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Volatiles Retention During Drying of Food Liquids

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The retention of trace volatile components in food liquids during low temperature drying processes is analyzed through a ternary diffusion model. Flux equations for both water and trace organic components are solved numerically for typical drying situations. Several effects are found with the ternary analysis which are not evident from a simpler binary model. The sugar-water composition gradient which develops during drying causes an appreciable transport of the trace volatile species. This transport can occur in the same direction as the transport resulting from the concentration gradient of the volatile species, or in the opposite direction, and can result in a local accumulation of the volatile species. Concentration profiles for both water and dilute volatile components were experimentally measured during nearly isothermal drying of gelled slabs of synthetic sugar solutions and natural fruit juice concentrates. The predicted internal maximum in volatiles concentration is borne out by the experiment, and a satisfactory agreement of observed with predicted volatiles retention is found, within the limits of the experiment.

Food liquids are complex aqueous mixtures containing numerous organic compounds. Natural fruit juices, coffee, tea, and other such substances have a high water content, generally between 80 and 98% by weight. From the standpoints of preservation, storage, and transportation it is advantageous to concentrate or totally dehydrate these food liquids. Unfortunately most juices are very sensitive to heat treatment, both because of degradative reactions and because of the volatilization of components essential to the flavor and aroma of the juice. These volatile flavor components are typically trace organic compounds having a high activity coefficient and hence a high volatility over the aqueous solution. These trace species govern the quality and attractiveness of the drink and their retention is of utmost importance. The particular organic compounds constituting the vapor space or aroma above fruit juices and other food liquids are different from substance to substance (*1* to *3*). A mixture of common sugars—two monosacharides, d-fructose and d-glucose, and one disaccharide, sucrose—makes up between 90 and 98 wt.% of the total dissolved solids in fruit juices (*4*, *5*). Thus, to a first approximation, most fruit juices can be treated as aqueous sugar solutions containing trace amounts of volatile organic components.

The retention of volatile flavor compounds during drying at lower temperatures is usually much better than that at higher temperatures. Thijssen and co-workers have analyzed volatiles loss as a selective diffusion process wherein the ratio of the rate coefficient of the transport of the trace organic species to the rate coefficient of transport of water becomes very low as the dissolved solids content increases (*6* to *8*). They show that this picture agrees well with a number of observed characteristics of volatiles loss during air drying of slabs and spray drying.

Freeze-drying gives particularly good volatiles retention. Data for the effects of several process variables upon volatiles retention during freeze-drying have been reported by Sauvageot et al. (*9*) for natural juices and by Flink and Karel (*10*) for synthetic sugar solutions. Flink and Karel (*11*) have demonstrated that rates of volatiles loss, and hence volatiles mobility, depend specifically upon the morphology of molecular aggregation and the degree of crystallinity. Discussions of the qualitative predictions of a diffusion model for the effects of freeze drying on volatiles retention have been presented by King (*12*) and Thijssen and Rulkens (*6*). King (*12* to *14*) has also reviewed the general problem of volatiles retention.

Previous quantitative interpretations of volatiles loss have been made using an effective binary analysis for calculations of diffusion coefficients (*8*, *15*) and for predicting rates of loss during drying. In one case a convective term depending upon the water flux was incorporated (*7*, *16*), but it was a small enough term so that it did not alter the predictions of the binary model greatly.

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Our contention is that it is necessary to analyze volatiles loss through a three-component diffusion model. Several effects are found with the ternary analysis which are not evident from a simpler binary model. One is the influence of the sugar concentration gradient upon the chemical potential gradient for the trace organic species; another is the importance of cross diffusion terms. Although in reality fruit juices contain many trace organic species and different dissolved sugars, a ternary model should adequately describe this system. The sugars are components that are chemically similar to one another and have no outward flux during drying. The trace components are present in such dilute concentrations that they can be assumed to have negligible effect on the transport of each other.

THEORY

The transport process in a ternary system of components 1, 2, and 3 is best described by means of the general equations for the fluxes of the two solutes 1 and 2 in a fixed volume frame of reference (*19, 20*):

$$J_1^v = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \tag{1}$$

$$J_2^v = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \tag{2}$$

D_{11}, D_{12}, D_{21} and D_{22} are multicomponent diffusion coefficients and are not identifiable, in general, with binary diffusion coefficients. An exception occurs if Component 1 is highly dilute, in which case D_{22} is the binary diffusion coefficient for a mixture of 2 and 3. Equations (1) and (2) are a generalization of Fick's equation for two independent diffusional flows.

The fluxes of Components 1 and 2 relative to the velocity of Component 3 are given by the following equations:

$$J_1^3 = C_1(v_1 - v_3) = J_1^v - \frac{C_1}{C_3} J_3^v \tag{3}$$

$$J_2^3 = C_2(v_2 - v_3) = J_2^v - \frac{C_2}{C_3} J_3^v \tag{4}$$

For the condition of a volume-fixed frame of reference, the fluxes J_1^v, J_2^v and J_3^v are related by Equation (5).

$$\frac{J_3^v}{\rho_3} = -\frac{J_1^v}{\rho_1} - \frac{J_2^v}{\rho_2} \tag{5}$$

Substitution of Equations (1), (2), and (5) into Equations (3) and (4) gives

$$\begin{aligned} J_1^3 = {} & \left[-D_{11}\left(1 + \frac{C_1\overline{V}_1}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right) - D_{21}\left(\frac{C_1\overline{V}_2}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right)\right]\nabla C_1 \\ & + \left[-D_{12}\left(1 + \frac{C_1\overline{V}_1}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right) - D_{22}\left(\frac{C_1\overline{V}_2}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right)\right]\nabla C_2 \end{aligned} \tag{6}$$

$$\begin{aligned} J_2^3 = {} & \left[-D_{11}\left(\frac{C_2\overline{V}_1}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right) - D_{21}\left(1 + \frac{C_2\overline{V}_2}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right)\right]\nabla C_1 \\ & + \left[-D_{12}\left(\frac{C_2\overline{V}_1}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right) - D_{22}\left(1 + \frac{C_2\overline{V}_2}{1 - C_1\overline{V}_1 - C_2\overline{V}_2}\right)\right]\nabla C_2 \end{aligned} \tag{7}$$

Equations (6) and (7) are completely general in nature. However, now we shall start restricting them to the special situation encountered for volatiles loss. Let us define Component 1 as the trace volatile component, Component 2 as water and Component 3 as the dissolved nonvolatile sugars. Since Component 1 is present in trace amounts, Equations (6) and (7) can be simplified considerably to give the following equations:

$$J_1^3 = -D_{11}\nabla C_1 - \left[D_{12} + D_{22}\left(\frac{C_1\overline{V}_2}{1 - C_2\overline{V}_2}\right)\right]\nabla C_2 \tag{8}$$

$$J_2^3 = -D_{22}\left(\frac{1}{1 - C_2\overline{V}_2}\right)\nabla C_2 \tag{9}$$

The cross diffusion coefficient D_{12} is given in terms of the other diffusion coefficients and the activity coefficients of the system by Equation (6) of the previous paper (*18*). Substituting for the cross diffusion coefficient D_{12} in Equation (8) gives

$$\begin{aligned} J_1^3 = -D_{11}\nabla C_1 - \frac{C_1}{C_2}\Bigg\{ & \left[\frac{\partial \ln \gamma_1}{\partial \ln C_2}(1 - C_2\overline{V}_2) + C_2\overline{V}_1\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln C_2}\right)\right]\left(\frac{D_{11}}{D_{22}} - 1\right) \\ & + \left(1 + \frac{\partial \ln \gamma_2}{\partial \ln C_2}\right)\frac{D_{21}}{D_{22}} + C_2\overline{V}_2\Bigg\} J_2^3 \end{aligned} \tag{10}$$

The large term in braces on the right-hand side of Equation (10) is a unique function of C_2. It will change sign for the same reasons that D_{12} does and will do so at about the same values of C_2. Volatiles loss corresponds to a flux J_1^3 in the same outward direction as J_2^3. If the term in braces in Equation (10) is positive, the J_2^3 term will augment the first term and accelerate volatiles loss; if the term in braces is negative, the J_2^3 term will offset the first term and reduce volatiles loss. In the latter case for a sufficiently high drying rate the J_2^3 term can cause a transport of volatile component locally inward from the drying surface.

The coefficient D_{22} can be taken as the binary diffusion coefficient for the water (2)-dissolved sugars (3) system. We have experimentally determined values of D_{11}, D_{21}, and D_{12} for ternary systems composed of water, fructose, or sucrose, and various volatile compounds which occur naturally in fruit juices (*18*).

MATHEMATICAL ANALYSIS

Procedure

For simplicity, we have carried out mathematical predictions of volatiles loss and volatiles concentration profiles for an initially homogeneous food material in the form of a slab which shrinks during drying. Because of the dependence of the volatiles transport rate upon the water concentration profile, it is necessary to include a simultaneous solution of the water concentration as a function of position and time along with the solution for the volatiles concentration profile. The rate-controlling step for water removal can be either heat transfer or mass transfer, external to or within the slab. The water concentration profile depends upon the balance between the external mass transfer coefficient and the internal rates of water diffusion. The effect of heat transfer upon the water profile and the volatiles diffusion process will come through the dependence of diffusion coefficients and vapor-liquid equilibrium ratios upon temperature; thermal diffusion is assumed negligible. Since the material in the slab will have a relatively high thermal conductivity, the temperature within the slab is assumed uniform and invariant. If heat transfer external to the slab is an important rate limit for water removal, this assumption corresponds to a particular temperature program for the heat source.

The surface boundary condition for water transport was applied as

$$J^3_{2,\text{ surface}} = -k_2\,(C_{2s} - C_{2e}) \qquad (11)$$

This expression corresponds to water evaporation from the surface into vacuum or a flowing air stream, with a constant gas phase mass transfer coefficient and a linearization of the water sorption isotherm. Because of the very high volatilities of most of the trace volatile compounds to be considered, k_1 for the volatiles in the equation analogous to Equation (11) was taken to be infinite in all cases. C_{1e} was taken to be 10^{-7} kg.-moles/m³. This corresponds to assuming that the surface concentration of volatiles drops immediately to a value near zero.

The concentration profiles at successive times and the rates of evaporation for both the trace organic species and water were obtained by evaluating solutions of the following equations:

$$\frac{\partial C_1}{\partial t} = -\frac{\partial}{\partial x}\,(J_1{}^3) \qquad (12)$$

$$\frac{\partial C_2}{\partial t} = -\frac{\partial}{\partial x}\,(J_2{}^3) \qquad (13)$$

The three boundary conditions for Equations (12) and (13) are:

1. At $x = 0$ (centerline or impermeable surface) and all t, by symmetry $\frac{\partial C_1}{\partial x} = \frac{\partial C_2}{\partial x} = 0$
2. For $x < l$ and $t = 0$, $C_1 = C_1{}^0$ and $C_2 = C_2{}^0$
3. At $x = l$ (evaporating surface) and $t > 0$, $C_{1e} = 10^{-7}$ kg.-moles/m³, and $C_{2e} = 10$ kg moles/m³. This corresponds to an equilibrium relative humidity of about 30%.

Equations (12) and (13) are highly nonlinear because

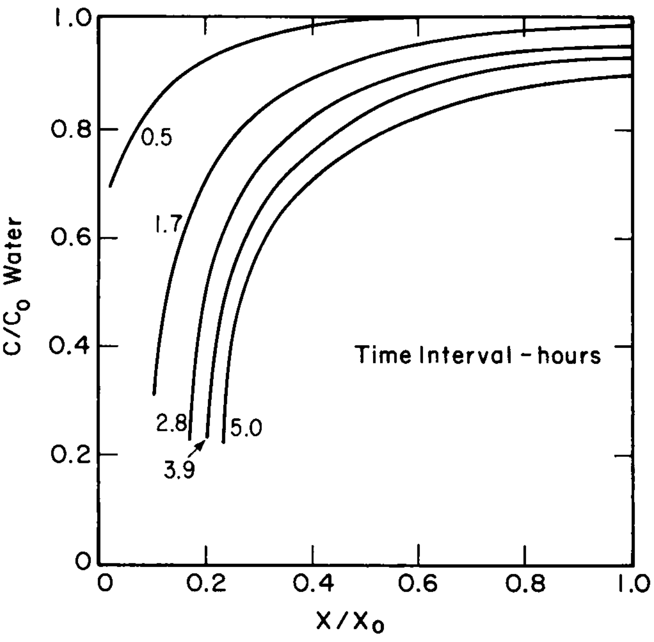

Fig. 1. Water concentration profiles in the sucrose slab during drying at 298K. Initial water concentration (C_0) = 45 kg.-moles/m³; slab thickness (X_0) = 1 cm.; surface mass transfer coefficient 1.25 x 10^{-5} cm/s. X/X_0 = Distance from initial surface position/initial thickness.

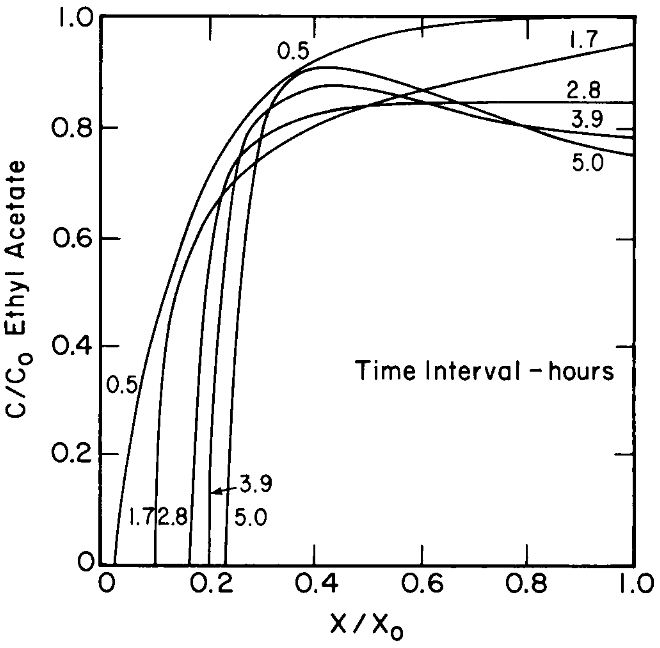

Fig. 2. Ethyl acetate concentration profiles during drying conditions of Figure 1. Surface concentration is assumed zero.

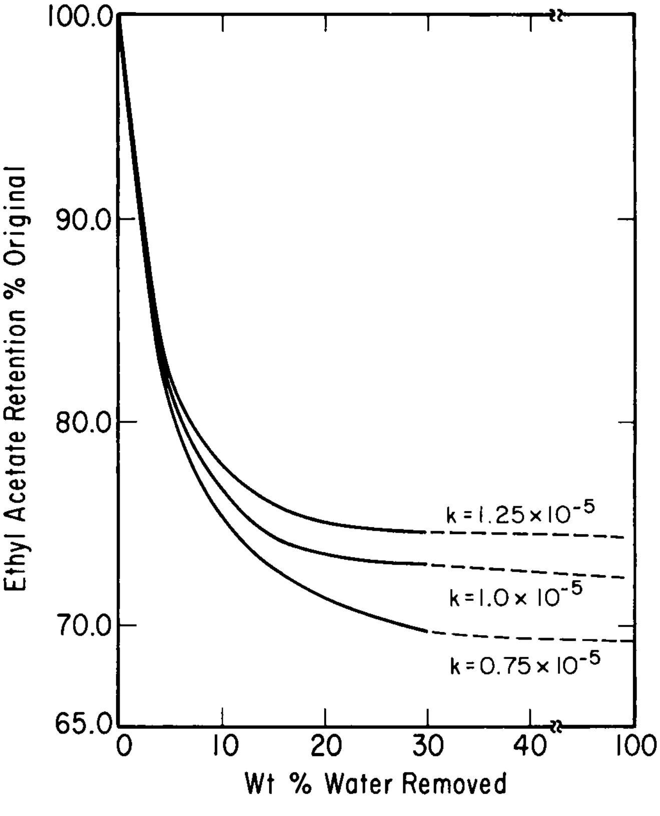

Fig. 3. Effect of the surface transfer coefficient on the retention of ethyl acetate in 25 wt. % sucrose solutions at 298K. Other conditions are those of Figure 1.

of the large variations in diffusion coefficients and are very difficult if not impossible to solve analytically. Several methods are available for solving finite difference approximations to the above equations (*21, 22*). In this study the symmetrical Crank-Nicholson implicit representation was employed. This approach was preferable since the coefficients of the finite difference equations changed markedly from point to point in the concentration network. The improved stability and convergence characteristics of the Crank-Nicholson scheme was necessary to cope successfully with this situation (*21*). The entire water profile was solved first for one value of time, after which the entire volatile profile was computed at that time. The entire water profile was then solved at the next time interval, etc.

The shrinkage resulting from the evaporation of water further complicates the solution to Equations (12) and (13). It was assumed that shrinkage was due solely to the water loss and that there are constant partial molar volumes of sugar and water and no other molar volume contraction effects. The mesh points were made immobile with respect to Component 3, and thus the actual distance increment changed accordingly from place to place and time to time. The concentration gradients near the evaporating surface are very steep because of the strong dependencies of the diffusion coefficients upon water concentration. For this reason, the increment size in the half of the concentration network nearest the surface was continually halved from slice to slice approaching the surface. However, the first three to four slices nearest the surface were kept of equal size. The results which are presented were obtained for a network with 30 distance slices. The convergence of this method was tested by doubling the increment size and altering the value of β. Solutions for equivalent values of β agreed within one percent and less. Details of the technique of evaluating the numerical solutions are given elsewhere (*17*).

Results

The results of a computer solution to Equations (12) and (13) for unidirectional isothermal evaporative drying of a sucrose-water slab at 298K are presented in Figures 1 and 2. The initial thickness of the slab is 1 cm with one face being impermeable. The initial concentration is 25 wt. % sucrose, with ethyl acetate as the high dilution volatile component. Figure 2 shows the moisture content as a function of distance into the slab. The left-hand end of the curve moves as time progresses because of shrinkage accompanying drying. Figure 3 shows the ethyl acetate content of the slab as a function of time and position. There is an internal maximum in volatiles concentration occurring within the slab after a certain length of time. This is a direct result of the sign change of the ∇C_2 term in Equation (8), stemming from the sign change of D_{12}. The flux of volatile is directed towards the maximum from either both directions—an inward flux from the left and an outward flux from the right, or one direction—the outward flux from the left being smaller than the outward flux from the right. Figure 3 shows the % retention of ethyl acetate as a function of the % water removal during drying, with the surface mass transfer coefficient as a parameter. The value of the surface transfer coefficient over the range considered has a small but significant effect on the retention. Higher values of k_2 tend to increase the sugar content near the surface more rapidly, resulting in an increased retention. A striking feature of Figure 3 is that the % retention begins to level out after about 15 or 20% water removal. The maximum loss of ethyl acetate occurs during the initial stages of drying. This conclusion agrees qualitatively with the simpler binary model of Thijssen et al. (*8*).

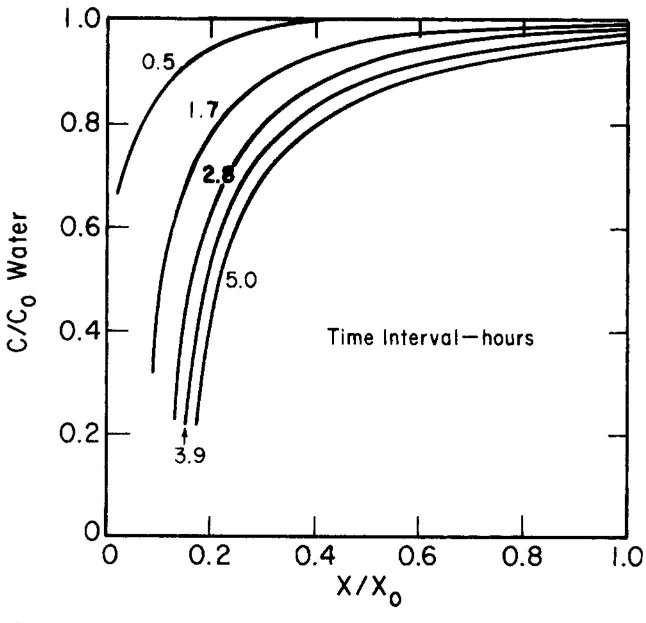

Fig. 4. Water concentration profiles in a sucrose slab during drying at 274K. Other initial conditions identical to Figure 1.

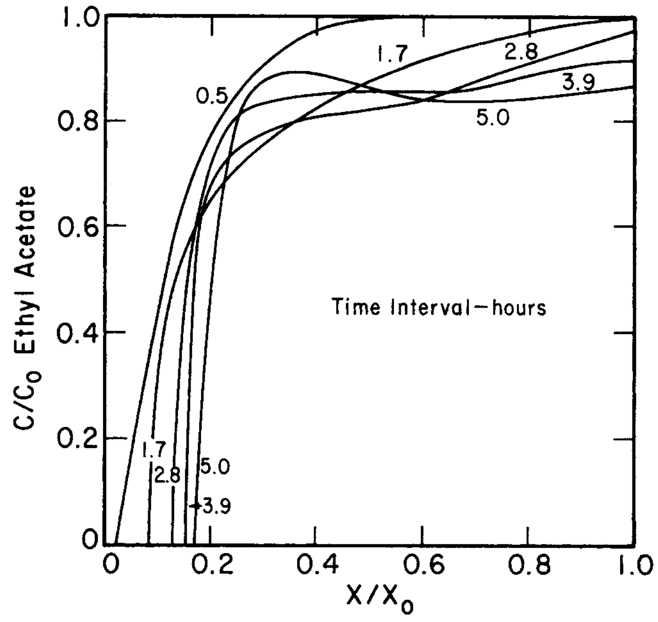

Fig. 5. Ethyl acetate concentration profiles during drying conditions of Figure 4. Surface concentration is assumed zero.

The effect of temperature can be shown by comparing Figures 1 and 2 with Figures 4 and 5, which are for isothermal unidirectional evaporative drying of a sucrose-water slab at 274K. The slab initially contains 25 wt. % sucrose, with ethyl acetate as the high dilution volatile component. Again there is an internal maximum in ethyl acetate concentration occurring within the slab after a certain length of time for the same reason. The retention of ethyl acetate is somewhat superior to that for isothermal drying at 298K. Qualitatively this is because the activation energy for D_{11} is greater than that for D_{22}. It was assumed that the activation energy was similar for D_{11} and D_{21}. At the temperature of 274K, the coefficient D_{12} changes sign at about the same values of C_2 as before (*17, 18*).

A series of computer solutions was obtained for temperatures of 274, 298, and 308K, for solutions of both d-fructose and sucrose, with initial concentrations ranging from 15 to 45 wt. % sugar (*17*). The internal maximum

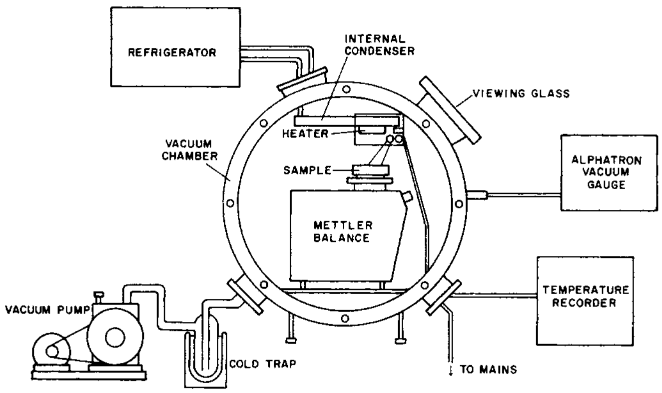

Fig. 6. Experimental apparatus.

in volatiles concentration was distinctly apparent for sucrose solutions of 15 and 25 wt. % initial sucrose content. With higher initial sucrose contents, and generally with fructose solutions, the volatile concentration profile tended to change monotonically within the bulk liquid, with a very sharp gradient at the surface. At times there was a tendency for a formation of a slight internal maximum. Volatiles retentions were somewhat improved in fructose solutions as compared to sucrose solutions because D_{22} is bigger for fructose than for sucrose, but D_{11} and D_{21} are unchanged. Furthermore, the retentions always increase with increasing sugar content, because the ratio D_{11}/D_{22} sharply decreases with solids concentration *(18)*.

EXPERIMENT

The purpose of the experimental portion of this work was to determine concentration profiles for both water and a dilute volatile component in slabs of aqueous sugar solutions, after partial drying. Comparison between experimental profiles and those predicted by the ternary diffusion model should shed light not only on the exactness of the model, but also on the controlling transport mechanisms of volatiles loss.

Drying Apparatus

The equipment used is shown in Figure 6. The drying chamber was a cylindrical vessel 0.51 m in diameter and 0.51 m long. An internal condenser connected to an external refrigerator was fixed to the top of the vessel. The chamber exhaust line passed through a large vapor trap which was immersed in liquid nitrogen and served as a condenser for volatile components and water. Two Marvac vacuum pumps of 1×10^{-3} m^3/s capacity were used to maintain an absolute chamber pressure of 1000 to 1500 μm Hg, as read by an Alphatron vacuum gauge connected to the side of the vessel. This pressure corresponds to an equilibrium water concentration C_{2e} of about 10 to 15 kg.-moles/m^3. Temperatures of the sample surface near the wall and center together with the bulk gas phase temperature were measured with three copper-constantan thermocouples connected to a Leeds & Northrup Speedomax multipoint temperature recorder. A 1000 W adjustable radiant heater was suspended from the top of the chamber.The weight of the sample was directly read on a Mettler balance which could be viewed through a glass window on the top side of the chamber.

The sample holder consisted of a stack of 8 Plexiglass plates, each of 1.6 mm thickness, with a central 51-mm diam. hole extending through the stack of plates. The 8 plates were held together by a pair of stainless steel plates and 4 bolts. The sample to be dried was poured into this central hole and was consequently 51-mm diam. and about 13 mm thick initially.

Experimental Procedure

An aqueous sugar solution was prepared containing 1 to 2 wt. % gelatin. Solutions were best prepared by thoroughly mixing the gelatin with the solid sugar and then adding hot water to this mixture. After this solution had cooled to room temperature, about 0.5 vol. % ethyl acetate was added through a syringe. This solution containing the volatile component was then poured into the sample holder, which in turn was placed in a kitchen refrigerator kept at about 288 K. About 3 to 4×10^{-3} kg. of the same solution was also poured into a covered 25 cm^3 beaker, to be used as the reference sample after the drying run.

The gelled solution in the sample holder was then dried for about 1.8×10^4 s in the vacuum drying chamber. Surface temperatures ranging from 298 to 308 K. were maintained during drying by adjustment of the radiant heater. Drying was slow enough for the samples to remain at an essentially constant and uniform temperature, as confirmed by spot checks with interior thermocouples. Shrinkage was quite uniform throughout the slab, but at times the surface had slight imperfections. At the end of the drying time, the sample holder was placed in the freezer compartment of the refrigerator, kept at 258 K. This low temperature caused the whole solution to solidify rapidly. The sample holder was dissassembled plate by plate, and slices were cut using a sharp serrated knife. In order to prevent cutting of the Plexiglass plate itself, the stainless steel plate was always placed on top and the actual cutting was done over it. The thickness of slices was obtained both by approximate measurement and by calculations after knowing the total weight and sugar content of the slice. The thickness of the first slice was generally smaller because the final position of the slab surface would not exactly coincide with a particular plate. Again, the thickness of the last slice was larger because it includes the thickness of the steel plate. The observed reduction in volume corresponded closely to the measured water loss in all cases.

These slices were then placed individually in 25 cm^3 beakers and were dissolved in 3 cm^3 of distilled water. The ethyl acetate content of each slice was determined by directly injecting 2.5 mm^3 of liquid into the flame ionization chromatograph. A 1.6 m $\times$ 6 mm I.D. Poropak-Q column was used. with a column temperature around 475 K. A similar precaution of inserting a 9 cm $\times$ 0.6 cm pyrex capillary tube in the injection port was followed *(18)*. At these low concentration levels, the peak areas were found experimentally to be linear with concentration. The water content within each slice

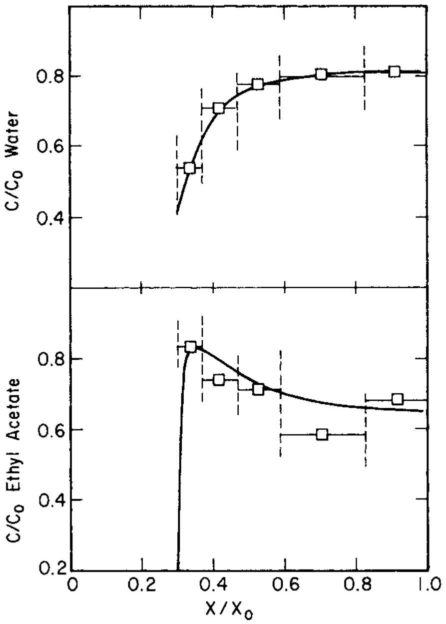

Fig. 7. Water and ethyl acetate distribution in a gelled aqueous sucrose solution after drying at 298K and 1 mm.-Hg pressure. Initial concentration 25 wt. % sucrose, 0.5 vol. % ethyl acetate, and 1.9 wt. % gelatin. Initial sample thickness $\simeq$ 1.2 cm.

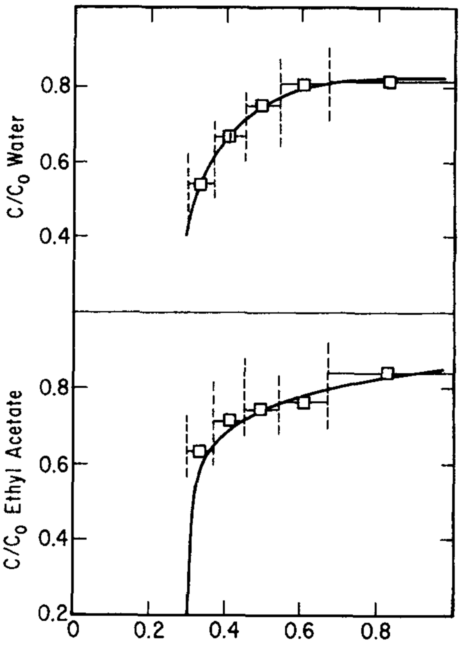

Fig. 8. Water and ethyl acetate distribution in a gelled aqueous fructose solution after drying at 298K and 1 mm-Hg pressure. Same initial conditions as in Figure 7 with fructose replacing sucrose.

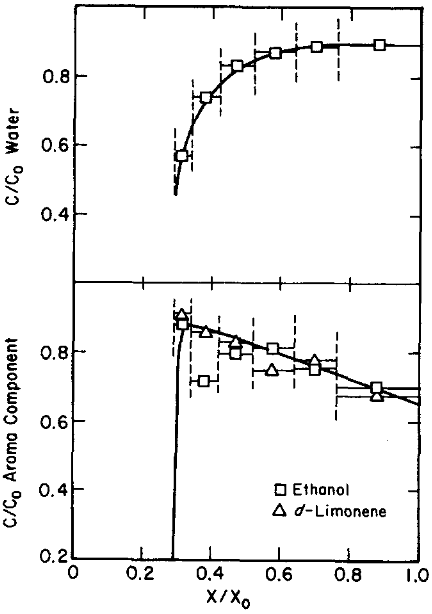

Fig. 9. Water and aroma component distribution in gelled orange juice after drying at 298K and 1 mm.-Hg pressure. Initial concentration 25 wt. % solids and 1.5 wt. % gelatin. Initial sample thickness = 1.2 cm.

was determined both by using an Abbé refractometer, and by drying the sample to dryness in a vacuum oven kept at 353 K. The results from the two methods agreed well.

In the case of fruit juices, the sample was prepared by dissolving the gelatin in water and adding this solution to the fruit juice to attain the required concentration prior to drying. Partially reconstituted commercial juice concentrates (Minute Maid frozen concentrated orange juice) were used for the experiments. Additional ethanol in the amount of 0.5 vol. % was added to the juice solution; d-limonene was monitored at its naturally occurring level.

The drying time was 1.8×10^4 s in all cases. After drying was stopped, the slices were dissolved in 15 cm^3 distilled water and placed in 250 cm^3 Erlenmeyer flasks sealed at the top with aluminum foil. The flasks were placed in a thermostated bath maintained at 298 ± 0.05 K. After the solution had been allowed to equilibrate, 5 cm^3 of the vapor space was taken with a gas tight syringe and injected as a vapor sample into the chromatograph. From the vapor phase concentrations, the liquid phase compositions can be obtained after correction for the activity coefficients (*18*). Water concentrations were obtained using the Abbé refractometer.

Results

Figures 7 and 8 show the retention of trace amounts of ethyl acetate and water for two gelled solutions of sucrose and fructose, respectively. The data points represent average compositions found in the slices of approximate thickness shown by the vertical dashed lines. The curves are the best fit through the experimental points. Figure 7 may be compared with the predictions of Figures 1 and 2 for a 5-hr. drying period. The predicted internal maximum for the 25 wt. % sucrose solution is borne out by the experiment. Figure 8 agrees similarly well with predictions of the diffusion model for that case. Experimental % retentions of ethyl acetate are in the neighborhood of 65 to 70% and compare favorably with the predicted values. However, comparisons to a high degree of precision cannot be made between the theory and experiment for several reasons: Temperature gradients have not been incorporated in the model; the drying conditions were not rigidly held at those postulated in the solution of the equations; k_2 was not determined independently; and no allowance has been made for the small amount of gelatin affecting the diffusional behavior of ethyl acetate and water. From the work of Friedman (*23*) we can say that at the levels of gelatin used in this study the effect should not be large.

Figure 9 shows the retention of volatile components and water in one of the gelled samples of orange juice. An internal maximum in the volatiles profile is quite evident from the results. Orange juice contains a large proportion of sucrose (approximately 60% of the total sucrose, fructose, and glucose), and this is the main reason for the similarity between the juice and pure sucrose solutions.

Results for the 8 other experimental runs of this sort which were made are similar to those shown here, and are presented elsewhere (*17*).

DISCUSSION

It is interesting to compare the predicted results of this study with those of Thijssen and Rulkens (*7, 16*) who analyzed the loss of acetone and ethyl acetate from slabs of aqueous maltodextrin solutions during drying. Their moisture content profiles were obtained from an equation identical to Equation (9) of this study, and their predicted water profiles are therefore quite similar to ours. However, in the volatile species flux equation [Equation (18) of (*16*)] the term involving $J_2{}^3$ is much less in absolute magnitude than the $J_2{}^3$ term in our Equation (10), and does not have the property of changing signs. As a consequence their solutions cannot predict the internal maximum of the volatile concentration.

The differences between the analysis of Thijssen and Rulkens and the analysis of this paper stem from several factors:

1. The analysis by Thijssen and Rulkens (*7, 16*) is based upon the Stefan-Maxwell equation, which is normally

applied to gases. Lightfoot et al. (*24*) show that this equation is valid for liquids only if it is modified to include a term $(\nabla \ln a_i/\nabla \ln x_i)$ and if allowance is made for unequal component volumes. The added term incorporates solution nonidealities and part of the impact of the water flux.

2. Thijssen and Rulkens hold their coefficient D_{aw} constant at a value equal to the binary diffusivity of volatile component in water at high dilution (*7, 16*). In reality this coefficient would be expected to vary with the dissolved solids content in a complex manner.

3. In the measurement of diffusion coefficients a water gradient necessarily develops along with the gradient in volatile component content; the resultant effect of the D_{12} term in Equation (1) is not accounted for by Menting et al. (*25*).

Despite these differences, most of the qualitative conclusions inferred previously about the directional effect of various processing variables upon volatiles retention in freeze-drying and drying from the liquid state remain valid (*6, 8, 12* to *15*). Important different predictions stemming from the ternary diffusion analysis include a different shape of the volatiles concentration profile within a substance during drying and at the conclusion of drying, altered quantitative predictions of volatiles retention, the possibility of achieving selective volatiles retention by combining a negative value of the cross coefficient D_{12} (at intermediate moisture content) and a high water gradient within the substance being dried, as well as by low solids content and low temperatures.

CONCLUSIONS

The ternary diffusion model appears to give an interpretation which matches quantitatively the essential features of the phenomenon observed experimentally—the amount of volatiles loss, the shape of the resulting concentration profiles for volatile species, and the effect of different processing variables. A particular result of interest is the possibility of achieving satisfactory retention of volatile compounds for fruit juices and other food liquids with evaporative drying processes, as well as with freeze-drying. The diffusion analysis should serve as the basis for conceiving improved drying processes and for predicting and analyzing their volatiles retention behavior.

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NOTATION

a = activity
C = molar concentration
C^0 = initial concentration
D = diffusion coefficient
h = distance increment
J = flux toward evaporating surface
k^* = time increment
k = surface transfer coefficient
l = distance of evaporating surface from centerline or impermeable surface
t = time elapsed
v = average velocity
$\overline{V}$ = partial molar volume
x = distance from centerline or impermeable surface toward evaporating surface

Greek Letters

γ = activity coefficient
ρ = density
∇ = gradient operator

Subscripts

1, 2, 3 = components 1, 2 and 3
e = equilibrium with prevailing value in gas phase
s = evaporating surface

Superscripts

0 = initial
3 = with reference to flux of Component 3
v = fixed volume frame of reference

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