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Interactive Effect of Food Compositions on the Migration Behavior of Printing Ink Solvent

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Abstract

The partitioning behavior of the five printing ink solvents in nine lab-made cookies with various sugar and water content at 25°C was studied to find out the presence and effects of interaction between the two ingredients on partitioning behavior in cookies. Solvents were ethyl acetate, hexane, isopropanol, methyl ethyl ketone and hexane. It was observed that the partition coefficient (the solvent concentration in food compared to that in air, Kp) decreased as sugar increased in all case and increased as water content increased for all compounds except toluene. Statistical analysis by the F-test method was used to determine the significance of sugar-water interactions, as well as other single factors on partitioning behavior of each solvent. Sugar content alone had no significant effects, but the crystallinity of sugar, as changed by water content, affected the partitioning behavior of the five solvents significantly. Parameter estimation for each significant factor by SAS program yielded a regression equation, which was used to predict the partitioning behavior in the finished cookie. Kp values from the regression equation could be determined more precisely by applying a correction term for the interaction between sugar and water to the Kp values of each ingredient after baking.

Key words: partitioning behavior, sugar and water interaction, F-test, regression equation, prediction of Kp value

INTRODUCTION

It is common practice to apply decorative coatings to flexible package materials to gain consumers' attention. The coating materials are generally dissolved or dispersed in solvents, and then applied to the packaging material with the subsequent removal of solvent by evaporation in the storage oven. However, a certain amount of residual solvents can remain (1), which can then migrate into the food by either direct contact or via the headspace inside the package. Migration of the residual solvents could generate off-flavor, deteriorate quality of the finished food, and even cause safety problems in the contained food.

The amount of solvent that enters the food depends on the partitioning of the solvents between the package materials and the contained food (2). Factors that influence this partitioning from the polymeric packaging materials into the single food compositions have been studied (3-7) and the results used to predict migration behavior (8,9). However, factors that influence the partitioning to the total foods system are less understood. These factors include the chemical structure of the migration solvent and its interaction with the target food substrate. Some studies (10,11) discuss the effects of structural change and interaction between some of the ingredients in the total food system on partitioning behavior is difficult to predict. Additional information about the effect of interactions between selected ingredients in the cookie is needed for understanding the migration behavior.

To satisfy this objective, factorial experiments were conducted to determine key interactions of several factors, and to derive a regression equation that could assign values to the included variables to predict Kp for different foods.

These factors included water and sugar, and the effect of sugar crystallinity on the partitioning behavior of the end product. Factorial experiment was conducted to determine the effects of sugar and water content of cookies at three different concentrations on the partitioning coefficient values of printing ink solvents. The other ingredients and their amounts were fixed at flour (37%), chips (22.5%), shortening (19%), whole eff powder (0.6%), whey (0.3%). Five solvents (ethyl acetate, hexane, isopropanol, methyl ethyl ketone, toluene) which represent different specific functional groups were used and gas chromatography was used to measure ingredient sorption a closed system.

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MATERIALS AND METHODS

Cookie ingredients and preparation of lab-made commercial cookie

Chocolate-chips (Keebler Co., USA), Flour (General Mills Co., USA), white and brown sugar (Domino Sugar Corp., USA) and dried whole egg powder (High-grade egg products Inc, USA), whey powder from Sigma Co. and vegetable shortening from Proctor and Gamble Co. were used for lab-made cookies. Table 1 shows previously determined fat and water content of raw and baked cookie ingredients. Shortening (19.1% of total weight), brown sugar (2.4%), white sugar (12.6%), whole egg powder (0.6%) and whey powder (0.3%) were added to mix with some water (5.6%). Finally flour (37.0%) and chocolate chips (21.8%) were added to make dough, the dough was stored overnight at room temperature, and then the cookies were baked at 260°C for 10 min.

Table 1. Fat and water content of each cookie ingredient (%)

Sample		Fat content	Water content
Shortening	Raw	93.2	0.0
	Baked	93.9	0.0
Whole egg	Raw	39.5	3.4
	Baked	41.7	1.1
Chocolate chips	Raw	25.6	1.8
	Baked	27.4	0.9
Flour	Raw	0.9	11.6
	Baked	1.1	5.6
Whey powder	Raw	0.0	9.3
	Baked	0.0	4.1
White sugar	Raw	0.0	0.1
	Baked	0.0	0.1
Brown sugar	Raw	0.0	0.3
	Baked	0.0	0.5

Factorial experiment design

Factorial experiments using a combination of three different concentrations each of sugar and water were conducted to determine the effects of the contents on the partition coefficients of printing ink solvents. Table 2 shows possible combinations (3×3) of sugar and water contents based on total cookie weight.

The other cookie ingredients and their amounts remained fixed at flour (37%), chips (22%), shortening (19%), whole egg powder (0.6%), and whey (0.3%). Table 3 shows formulation of cookie model systems for factorial experiments designed to study the effect of sugar and water concentration combinations on partitioning behavior of printing solvents. Lab-made cookies were prepared based on the cooking method of commercial recipes.

Presence of interaction or dependency between sugar and water at each level of the 9 combinations can be determined by drawing a diagram in which partition co-

Table 2. Combination of sugar and water contents for factorial experiment in 9 lab-made cookie

		Sugar		
		10%	15%	20%
Water	3%	10% Sugar 3% Water	15% Sugar 3% Water	20% Sugar 3% Water
	6%	10% Sugar 6% Water	15% Sugar 6% Water	20% Sugar 6% Water
	9%	10% Sugar 9% Water	15% Sugar 9% Water	20% Sugar 9% Water
Total case				9

Table 3. Formation of cookie model systems for factorial experiment design to study the effect of sugar and water contents on partitioning behavior of printing solvents

Ingredients[1)]	Weight compositions (%)								
Sugar	10	15	20	10	15	20	10	15	20
White sugar	8.4	12.6	16.8	8.4	12.6	16.8	8.4	12.6	16.8
Brown sugar	1.6	2.4	3.2	1.6	2.4	3.2	1.6	2.4	3.2
Water	2.7	2.7	2.7	5.1	5.1	5.1	9.4	9.4	9.4
Flour	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Chips	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8	21.8
Shortening	19.1	19.1	19.1	19.1	19.1	19.1	19.1	19.1	19.1
Whole egg	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Whey powder	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

[1)] Weight compositions of each ingredient based on cookie weight (100 grams).

efficient values were chosen as Y-axis and sugar or water factors were selected as X-axis, alternatively. While parallel lines indicate that no interaction exists between sugar and water, intersecting lines imply that an interaction occurred between each factor.

Measurement of fat and water content of 9 lab-made cookies

Fat content of each lab-made cookie (5.0 g) was measured by the Soxhlet extraction method (12) with cellulose extraction thimble (from Whatman Ltd. with 33mm (ID)×94 mm (length)). After pouring 150 mL hexane in the extraction flask (250 mL), the flask was fitted to the extraction apparatus and boiled at such a rate that the hexane refluxed gently for seven hours, the heating was stopped and the thimble was removed from the extraction apparatus. After evaporating hexane for 7 hr, the concentrated solution was placed in a desiccator overnight to remove trace amounts of hexane. Moisture content was measured by drying oven method (13). Triplicate samples (5.0 g) were heated in the oven at 130°C for 1 hr and then stored in the desiccator for 30 min.

Determination of partition coefficient values for each solvent on various cookie models for factorial experiment

Previously determined partition coefficient values (10) of commercial lab-made cookies were: isopropanol (0.13951±0.00420), methyl ethyl ketone (0.11429±0.00491), toluene (0.12163±0.00496), ethyl acetate (0.07427±0.00351), and hexane (0.04683±0.00142). Kp value of 9 lab-made cookie models with various water and sugar content were determined in a closed system based on the method of Biran et al. (14). Vials (60 mL) with each cookie (5.0 g) and blank vials were prepared with sealing of rubber septa and then 0.4 μL of each solvent was injected. 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 gas chromatograph (GC) by syringe. These experiments were repeated three times. Partition coefficients of each solvent between each sample and headspace were calculated by the following equation.

$$Kp = \frac{\text{Concentration of solvent in food}}{\text{Concentration of solvent in air}}$$

RESULTS AND DISCUSSION

Partition coefficient values for each solvent on various cookie models for factorial experiment

Partition coefficient values for nine lab-made commercial cookie with commercial compositions and nine lab-made cookies with variable sugar and water content measured at 25°C are shown in Table 4 and were used to identify the presence and effects of interaction between the two ingredients in the cookies. The presence of any interaction between two ingredients can be judged by diagram and statistical analysis, which are discussed in greater detail below.

Determination of interaction between sugar and water content by using a diagram method

The presence of interaction between sugar and water means that a change in sugar produces a different change in the partition coefficient value at other levels of water, and can be judged by diagram study. If the regression lines are not parallel, there is interaction between the two factors (15). On the other hand, if the regression lines are parallel, no interaction is considered to occur. The regression lines were not parallel to each other, so the partitioning behaviors of all five solvents were affected by sugar and water interactions to some extent. For hexane and toluene, the interactions were relatively

Table 4. Kp for printing ink solvents in cookie model systems where X_1 is sugar[1)], X_2 is water and X_3 is fat[2)]

X_1	X_2	X_3	Ethyl acetate (±STD)	Hexane (±STD)	Isopropanol (±STD)	Methyl ethyl ketone (±STD)	Toluene (±STD)
	Group I						
10	2.5	29.5	0.0770±0.0004	0.0496±0.0003	0.0687±0.0012	0.0929±0.0012	0.1418±0.0010
10	5.4	27.8	0.0840±0.0008	0.0494±0.0003	0.1372±0.0012	0.1199±0.0010	0.1381±0.0002
10	8.3	27.1	0.0920±0.0001	0.0501±0.0001	0.2052±0.0034	0.1528±0.0009	0.1361±0.0003
	Group II						
15	3.5	27.2	0.0748±0.0003	0.0473±0.0002	0.0878±0.0024	0.0918±0.0004	0.1354±0.0003
15	6.0	25.9	0.0821±0.0003	0.0479±0.0001	0.1440±0.0044	0.1188±0.0011	0.1326±0.0002
15	8.6	25.0	0.0896±0.0004	0.0487±0.0001	0.1957±0.0035	0.1412±0.0011	0.1311±0.0001
	Group III						
20	2.9	26.0	0.0734±0.0005	0.0456±0.0003	0.0806±0.0015	0.0836±0.0012	0.1317±0.0002
20	5.7	24.8	0.0802±0.0005	0.0470±0.0001	0.1339±0.0003	0.1075±0.0011	0.1298±0.0003
20	8.5	23.4	0.0860±0.0007	0.0479±0.0002	0.1770±0.0030	0.1282±0.0013	0.1271±0.0001

[1)]X_1 is % in cookie dough, X_2 and X_3 are final % in the baked cookie product.
[2)]Average of determinations on 3 samples at 1 concentration over 50 ppm～70 ppm, N=27.

minor compared to those of the polar solvents. For ethyl acetate and methyl ethyl ketone, under increasing sugar content (from 10% and 15% to 20%), the regression lines were more anti-parallel and the interactions were relatively stronger at all cases compared to those of other solvents. Qualitatively, it is seen that Kp decreased as sugar increased in all cases. Also, Kp increased as water increased for all cases except toluene. However by just using the factorial diagram method, it was not possible to measure the significance of sugar and water interaction.

Determination of interaction between sugar and water content by using a statistical analysis

Statistical analysis by the F-test method was used to determine the significance of sugar and water interactions and the other single factors on partitioning behavior of each solvent. The partition coefficient values for the factorial experiments on nine lab-made cookies were analyzed statistically by the SAS (JUMP) program using the F-test. The results on the five solvents are shown in Tables 5～9. The F-test indicates whether sugar, water, and sugar-water interaction affected partition coefficient values significantly. In this factorial work, total observations (N) were 27 and total parameters (P) were 5 (intercept, sugar, water, sugar-water interactions and fat). According to the ANOVA table, degree of freedom of each parameter V1 was 1 (P-1) and degree of freedom V2 was 22 (N-P). At the 5.0% significance level, the F value is 4.30. Therefore, to affect partition coefficient values significantly, the F ratio of the parameter should be higher than 4.30.

The effect of sugar: For each solvent, the F-value of sugar parameter is smaller than the tabulated F value (4.30) at the 5.0% significance level. This result showed that sugar did not affect partitioning behavior of the five solvents significantly.

The effect of water: For polar solvents (ethyl acetate, isopropanol and methyl ethyl ketone), the F-value of water is larger than the tabulated F value at the 5.0% significance level, and for non-polar solvents (hexane and toluene), the F-value of water is below the significance level. These behaviors indicated that water affected partitioning behavior of the polar solvents significantly, while

Table 5. ANOVA (corrected[1)]) table of ethyl acetate for factorial work and parameter estimate of each significant factor for determination of regression equation[2)]

Source	Degree of freedom	Sum of square	F-value	Estimates
Slope	4	0.00100218		
Sugar	1	0.00000111	2.9204	
Water	1	0.00006451	169.8422	0.0038567
Sugar × Water	1	0.00000186	4.8921	-0.000028
Fat	1	0.00000456	12.0046	0.0021464
Intercept				0.001012
Error	22	0.0000836		
Total (C[1)])	26	0.00101054		

[1)]Corrected means deletion of intercept from the ANOVA table.
[2)]$Kp = 0.001012 + 0.0038567X_2 + 0.0021464X_3 - 0.000028X_1X_2$ (R^2=0.99). X_1 is % of sugar in cookie dough, X_2 and X_3 are final % of water and fat in baked cookie.

Table 6. ANOVA (corrected[1)]) table of hexane for factorial work and parameter estimate of each significant factor for determination of regression equation[2)]

Source	Degree of freedom	Sum of square	F-value	Estimates
Slope	4	0.00005002		
Sugar	1	0.00000021	3.2907	
Water	1	0.00000011	1.7479	
Sugar × Water	1	0.00000327	51.9821	0.0000376
Fat	1	0.00000116	18.4526	0.0010838
Intercept				0.0177938
Error	22	0.0000139		0.001012
Total (C[1)])	26	0.00005140		

[1)]Corrected means deletion of intercept from the ANOVA table.
[2)]$Kp = 0.0177938 + 0.0010838X_3 + 0.0000376X_1X_2$ (R^2=0.96). X_1 is % of sugar in cookie dough, X_2 and X_3 are final % of water and fat in baked cookie.

Table 7. ANOVA (corrected[1)]) table of isopropanol for factorial work and parameter estimate of each significant factor for determination of regression equation[2)]

Source	Degree of freedom	Sum of square	F-value	Estimates
Slope	4	0.05999161		
Sugar	1	0.00002847	2.2922	
Water	1	0.00366567	295.105	0.0290727
Sugar × Water	1	0.0009681	77.9368	-0.000646
Fat	1	0.00000311	0.2504	
Intercept				0.0475888
Error	22	0.00027327		
Total (C[1)])	26	0.06026488		

[1)]Corrected means deletion of intercept from the ANOVA table.
[2)]$Kp = 0.0475888 + 0.0290727X_2 - 0.000646X_1X_2$ (R^2=0.99). X_1 is % of sugar in cookie dough, X_2 is final % of water and fat in baked cookie.

Table 8. ANOVA (corrected[1)]) table of methyl ethyl ketone for factorial work and parameter estimate of each significant factor for determination of regression equation[2)]

Source	Degree of freedom	Sum of square	F-value	Estimates
Slope	4	0.01317199		
Sugar	1	0.00000194	0.9720	
Water	1	0.00082466	414.0183	0.0137894
Sugar × Water	1	0.00011471	57.5896	-0.000222
Fat	1	0.00000991	4.9740	0.0031639
Intercept				-0.033988
Error	22	0.0004382		
Total (C[1)])	26	0.01321581		

[1)]Corrected means deletion of intercept from the ANOVA table.
[2)]$Kp = -0.033988 + 0.0137894X_2 + 0.0031639X_3 - 0.000222X_1X_2$ (R^2=0.98). X_1 is % of sugar in cookie dough, X_2 and X_3 are final % of water and fat in baked cookie.

Table 9. ANOVA (corrected[1)]) table of toluene for factorial work and parameter estimate of each significant factor for determination of regression equation[2)]

Source	Degree of freedom	Sum of square	F-value	Estimates
Slope	4	0.00048889		
Sugar	1	0.00000065	3.1487	
Water	1	0.00000034	1.6618	
Sugar × Water	1	0.00000192	9.3488	0.0000288
Fat	1	0.00000562	27.3265	0.0023827
Intercept				0.0741477
Error	22	0.0000452		
Total (C[1)])	26	0.00049341		

[1)]Corrected means deletion of intercept from the ANOVA table.
[2)]$Kp = 0.0741477 + 0.0023827X_3 + 0.0000288X_1X_2$ (R^2=0.89). X_1 is % of sugar in cookie dough, X_2 and X_3 are final % of water and fat in baked cookie.

it did not affect the non-polar solvents. These results were in accord with hydrogen bonding attraction between the polar solvents and water.

The effect of sugar and water interaction: For all of the solvents, the F-value of sugar and water interaction is larger than the tabulated F value at the 5.0% level, which means sugar-water interaction affected partitioning behavior significantly. This result indicated that there could be a crystallinity effect that depends on a competition for the water. For example, the sugar can crystallize and cover active sites or produce interaction between the flour and fat. This would change the ability of the sol-

Table 10. Calculated Kp by using a regression equation with % H_2O, % fat and % sugar, and experimental Kp values for lab-made cookies for each solvent

Solvent	Calculated Kp[1)]	Experimental Kp	Difference[2)]
Ethyl acetate	0.07287	0.07427	1.92%
Hexane	0.04779	0.04683	2.01%
Isopropanol	0.15182	0.13951	8.11%
Methyl ethyl ketone	0.10094	0.11429	13.23%
Toluene	0.13568	0.12163	10.36%

[1)]Kp values by using regression equation from the factorial experiment.
[2)]% difference between the calculated Kp by regression equation and the experimental Kp of #2 lab-made cookie.

vents to penetrate and interact.

The effect of fat: For toluene, hexane, ethyl acetate and methyl ethyl ketone, the F-value of fat is larger than the tabulated F value at the 5.0% level, and for isopropanol, the value is smaller. This behavior means fat affected partitioning behavior significantly in all of solvents except isopropanol. Among them, toluene was affected most significantly.

Prediction of partitioning behavior of cookie with regression equation using % H_2O, % fat and % sugar

Statistical analysis by the SAS computer program determined a parameter estimation of each significant factor in each solvent and yielded a regression equation and are shown in Tables 5～9. Kp can be calculated by inserting % water and % fat found by analysis in the cookie, and % sugar in the cookie formula. For example, the hexane regression equation was as follows:

$$\text{Kp} = 0.0177938 + 0.0010838 \times 24.83 \text{ (fat content)} + 0.0000376 \times 15.18 \text{ (sugar content)} \times 5.41 \text{ (water content)} = 0.04779$$

The calculated Kp values using this regression equation and experimental Kp of representative lab-made cookies for each solvent were shown in Table 10. The % difference between the calculated Kp and the experimental Kp of lab-made cookies in five solvents ranged from 1.92% to 13.23%. Previous research (11) showed the % difference between the Kp calculated by using baked cookie ingredient composition and experimental Kp of lab-made cookie in five solvents ranged from 11.25 to 18.20. Therefore, the calculated Kp values determined with the correction factor were more reflective of the interaction between sugar and water than the Kp values of each ingredient after baking.

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