Chemical and Organoleptic Properties of Dried Emulsions

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ABSTRACT

Safflower oil was incorporated into a model emulsion system containing emulsifier, carbohydrates, antioxidants, and protein. Emulsions were spray dried and the dry powders were stored at 60 C. Their oxidation rates were measured by headspace gas analysis (Oxygen absorption and carbon dioxide generation); peroxide and carbonyl values also were run. Although these objective tests all gave good correlation with average flavor scores, results show that oxygen absorption was superior to others as an indicator of flavor deterioration. Stepwise, multiple linear regression analysis showed that oxygen absorption and carbonyl value gave an equation which can predict flavor scores with a high degree of accuracy.

INTRODUCTION

In the first study in this series (1) we sought a correlation between chemical and organoleptic properties of various oxidized fats. The results showed that measurements involving the primary oxidation step (peroxide value, oxygen absorption, and pentane value) generally gave a good correlation, while those measuring the secondary oxidation products (benzidine, thiobarbituric acid, and octanoic acid values) gave a poor correlation. It was evident from this study that the correlations found varied significantly with the particular fat under study and, to a lesser extent, with the conditions of oxidation. Regardless of the fat used, however, a high correlation between oxygen absorption, peroxide value, and pentane level characterized the results. There was a straight line relationship among these 3 parameters, indicating that when an oil was oxidized alone, the rate of peroxide decomposition was negligible compared to its rate of formation, at least in the range studied. We had reason to believe that this was not true of an oil which was part of a multicomponent system. It was the purpose of this study to confirm this difference, to determine its dimensions, and to ascertain, if possible, its importance to the development of oxidative flavor. As often repeated in the literature (2), peroxides are not in themselves flavorful; it is their decomposition that results in off flavors. It seemed fruitful for us to focus on this aspect of the oxidative problem.

To put some dimensions on peroxide decomposition, we oxidized safflower oil both alone and in the presence of other components in the form of a dried emulsion. The results obtained by heating safflower oil alone, as shown in Table I, verify what had been seen in the earlier study (1). The similarity between peroxide values (PV) and O_2 absorption values was apparent. The last value was the exception, indicating that a high degree of oxidation had to be reached before a discrepancy between the two appears. When this same oil was incorporated into a carbohydrate-protein matrix, however, the difference appeared much earlier. As shown in Figure 1, O_2 absorption and the PV curve were appreciably different after ca. 1 week at 50 C, indicating a faster decomposition rate of peroxides.

TABLE I

PV and O_2 Absorption of Safflower Oil at 50 C

Time (Days)	O_2 Absorption (Meq/Kg)	PV (Meq/Kg)
0	3.0[a]	3.0
1	4.3	4.4
2	5.9	5.8
3	7.3	7.5
6	14.3	13.8
11	19.8	19.3
22	44.5	43.5
56	273.3	241.8

[a]3.0 Meq/Kg (initial PV) added to all absorption values.

EXPERIMENTAL PROCEDURES

Materials

In most experiments, antioxidant-free safflower oil was used. The oil was purchased from Welch, Home and Clarke Co. (New York, NY). Prior to use in the emulsion, the oil was stabilized with 0.02% antioxidant. The antioxidant best suited for this oil seemed to be *tertiary*-butylhydroquinone (TBHQ) (Eastman Chemical Products, Inc., Kingsport,TN.) The emulsifier used, Acidan Z-1, was produced by Grindstedvaerket, (Aarhus, Denmark), and was used at the 1% level. Various laboratory prepared protein isolates were tried, including milk, cottonseen, soy, and chickpea. Commercial sodium caseinate (Land O' Lakes Co., Minneapolis, MN) was favored because it was readily available and highly dispersible. The carbohydrate used was Mor-Rex 1435, a high maltose corn syrup (Corn Products Co., Argo, IL).

Methods

Typically about 2 Kg wet emulsion was prepared by mixing 105 g safflower oil, 890 g corn syrup, 10 g emulsifier, 50 g protein, and 850 g water in a Waring Blender for 5 min. The resulting emulsion then was spray dried in a Nichols-Niro portable spray dryer. The inlet temperature

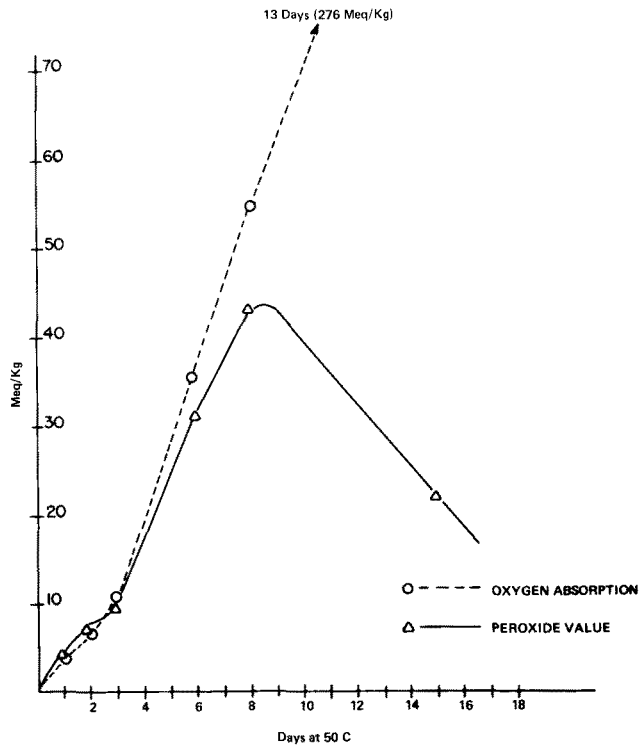

FIG. 1. Oxidation of a dried emulsion: peroxide value vs oxygen absorption.

TABLE II

Dried Emulsion Composition

Components	Sample Number (% dry wt)				
	I	II	III	IV	V
Safflower oil	20.5	20.5	20.5	20.5	20.5
Corn syrup[a]	78.4	78.4	73.1	73.1	78.4
Emulsifier[b]	1.1	1.1	1.1	1.1	1.1
Sodium caseinate	-	-	5.3	5.3	-
Antioxidant	-	c	-	c	d

[a]High maltose.

[b]Citrated monoglycerides.

[c]*tertiary*-butylhydroquinone (TBHQ) (0.02% based on fat).

[d]Tenox 20 (20% TBHQ, 20% citric acid, 60% propylene glycol); 0.1% based on fat.

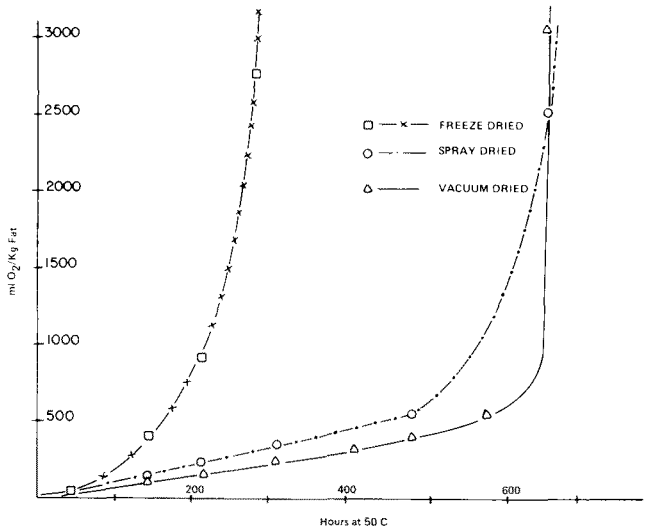

FIG. 2. Type of drying and oxidation rate.

ranged from 160-175 C; the outlet temperature from 70-90 C.

The spray dried powders were stored at -17 C under N_2 until used. The oxidation was carried out in pint sized brown bottles stoppered with air tight rubber septa. A number (10-15) of 100 g portions of each sample were introduced into the bottles with a powder funnel. The bottles were placed in a dark room at 32 ± 1 C, and samples were removed periodically for headspace analysis (O_2 and CO_2 determinations). At the proper O_2 absorption level, the sample was removed from the hot room and 50 g was slurried in 150 ml hot water for flavor evaluation. The remaining 50 g were used for other tests. Peroxide value (PV) was obtained by dispersing 10.0 g dry powder (2.0 g fat) in acetic acid:chloroform solution and titrating in the usual manner (3).

Headspace analysis for O_2 has been reported in detail elsewhere (1). CO_2 determination was carried out by injecting 0.50 ml of headspace into a Hewlett-Packard Model 5750 gas chromatograph. The stainless steel column (12 ft. x 1/8 in. outer diameter) was filled with 80-100 mesh Chromosorb 102 obtained from Johns-Manville (Lompoc, CA) The column was operated at 100 C, and the thermal conductivity detector was set at 240 milliamps. Helium was the carrier, and it was used at 40-60 ml/min.

The flavor evaluation was similar to that done in the previous study (1). The panel consisted of about 20 colleagues, most of whom had participated in the prior test. Before the first actual evaluation session, each panel member was acquainted with the flavor ballot which was identical to that used previously. At this time, the panelist also was allowed to taste both oxidized and unoxidized samples typical of dried emulsions at various stages of oxidation. During the actual test 5 controls and 5 oxidized samples were slurried in 150 ml hot spring water (60-70 C). The beakers containing the samples were placed in a beaker warmer controlled at 60 ±2 C. The panelist was asked to taste and rate the control of each set first, and then, according to the scale on the ballot, rate the difference between it and the oxidized sample. The scores of all the tasters were added and the average was obtained. In computing the average flavor score (AFS) for each sample, those judgments that differed by more than 2 units from the mean were discarded. For any given sample, a maximum of 15% of the judgments were eliminated this way.

For the spectrophotometric determinations, 10.0 g of dried emulsions were dispersed in 60 ml deionized water, acidified with 10 ml 4N HCl and mixed in a Waring Blendor at high speed for 2 min. A 35 ml aliquot was transferred to a micro kjeldahl distilling set-up with a 15 ml water rinse and 2-3 drops silicone antifoam (SAG 470, Union Carbide Corp., New York, NY). The first 25 ml of distillate was collected in ca. 10 min; 10.0 ml of this distillate was pipetted into a stoppered test tube containing 10.0 ml 0.1% dinitrophenylhydrazine in 1N HCl, and heated at 60 C in a water bath for 30 min. The sample then was cooled to room temperature under running tap water. While shaking vigorously, 20.0 ml of a 4% KOH solution in absolute ethanol (prepared daily) was added; the solution was allowed to stand for 10-15 min; the optical density at 460 and 500 nm then was measured using a Model 240 spectrophotometer (Gilford Labs, Inc., Oberlin, OH). The optical density thus obtained was arbitrarily called the carbonyl value (CV) of the sample. Each sample was run in duplicate, and the CVs reported are the average of 2 determinations.

RESULTS AND DISCUSSION

Of the parameters investigated in the initial phase of this work, none seemed to be as important as the method used to produce the dried emulsion. As Figure 2 shows, the drying procedure definitely influenced the oxidative stability of the product. Freeze drying produced an emulsion of great surface area. Vacuum and spray drying consisted in forming a plastic film which shrunk as the drying progressed. This resulted in a product of greater density, lower surface area, and higher oxidative stability than a freeze dried emulsion. Of these two, spray drying was chosen because it was more rapid and reproducible.

The compositions of the 5 dried emulsions prepared and tested appear in Table II. They are numbered I-V, and, for the sake of brevity, are referred to simply as: control, TBHQ, caseinate, caseinate + TBHQ, and Tenox 20, respectively.

Some characteristics of these 5 dry powders appear in Table III. The moisture, iron, and copper content were all about the same; their bulk densities also were comparable. The only significant difference here was the smaller emulsion particle size of the caseinate containing samples. The average particle size was determined by using a Model TA II Coulter Counter with Isoton® as the dispersant. Both of these were purchased from Coulter Electronics (Hialeah, FL).

What is shown in Figure 3 is typical of the results obtained. The lower curve shows the actual distribution of particle sizes ranging from 0.5-12.7 microns. The upper curve is a cumulative distribution which was helpful in determining the average particle size of the mixture. With this sample (control), over 60% of the particles fell in the 0.6-2.5 micron range, and the average particle size was ca. 1.5 microns.

The above preliminary testing was followed by organoleptic and objective tests. The initial AFS in this study were somewhat lower than the previous study and ranged

TABLE III

Dried Emulsion Properties

	Sample Number				
	I (Control)	II (TBHQ)[a]	III (Caseinate)	IV (Caseinate + TBHQ)[a]	V (Tenox 20)
Moisture (%)	1.4	1.3	1.6	1.6	1.2
Iron (ppm)	4.8	4.0	6.1	6.1	4.6
Copper (ppm)	0.5	1.2	0.8	0.9	0.9
Average particle size (microns)[b]	1.57	1.45	0.98	0.97	1.85
Bulk density	0.55	0.55	0.52	0.53	0.56

[a]TBQH = *tertiary*-butylhydroquinone.

[b]Measured in dilute NaCl solution.

between 7-8. This was to be expected because the substance tasted here was not a bland oil, but a sweet powder. The taste panel members were asked to disregard this sweet note and concentrate on off or rancid notes, i.e., to focus on the difference between the starting material and the corresponding oxidized sample. Again, we found that the reproducibility was ±1 AFS units. Bias due to the order of testing (identifying a sample as oxidized when it was not) caused the AFS to drop by ca. 0.5; for this reason, a change of 0.5 or less in AFS was not considered significant. Figure 4 shows the change of AFS of the 5 samples with time. From this is was evident that the caseinate-TBHQ sample (IV) was the most stable to oxidation, while the caseinate sample (III) was the least stable. The latter was hard to explain, because previous work in this laboratory and elsewhere (4) had always shown that protein served to stabilize a dried emulsion against oxidation. Because this was not the main thrust of the study, this anomaly was not pursued further.

From an analytical standpoint, an analysis of the fat in the dried emulsion was considered preferable because the conventional methods would be applicable. Some preliminary testing convinced us, however, that this would be undesirable. Besides extra time required to extract fat from the powders, it soon became clear that it was not possible to remove fat quantitatively without using harsh methods, e.g., acid digestion, which would destroy compounds of interest. Previous experience had indicated that the oxidized fat fraction was more difficult to extract. For this reason, the PVs were measured directly on the powder. This made the end point somewhat indistinct, especially in the case of the caseinate containing samples. However, results on a 10.0 g powder sample were reproducible.

Because of the reasons cited above, the pentane and octanoic value determinations used in the first study were not run in this case. The powders were dispersed in acidified, deionized water and steam distilled in a micro Kjeldahl

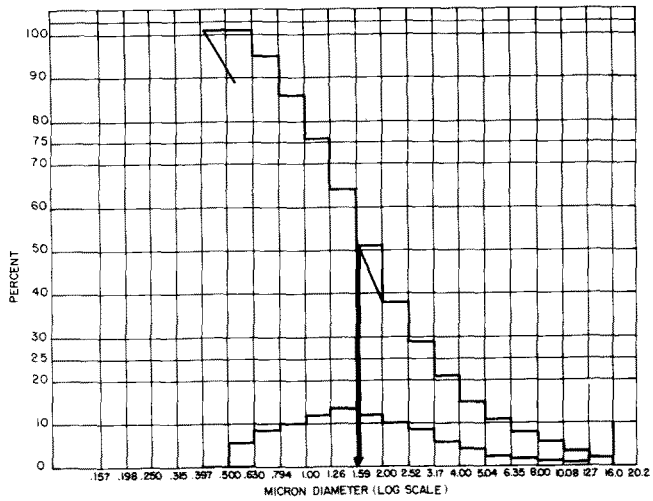

FIG. 3. Particle size analysis of sample I (control). Aperture = 30μ; average particle size = 1.57μ.

apparatus in a manner similar to that described for soybean flakes (5). Aliquots of the distillate were analyzed spectrophotometrically after adding p-anisidine (6), thiobarbituric acid (7), or dinitrophenylhydrazine (DNPH) reagent. The absorptivity with the first 2 reagents was too low to be of practical use. The DNPH reagent gave substantial optical density (OD) and was used routinely for all samples. According to Jordan and Veatch (8), the wine red color obtained with dinitrophenylhydrazones in the presence of alkali was linear with concentration from 400-500 mμ. A reading was taken at 460 mμ, because previous work indicated that this was where a maximum for unsaturated carbonyls occurred (9); 500 mμ was used because the method gave maximum OD at this wave length.

Table IV shows the complete evaluation data of sample I

TABLE IV

Complete Evaluation: Sample I (Control)

Days at 32 C	Average flavor score (AFS)	Oxygen absorption (Meq/Kg oil)	Peroxide value[a]	CO_2 evolved (mM/Kg oil)	Carbonyl[b] value 460mμ	Carbonyl[b] value 500mμ
0	7.7	-	9.5	-	-	-
1	7.1	0.9	14.0	0.17	0.19	0.23
2	7.6	2.1	14.5	-	0.24	0.28
3	6.7	2.4	17.0	0.24	0.29	0.38
4	7.2	10.1	15.0	0.19	0.25	0.38
5	6.3	18.1	33.0	0.19	0.36	0.50
6	4.4	70.9	67.0	0.67	0.57	0.74
7	4.1	87.1	97.5	1.04	0.78	1.19

[a]Meq/Kg, determined on 10.0 g of powder (2.0 g fat).

[b]Optical density, 1.00 cm cells.

TABLE V

Complete Evaluation: Sample II (TBHQ)[a]

Days at 32 C	Change in flavor[b] (ΔAFS)	O_2 Absorption	Peroxide value	CO_2 Evolution	CV[c] 460	CV[c] 500
0	0	0.0	9.0	-	-	-
1	0.5	0.6	8.5	0.09	0.26	0.33
2	0.6	0.8	12.5	0.10	0.21	0.28
3	0.5	2.4	15.0	0.29	0.38	0.48
4	0.7	7.1	13.5	0.22	0.30	0.38
5	1.3	17.3	27.5	0.23	0.43	0.58
6	1.4	36.1	31.0	0.25	0.46	0.62
7	3.7	69.4	65.5	0.73	0.57	0.79

[a]TBHQ = *tertiary*-butylhydroquinone.

[b]Average initial average flavor score (AFS) = 7.6; range = 7.4-7.9.

[c]CV = Carbonyl value; optical density (OD) at the respective wavelengths; units of the other determinations are the same as those in Table IV.

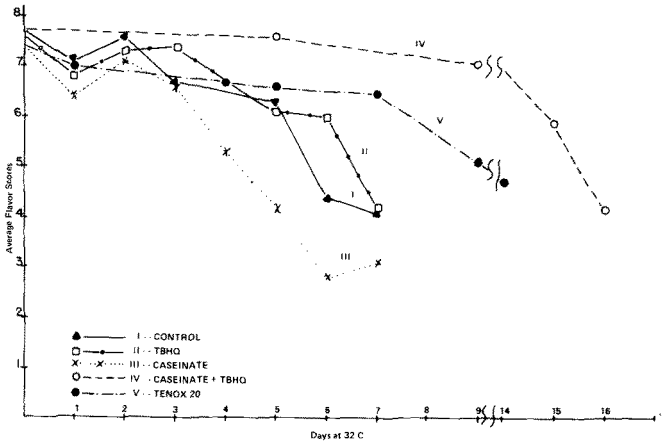

FIG. 4. Change of average flavor scores of the dried emulsions with time. TBHQ = *tertiary* butylhydroquinone.

(control). As expected, all parameters increased with decreasing AFS; the most notable change occurred between the fifth and sixth day. Note the fairly high initial PV and the fact that when this was added to the oxygen absorption column, the values were fairly close. For the lower PV, the amount of CO_2 generated was somewhat erratic, probably due to the poor sensitivity of the method. Loury has postulated mechanisms whereby a CO_2 molecule is generated when various hydroperoxides decompose (10). In our laboratory we have sought to measure this decomposition by assaying the amount of CO_2 in the headspace, and to correlate this value to off flavor development. It immediately became evident that CO_2 increased with increased oxidation. From Table IV and V, it was evident that the CO_2 data corresponded quite closely to a change in flavor and to the increase in carbonyl level. In Table V, the initial PV has been added to the oxygen absorption data. The values were almost identical until the later stages, when substantial oxidation had occurred. Similar results were ob-

TABLE VI

Complete Evaluation: Sample III (Caseinate)

Days at 32 C	ΔAFS[a]	O_2[b] Absorption	PV[c]	CO_2 Evolution	Carbonyl value 460	Carbonyl value 500
0	0.0	0.0	0	-	-	-
1	0.5	0.8	0	0.38	0.14	0.14
2	0.3	1.1	5.0	0.15	-	-
3	0.7	6.2	6.6	0.39	0.16	0.16
4	2.2	28.2	23.0	0.51	0.57	0.79
5	3.3	55.2	34.5	1.24	0.40	0.58
6	4.1	32.5	29.2	0.82	0.49	0.68
7	4.9	102.9	23.5	3.63	0.56	0 68

[a]AFS = average flavor score; average initial AFS = 7.4; range = 6.9-8.0.

[b]Units and conditions for data presented are the same as those in Tables IV and V.

[c]PV = peroxide value.

TABLE VII

Correlation Matrix of Variables[a]

	AFS[b]	ΔAFS[b]	PV	O_2	CO_2	CV[d] 460	CV[d] 500
AFS	1.000						
ΔAFS	-0.979	1.000					
PV	-0.632	0.634	1.000				
O_2	-9.860	0.882	0.761	1.000			
CO_2	-0.751	0.795	0.323	0.811	1.000		
CV_{460}	-0.756	0.761	0.873	0.816	0.520	1.000	
CV_{500}	-0.778	0.776	0.884	0.801	0.494	0.985	1.000

[a]N = 29; 99% confidence level r = 0.470; 95% confidence level r = .367.

[b]AFS = average flavor score.

[c]PV = peroxide value.

[d]CV = carbonyl value.

PREDICTION EQUATION

$$Y = a - 0.02341\ X_1 - 2.6787X_2$$

WHERE Y = PREDICTED AFS
X_1 = ACTUAL O_2 DETERMINATION
X_2 = ACTUAL CV_{500} DETERMINATION

SAMPLE	a
CONTROL	8.18
TBHQ	8.18
CASEINATE	6.99
CASEINATE + TBHQ	7.16
TENOX 20	7.38

$$R^2 = 0.872$$

FIG. 5. Equation predicting average flavor scores (AFS) on the basis of oxygen absorption and the carbonyl value of a sample. TBHQ = *tertiary* butylhydroquinone. AFS = average flavor score.

tained in sample V, where the antioxidant was complemented by the use of a known metal deactivator (citric acid). The latter was, undoubtedly, responsible for its significantly slower rate of oxidation and the more gradual drop in AFS (Fig. 4). The results were less clear cut with the casein containing samples (III and IV), but the general trends remained the same as shown in Table VI. The initial PV was zero for samples III and IV, indicating a tendency of the protein to bind and/or decompose the peroxides. In these samples we saw the largest discrepancy between PV and O_2 absorption values and the highest CO_2 values.

The complete data for the 5 samples was submitted for statistical analysis to establish a correlation between the organoleptic and the objective determinations. The results are summarized in Table VII. The simple correlation matrix shown there indicates that AFS, Δ AFS, and all chemical tests run correlated with each other very well in most cases. The best single correlation with AFS was obtained with O_2 absorption; the worst with PV. As suspected, for a multicomponent system, O_2 absorption gave a better indication of flavor deterioration than PV.

The complete data were analyzed using stepwise multiple linear regression. The best relationship was obtained by using O_2 absorption and CV_{500}. The prediction equation thus evolved is shown in Figure 5. This equation has an $R^2 = 0.872$. From this prediction equation, a set of contour plots for each of the 5 samples was obtained. One of these sets is shown in Figure 6; this represented the control dried

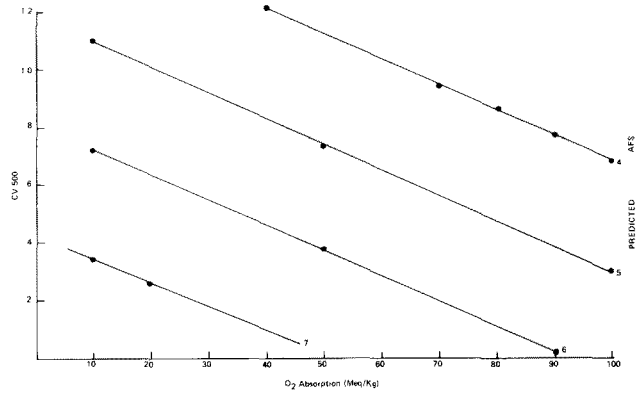

FIG. 6. Contour plots of the predicting equation for sample I (control).

emulsion (sample I). It predicts that an AFS 7 can be achieved only if the O_2 absorption is <50 meq/Kg and if the CV_{500} is <0.4. The correlation between the observed AFSs and the predicted AFSs are high. The lowest was 0.86 (sample III). All others were 0.94-0.99. In the future, it will be interesting to know how these predicted curves fit the flavor data obtained from different multicomponent systems.

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