

Partitioning Behavior of Selected Printing Ink Solvents between Headspace and Chocolate Cookie Samples

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Abstract

Static Headspace Gas Chromatographic analysis was used to study the partitioning behavior of five organic printing ink solvents between chocolate cookie/air systems. Three cookie sample formulations varied with respect to chocolate type and overall percentage of constituents. Major considerations involved differences in fat content and type and resulting variability in chemical and physical structure. Each of the solvents studied (ethyl acetate, hexane, isopropanol, methyl ethyl ketone, toluene) represents a general class of printing ink solvents based on predominate functional group. Values of the partitioning coefficient (K_p) were determined at equilibrium using measured quantities of both solvent and cookie sample in closed systems at temperature of 25, 35, and 45°C. In each of the three cookies at the three test temperatures, toluene always exhibited the greatest value of partitioning to cookie and hexane always exhibited the least. Results also showed that the partitioning behavior of solvents is generally inversely related to temperature and that solvent affinity, though constant for a particular cookie type over all test temperatures, varies significantly among the three cookie types. The preference of each of the five solvents for each cookie sample was also found to vary with temperature. No correlation was found between the extent of partitioning and cookie formulation or physical characteristic of solvent. The Hildebrand parameter, related to ΔH_{mix} (heat of mixing), may be used to describe differences in partitioning based on the overall potential of a solvent/cookie interaction to occur. The potential for interaction is dependent upon the chemical structure of the cookie sample and thus the availability of 'active-sites' required for a given solvent.

Key words: partition coefficient, printing ink solvents, cookie and cookie formulation, Hildebrand parameter

INTRODUCTION

With the increasing use of plastic films for the packaging of food products, it has become necessary to evaluate any and all possible food/package interactions that might occur in their relationship to food safety and quality. Food/package interaction may occur in either or both of two directions: either the migration of food components to package films or the migration and subsequent interaction of film components to foodstuff (1-5). An example is that of residual printing ink solvents remaining on the film surface following insufficient drying after printing (6). Various organic solvents are used as a medium within which dyes, being either dispersed or solubilized, can be carried to the film surface for the printing of various decoration and information pertaining to the sale and subsequent use of the contained food product. It has been shown that residual levels of such solvents in package of plastic films are capable of migration, followed by flavor changes to contained foods, resulting in a decrease of product quality (7-9). At this point, there is still limited data surrounding the determination of the

variables concerned with the interaction of such organic solvents with foods and the resulting loss in product quality. It is therefore the focus of this research to determine the variables concerned with the interaction of selected organic solvents with chocolate cookie samples in an attempt to alleviate the potential problems discussed. The specific objectives of this research were to determine partition coefficients of five printing ink solvents (hexane, toluene, isopropanol, ethyl acetate, methyl ethyl ketone) between headspace and three different chocolate cookie samples (chocolate chip, magic middles, swirls) at three temperatures (25, 35, 45°C), and to study the factors affecting such partitioning behavior.

MATERIALS AND METHODS

Cookie types and formulation

Three chocolate cookie types were used in our experiments. Each consists of a particular chocolate type incorporated into vanilla dough. The chocolate cookie contains discrete chocolate chips, magic middles a chocolate cream center, and the swirls a chocolate liquor mixed

Table 1. The composition of chocolate swirls ingredients

	Part A	Part B
White enriched flour	31.6	9.2
Soybean oil	18.9	8.7
Sugar	10.5	11.9
Salt	0.5	0.1
Water	3.5	—
Sodium bicarbonate	0.3	—
Chocolate liquor	—	4.1
Powdered egg (whole)	—	0.8

Values listed above given as percentage of final dough weight.

throughout the entire cookie. The chocolate chip and magic middles cookie were obtained from a local food company while the swirls were made in our laboratory.

The cooking method (baking at 260°C for 12 min) of the commercial cookies was used for the preparation of lab-made cookies. The baking conditions were selected based on previous work and commercial recipes. Two separate batches of ingredients were prepared (Table 1).

Part A and B: Dry ingredients were sifted together, water and oil were then added and the components were mixed by hand. Part A and B were then lightly mixed together, rolled out with a small amount of flour and the dough cut into circles. The cookies were then baked and cooled on the baking sheet to ambient temperature.

Solvents

Five printing ink solvents were used for determining partition coefficient value. Hexane, toluene, isopropanol, methyl ethyl ketone and ethyl acetate, which have 99.9% purity, were from Fisher Scientific Co. Reagents to analyze fatty acid compositions were: sodium hydroxide, methanolic solution of BF₃ (12.5% BF₃ content and 99.9% purity), hexane (99.9% purity), and anhydrous sodium sulfate, all from Fisher Co. (Fairlawn, NJ, USA). Saturated sodium chloride was obtained from Sigma-Aldrich Co. (St. Louis, MO, USA).

Extraction of fat content and fat component in each cookie sample

The modified method of Paquot and Hautfenne (10) was used to determine fat content. Duplicate samples of each type were put into a cellulose extraction thimble (33 mm (ID) × 94 mm (length), Whatman Ltd., Picataway, NJ, USA), which was placed in a Soxhlet extraction apparatus with 150 mL hexane for 7 hr. Hexane was removed by distilling into the extraction apparatus, and the concentrated solution was transferred to a tared 100 mL flask to complete removal. The flask was cooled in a dessicator and weighed for determining fat weight. The fatty material was converted to esters by boiling with 7 mL methanolic NaOH solution followed by 10

mL methanolic solution of BF₃. Ten mL hexane was added and then saturated sodium chloride solution was added to the neck of the flask (100 mL). The mixture was separated in a separatory funnel (100 mL) and the upper level was dried with anhydrous sodium sulfate 0.3 ~ 0.5 g. One microliter of each was injected into a Varian 3300 Gas Chromatograph with flame ionization detector and silica capillary column (Supelcowax 10, 0.32 mm × 30 m, Supeclo Co., Bellefonte, PA, USA). Operating conditions included He carrier gas at 1.5 cc/min and injection port at 230°C, column 145°C, and detector 230°C. Fatty acid components were identified and determined by comparing with authentic standard fatty acid methyl ester peak retention times and peak areas.

Measurement of water content

Moisture content was measured by using drying oven method (11). Triplicate samples (5.0 g) were put in a weighing dish and stored in a preheated oven at 130°C for 1 hr. The heated sample was transfer to dessicator and stored for 30 min, and weighed at room temperature for water weight.

Melting range of chocolate samples

Three cookie samples have different type of chocolate (chocolate chips, chocolate cream and chocolate liquor), each of which has different fat components. Melting range was determined on 0.3 g of each sample between covered glass on a thermal hot stage under a Bristoline thermal microscope with polarizer and thermometer. The temperatures at which the first and last crystals disappeared at a heating rate of 0.2°C/min were recorded.

Determination of equilibrium day for each solvent on each cookie

Each of the five solvents was tested in conjunction with each of the three cookie samples at 25, 35 and 45°C. These specific temperatures were chosen as they reflect values below, at and above the melting points of the various chocolates contained in our cookie samples (12). Analysis at these temperatures would result in phase transitions of the fat portion of the chocolate within our samples. It is speculated that these phase transitions may affect values of partition coefficients and so we deemed these temperatures as important variables for consideration. For each test temperature, time periods of testing were either one, three or five days. For each time period, at least three of both sample and control vials were prepared. Initially, 5.0 g of each sample was placed into a 60 mL vial and sealed with rubber and cap. Blank vials without sample were also prepared. After injection of 0.5 µL of each solvent into each blank vial and vial

with sample, the vials were stored in a water bath at 25°C. A 200 µL sample of headspace from each vial was injected into the GC every other day. Equilibrium day was determined by plotting % difference between control and sample headspace values until they did not change.

Determination of partition coefficient values

Partition coefficient values were determined in a closed system based on the method of Biran et al. (13). Sixty milliliter vials with individual cookie samples weighed (5.0 ± 0.1 g) and blank bottles were prepared with sealing of septa. For 25, 35 and 45°C determinations, bottles were injected with 0.5 µL of each solvent. Volumes were converted to mass for Kp determination from densities of the pure solvents. Equilibrium time varied from 1 to 3 days, according to solvent and storage temperature. 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 GC by gas tight syringe. 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:

$$K_p = \frac{\text{Wt. of solvent in headspace in blank} - \text{Wt. of solvent in headspace in bottle with sample}}{\text{Weight of sample} / \text{Weight of solvent in 1 mL headspace in bottle with sample} / \text{Density of air}}$$

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

Table 2. Percentage of water and fat content in cookies¹⁾

	Moisture content (Average ± SD)	Fat content (Average ± SD)
Chocolate chips	3.80 ± 0.02	25.24 ± 0.15
Magic middles	2.54 ± 0.04	29.13 ± 0.32
Swirls	1.16 ± 0.00	34.70 ± 0.31

¹⁾% of total weight after baking.

RESULTS AND DISCUSSION

Water, fat content and fat composition of cookie samples

Part of our research was to determine the relative effects of % fat and % water contents on Kp of the each cookie sample. The moisture content of a cookie product is generally considered to be relatively low compared to other baked products. The moisture contents of the three cookie types ranged from 1.16% to 3.80% (Table 2). Despite the presence of relatively small amounts, water may remain available in the cookie for interaction with polar solvents. The possible differences in the potential for polar solvents to hydrogen bond to the water available in each of the three cookie types may be considered as an important factor in the partitioning of these solvents and should be investigated further.

The relative effects on Kp of differences in % fat content and degree of crystalline structure of chocolates were determined. Each cookie sample had different ratios of fatty acids. Among the fat components, the decreasing order of melting point was stearic acid (69.6°C) > palmitic acid (62.9°C) > oleic acid (13.4°C) > linoleic acid (-5.0°C). The ratios of each fatty acid component were compared (Table 3) as well as the melting point range of each chocolate types (Table 4). Chips had the highest and longest melting range. The chocolate chips were the most crystalline at 25°C, and were molten at 35°C. The cream in magic middles was the least crystalline at 25°C and melted rapidly, as expected from its composition. Liquor in swirls was partially melted at 25°C, and was molten at 35°C.

Table 3. Analysis of fat compositions

Sample (% fat)	Fatty acids	Mass ratio	Ratio (saturated/unsaturated) ¹⁾
Chocolate chips (26.89 ± 0.26)	Palmitic, stearic, oleic and linoleic	2.4:2.6:3.1:1.0	1.42:1.00
Magic middles (28.52 ± 0.46)	Palmitic, stearic, oleic and linoleic	2.3:1.9:3.5:1.0	0.91:1.00
Swirls (30.70 ± 0.99)	Palmitic, stearic, oleic and linoleic	2.0:2.1:2.9:1.0	1.03:1.00

¹⁾Palmitic acid (mp: 62.9°C), stearic acid (mp: 69.6°C), oleic acid (mp: 13.4°C), linoleic acid (mp: -5.0°C).

Table 4. Melting ranges of three types of chocolate

Chocolate sample	Starting point	Ending point	Melting time ¹⁾
Chips	36.0°C	37.5°C	12 min
Cream	33.0°C	33.5°C	4 min
Liquor	34.5°C	35.5°C	8 min

¹⁾Heating rate of 0.2°C/min.

Partition coefficient variations with temperature

Kps for each solvent at 25, 35, 45°C (Table 5) generally decreased with increasing temperature except for the chocolate chip cookie. There are several possible explanations for this result. (1) As the temperature is increased, the kinetic energy of the solvent also increases. Therefore, there is less potential for any number of solvent molecules to associate and interact with cookie samples. (2) The temperature increases may alter the preference of the interaction of components within the samples for other components of the sample rather than for interaction with solvent. (3) If the majority of interactions between solvent and cookie samples reflect adsorption to the samples rather than absorption, increases in temperature would cause a much easier release of solvent from the surface of the samples. The only exception to this behavior was seen in the case of the chocolate chip cookie, where Kp with each of the solvents did not decrease with increasing temperature. The results show an increase in Kp value at 35°C from 25°C and then a decrease at 45°C. The results shown for these systems may reflect a change in the types of component such as melting points of the fats.

Because of relative high ratio of unsaturated fatty acid (Table 3) in magic middles (chocolate cream) and swirls (chocolate liquor), and the reduced crystallinity at room temperature, increasing the temperature did not affect the partition coefficient value of printing ink solvent. How-

ever, chocolate chip cookies (chocolate chip) have a relative high ratio of saturated fatty acids and greater crystallinity at room temperature. Therefore, by increasing the temperature from 25°C to 35°C, the fat in chocolate chip cookies melted and so more solvent could migrate into the chocolate, which result in an increased Kp.

Effect of solvent properties on the partition coefficient

At each experimental temperature, the order of Kp values for each solvent in the three cookie samples remained constant, and in the order shown below.

Chips: toluene>isopropanol>methyl ethyl ketone>ethyl acetate>hexane

Magic middles: toluene>methyl ethyl ketone>ethyl acetate>isopropanol>hexane

Swirls: toluene>methyl ethyl ketone>ethyl acetate>isopropanol>hexane

In each of the three cookies at the three test temperatures, toluene always exhibited the greatest value of partitioning to cookie and hexane always exhibited the least. By definition of Kp (the concentration of solvent in cookie/concentration of solvent in headspace), the extremely high Kp values for toluene indicate that in all cases, toluene is absorbed most by the cookie than any other of the solvents tested, while hexane is absorbed the least. While both of these solvents are relatively insoluble in water and have similar molecular weights, their boiling points lie at the extremes of the five solvents – 110.6°C (toluene) and 68.95°C (hexane). Hexane, with a lower boiling point, is a more volatile solvent and is thus less easily held by the cookie samples, resulting in lower Kp values, while toluene, on the other hand, is relatively non-volatile and tended to remain in the cookie samples more at all test temperatures. The remaining three solvents, with boiling points intermediate to those of both toluene and hexane, exhibit Kp values

Table 5. Average Kp for each solvent at 25, 35, and 45°C

Cookie sample	Solvent	25°C	35°C	45°C
Chocolate chips	Ethyl acetate	0.0723 ± 0.0038	0.1064 ± 0.0024	0.0943 ± 0.0056
	Hexane	0.0494 ± 0.0024	0.0511 ± 0.0009	0.0316 ± 0.0003
	Isopropanol	0.1106 ± 0.0025	0.1456 ± 0.0022	0.1142 ± 0.0078
	MEK	0.1084 ± 0.0039	0.1177 ± 0.0012	0.0988 ± 0.0024
	Toluene	0.2621 ± 0.0040	0.2839 ± 0.0054	0.1743 ± 0.0113
Magic middles	Ethyl acetate	0.2080 ± 0.0054	0.1381 ± 0.0041	0.0794 ± 0.0040
	Hexane	0.0654 ± 0.0052	0.0516 ± 0.0010	0.0371 ± 0.0017
	Isopropanol	0.1219 ± 0.0064	0.0979 ± 0.0048	0.0765 ± 0.0007
	MEK	0.2190 ± 0.0125	0.1458 ± 0.0091	0.0854 ± 0.0037
	Toluene	0.5172 ± 0.0176	0.3269 ± 0.0010	0.2314 ± 0.0042
Swirls	Ethyl acetate	0.1536 ± 0.0084	0.1375 ± 0.0090	0.0971 ± 0.0014
	Hexane	0.0619 ± 0.0008	0.0471 ± 0.0015	0.0342 ± 0.0009
	Isopropanol	0.1183 ± 0.0034	0.1123 ± 0.0003	0.0753 ± 0.0030
	MEK	0.1585 ± 0.0044	0.1445 ± 0.0003	0.1065 ± 0.0044
	Toluene	0.4294 ± 0.0011	0.3083 ± 0.0045	0.2065 ± 0.0054

Table 6. Hildebrand solubility parameter value of each solvent and triglyceride

Solvent	δ (MPa ^{1/2})
Isopropanol	21.0
Toluene	18.7
Methyl ethyl ketone	18.4
Ethyl acetate	17.9
Hexane	14.9
Triglyceride	18.6

between those of both toluene and hexane in all cases. Although there are some shifts in the partitioning order for these solvents among the cookie types, each cookie type does exhibit a distinct solvent order at all temperatures. Slight deviations from these standard orders based on the fact that some data points cannot be considered as distinct from each other all occur for a given system at specific temperatures. More explanations are needed on the possible solvent/cookie interactions that may occur based on such variations.

Solvent affinity order

Variations in solvent order based on K_p value between the three cookie types may be explained by comparing Hildebrand solubility parameter (δ) values for the solvent and triglyceride of cookies (14) (Table 6). The order of K_p values for each solvent in each cookie was the same at all temperature except isopropanol: toluene>methyl ethyl ketone>ethyl acetate>hexane. The Hildebrand equation for heat of mixing shown below predicts that compounds with similar δ have a greater tendency to mix (15).

$$\Delta H_{\text{mix}} = V_1(\delta_1 - \delta_2)^2 \varnothing_2 \quad [1]$$

where ΔH_{mix} is the partial molar heat of mixing; V_1 is the partial molar volume of the penetrant; \varnothing_2 is the volume fraction of the absorbent in the mixture; δ_1 and δ_2 are the square roots of the cohesive energy density of the absorbent and penetrant.

Using Eq. [1] and the δ values (Table 6) yields the following increasing order of ΔH_{mix} values in J/mol: toluene 0.5, MEK 5, ethyl acetate 52, isopropanol 439 and hexane 1811. Thus, toluene would mix more easily than hexane, for example, and the data predicts the series that was found experimentally, except for isopropanol. The isopropanol may be an anomaly due to the high polarity of its -OH functional group that can participate

in hydrogen bonding in the chocolate compositions and predominate over the order of attractive forces indicated by its δ value, which is influenced only by dispersion forces.

REFERENCES

1. Gilbert SG. 1976. Migration of minor constituents from food packaging materials. *J Food Sci* 41: 955-958.
2. Halek GW, Levinson JJ. 1989. Partitioning and absolute flavor threshold interaction of aliphatic and aromatic food packaging solvents in high fat cookies. *J Food Sci* 54: 173-176.
3. Vivek G, John DF. 1997. Migration and sorption phenomena in packaged foods. *Crit Rev Food Sci Nutr* 37: 519-559.
4. Charara ZN, Williams JW, Schmitt RH, Marshall MR. 1992. Orange flavor absorption into various polymeric packaging materials. *J Food Sci* 57: 963-966.
5. Koneczal JB, Harte BR, Hoojjat P, Giacini JR. 1992. Apple juice flavor compounds sorption by sealant films. *J Food Sci* 57: 967-970.
6. Halek GW, Levinson JJ. 1988. Partitioning behavior and off-flavor thresholds in cookies from plastic packaging film printing ink compounds. *J Food Sci* 53: 1806-1808.
7. Kim HK. 1990. Volatiles in packaging materials. *Crit Rev Food Sci Nutr* 29: 255-271.
8. An DJ. 2009. Determination and prediction of partition coefficient value (K_p) for printing ink solvents on cookie from K_p of each cookie ingredient. *J Food Sci* 14: 246-251.
9. Halek GW, Chan A. 1994. Partitioning and absolute flavor threshold interactions of aliphatic food packaging solvents homologs in high-fat cookies. *J Food Sci* 59: 420-423.
10. Paquot C, Hautfenne A. 1987. Preparation of the fatty acid methyl esters. In *Standard Methods for the Analysis of Oils Fats and Derivatives*. 7th ed. Blackwell Scientific Publications, Cambridge, MA, USA. p 123.
11. AOAC. 1980. *Official methods of analysis*. 14th ed. Association of Official Analytical Chemists, Washington, DC, USA. p 211.
12. An DJ. 2004. Compositional and Structural effects on migration behavior of printing ink solvents on lab-made cookies. *Food Sci Biotechnol* 13: 707-711.
13. Biran D, Giacini JR, Hayakawa K, Gilbert SG. 1979. Sorption of vinylchloride by selected food constituents. *J Food Sci* 44: 59-61.
14. Barton AFM. 1991. Homologous series and homomorphs. In *Handbook of Solubility Parameters and Other Cohesion*. CRC Press, Boca Raton, FL, USA. p 61.
15. Hildebrand J, Prausnitz J, and Scott R. 1970. *Regular and related solutions*. Van Nostrand Reinhold Publ. Co., New York, NY, USA. p 631.

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