involved in hydrogen bonding with water are very much decreased in the baked flour sample. However, the non-polar solvents, which create hydrogen bonds with fat rather than water, showed very similar partition coefficient values to those in the raw flour sample. Even though the baking process increased fat content only slightly, the increased fat content was too small to effect partitioning behavior of non-polar solvents.

Ingredients with crystalline structure (sugar and whey *powder)*: The Kp values of sugar and whey are very much smaller than those of other ingredients, even though the sugar sample has a lot of -OH polar groups and the whey sample contains high water content with a lot of -OH groups. The low Kp values can be explained by the high degree of crystalline structure of sugar and whey, which can prevent migration reaction of solvents.

The Kp values in baked sugar and whey samples for the polar solvents were lower than those of raw sugar and whey, while the Kp values of the non-polar solvent in baked sugar and whey samples are very close to or a little bit higher than those or raw sugar and whey. After the baking process, water content in baked sugar and whey was decreased. Therefore, the Kp values of polar solvents which are involved in hydrogen bonding with water decreased in baked sugar and whey samples, while non-polar solvents, which are dependent on fat for hydrogen bonding, showed very similar partition coefficient values to those in raw sugar and whey sample. Moreover, the low Kp values of all five solvents for baked sugar and whey showed the retarding effect of crystallinity and the baking process used in this work is not enough to change high crystallinity structure to amorphous or less crystalline structure in sugar and whey.

Comparison of calculated Kp values by cookie ingredients with experimental Kp values of lab-made cookies

To determine if the Kp value of a food could be predicted from summing the Kp of each ingredient multiplied by its weight factor in the cookie formula, this study determined the effect of the state of the individual ingredients on Kp by measuring the partition coefficient (Kp) values of selected printing ink solvents on each ingredients of a cookie at each of two states (as it is and after being baked at 260°C for 10 min).

Calculated Kp values of the solvents from the Kp of each raw cookie ingredients

The calculated partition coefficient values (Kp) of each solvent was determined by summing the Kp of each raw ingredient multiplied by its weight factor in the cookie formula to determine if one could predict Kp of cookie:

$$\text{Expected Kp}=A\times(1)+B\times(2)+ \text{----------} \ H\times(8).$$

The aliphatic character is the partition coefficient value of each solvent raw cookie ingredient and the Arabic number is the weight composition of each cookie ingredient.

For example of hexane:
raw flour Kp = 0.00380 weight compositions 36.97%
raw chocolate chips Kp = 0.01759 weight compositions 21.83%
raw shortening Kp = 0.17807 weight compositions 19.09%
raw white sugar Kp = 0.00018 weight compositions 12.71%
water Kp = 0.00012 weight compositions 5.58%
baked brown sugar Kp = 0.00016 weight compositions 2.43%
baked egg powder Kp = 0.09379 weight compositions 0.55%
baked whey powder Kp = 0.00008 weight compositions 0.27%

Then, the calculated Kp value for hexane is as follows. Calculated Kp = 0.00380 × 36.97% + 0.01759 × 21.83% + 0.17807 × 19.09% + 0.00018 × 12.71% + 0.00012 × 5.58% + 0.00016 × 2.43% + 0.09379 × 0.55% + 0.00008 × 0.27%.

The comparison between the experimental Kp values on lab-made cookies and the calculated Kp values by using the Kps of each raw cookie ingredient for each solvent were listed in Table 4. The % difference between the calculated Kp and experimental Kp of lab-made cookies in five solvents ranged from 17.69% to 44.76%.

Calculated Kp values of the solvents from the Kp of each baked cookie ingredients: The calculated partition coefficient values (Kp) of each of the five solvents were also determined by summing the Kp of each baked ingredients multiplied by its weight factor in the cookie

Table 4. Calculated Kp of lab-made cookies by using each raw cookie ingredient's Kp and difference between calculated and experimental Kp

Solvent	Calculated Kp[1]	Experimental Kp	Difference[2]
Ethyl acetate	0.12302	0.07427	39.63%
Hexane	0.03979	0.04683	17.69%
Isopropanol	0.25254	0.13951	44.76%
Methyl ethyl ketone	0.18701	0.11429	38.89%
Toluene	0.10549	0.12163	15.30%

[1] Kp values by using Kps of each raw cookie ingredient.

[2] % difference between the calculated Kp by using Kp of raw cookie ingredients and experimental Kp of lab-made cookie.

Table 5. Calculated Kp of lab-made cookie by using each baked cookie ingredient's Kp and difference between calculated and experimental Kp

Solvent	Calculated Kp[1]	Experimental Kp	Difference[2]
Ethyl acetate	0.08373	0.07427	11.30%
Hexane	0.04066	0.04683	15.17%
Isopropanol	0.17055	0.13951	18.20%
Methyl ethyl ketone	0.12878	0.11429	11.25%
Toluene	0.10838	0.12163	12.23%

[1] Kp values by using Kps of each baked cookie ingredient.

[2] % difference between the calculated Kp by using Kp of baked cookie ingredients and experimental Kp of lab-made cookie.

formula. The comparison of Kp values between the calculated and lab-made cookie is shown in Table 5. The % difference between the calculated and experimental Kp of lab-made cookie in five solvents ranged from 11.25% to 18.20%. It was significantly improved for polar solvents like ethyl acetate, methyl ethyl ketone and isopropanol, and somewhat improved for hexane and toluene.

The Kps calculated by the two different methods may be compared to find the best method for prediction of Kp values on lab-made cookie. While prediction with raw ingredients showed significant differences between calculated and experimentally found values, prediction with baked ingredients showed much smaller differences.

Decreased water content in each sample by the baking process (260°C for 10 min) generally affected partitioning behavior of polar printing ink solvents, but did not affect that of the non-polar solvents. Structural changes in cookie ingredients during the baking process caused some changes in migration behavior. For example, loss of water and interaction between ingredients, and changes in crystallinity affected partitioning behavior. This is supported by better prediction of experimental Kp by Kp of baked cookie ingredients, especially for polar solvents. The closest correspondence between calculated and experimental values was found when data involving similar processing condition among the ingredients were treated.

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