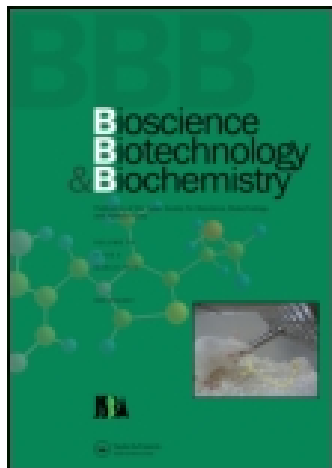


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Mathematical Analysis of the Effective Thermal Conductivity of Food Materials in the Frozen State

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The effective thermal conductivity of binary aqueous solutions or gel systems of glucose, sucrose, potato starch, gelatin, and egg albumin in the frozen state were theoretically investigated. Structural models were used for evaluating heat conduction combined with the ice fraction measured for the same sample as that used in the measurement of effective thermal conductivity. The temperature-dependency of the ice fraction was determined by the phase diagram or DSC method. The structural models employed, with no fitting parameters involved, were the series, parallel, and Maxwell–Eucken models with ice as the dispersed phase (ME1 model) and as the continuous phase (ME2 model). The intrinsic thermal conductivity for each component was determined from measurements taken on unfrozen sample. Although all of the four models were applicable to the unfrozen sample with no substantial difference in prediction, the ME1 model, which was composed of the dispersed ice phase and continuous thick solution phase, was the only model applicable to the frozen sample for predicting the effective thermal conductivity within 10% accuracy. With all the samples tested, the ME1 model gave the best results of the four models, suggesting the wide applicability of this model for predicting the effective thermal conductivity of frozen food materials.

A systematic description of the effective thermal conductivity is very important for accurate prediction and control of the freezing and thawing processes involved with foods.^{1,2)} In the unfrozen state, the effective thermal conductivity can be predicted from the intrinsic thermal conductivity combined with an appropriate heat transfer model, and from the volume fraction of each component.³⁾ The effective thermal conductivity of a frozen food, however, is one of the most complex physical properties to describe, since it is strongly dependent on temperature because of the nearly four-fold difference in the thermal conductivity between ice and water.

The selection of an appropriate heat transfer model is important for a mathematical analysis of the effective thermal conductivity of frozen food material. Among the heat transfer models, the Maxwell–Eucken model (ME model) has been used for an analysis of the effective thermal conductivity of gelatin gel.⁴⁾ Barrera and Zaritzky,⁵⁾ and Renaud *et al.*⁶⁾ have also applied the ME model for evaluating the effective thermal conductivity of beef liver and of solutions of gelatin, egg albumin, starch, and sucrose in the frozen state. Heldman⁷⁾ applied the Kopelman model for frozen lean beef, while Murakami and Okos⁸⁾ employed the parallel-perpendicular model for frozen red fish and lean beef. In all of these investigations, ice was assumed to be the dispersed phase. On the contrary, Pham and Willix⁹⁾ assumed ice as the continuous phase and applied Levy's model, a modified version of the ME model, in their theoretical analysis of the effective thermal conductivity of frozen fresh lamb meat, offal, and fats.

The use of accurate data for the temperature-dependency of the ice fraction is the other prerequisite for accurately predicting the effective thermal conductivity of frozen food. In the literature already mentioned concerning the effective

thermal conductivity, however, the ice fraction and its temperature-dependency were not measured and were estimated from the theoretical models, typically by the ideal solution theory.^{6–8)} The ideal solution theory, however, is of limited applicability to real foods at high concentrations.

In the preceding papers, we measured the effective thermal conductivity of binary aqueous solutions of glucose, sucrose, gelatin, and egg albumin at various concentrations and temperatures between -20 and 20°C by the steady-state method,³⁾ and also the temperature-dependency of the ice fraction for the same sample.¹⁰⁾ In this paper, the effective thermal conductivity of frozen food is analyzed by applying structural models for heat conduction based on measured data for the ice fraction of the same sample.

Materials and Methods

In this paper, we examine the mathematical models for evaluating the effective thermal conductivity of frozen food materials by using the experimental data reported previously,³⁾ except for potato starch which was obtained from Nacalai Tesque and was used as supplied. The method used for obtaining the data was to measure the effective thermal conductivity of unfrozen and frozen samples with the concentration varied at various temperatures by a steady state method, using the coaxial dual-cylinder apparatus previously described.³⁾ The ice fraction was measured by the phase diagram method for the glucose and sucrose solutions, and by the DSC method for those systems with high molecular weight such as potato starch, gelatin, and egg albumin.¹⁰⁾




Structural Models for Heat Conduction

Thermal conductivity is a non-additive property which cannot be determined only from the compositions of a material. The structure affects the type of mathematical formulation for evaluating the effective thermal conductivity. The relationship between the intrinsic thermal conductivity and the volumetric fraction of each component is described by the following equation:

$$\lambda_e = f(\lambda_1, \lambda_2, \dots; x_1^v, x_2^v, \dots) \quad (1)$$

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Table I. Structural Model for Heat Conduction Used in This Work

Model	Theoretical equation ($\sum x_i^v = 1$)	
Series	$\lambda_c = \frac{1}{\frac{x_w^v}{\lambda_w} + \frac{x_s^v}{\lambda_s}}$	
Parallel	$\lambda_c = \lambda_w x_w^v + \lambda_s x_s^v$	
Maxwell-Eucken	$\lambda_c = \lambda_c \left\{ \frac{\lambda_d + 2\lambda_c - 2x_d^v(\lambda_c - \lambda_d)}{\lambda_d + 2\lambda_c + x_d^v(\lambda_c - \lambda_d)} \right\}$	

Note: $x_i^v = \frac{x_i^w / \rho_i}{\sum x_i^w / \rho_i}$

Subscripts: s = solid; w = water; c = continuous phase; d = dispersed phase.

Superscripts: v = volumetric fraction, w = weight fraction.

Table II. Intrinsic Thermal Conductivity of Solute Components, λ ($\text{W m}^{-1} \text{K}^{-1}$), Determined by Various Structural Models for the Unfrozen Samples

Model	Glucose	Sucrose	Potato starch	Gelatin	Egg albumin
Series	0.351	0.345	0.414	0.340	0.377
Parallel	0.257	0.257	0.362	0.237	0.299
Maxwell Eucken	0.295	0.293	0.382	0.280	0.331

Table III. Thermal Conductivity and Density of Pure Components⁸⁾

	Material	Equation
λ ($\text{W m}^{-1} \text{K}^{-1}$)	Water	$0.5711 + 1.763 \times 10^{-3}t - 6.704 \times 10^{-6}t^2$
	Ice	$2.220 - 6.249 \times 10^{-3}t + 1.015 \times 10^{-4}t^2$
ρ (kg m^{-3})	Water	$997.2 + 3.144 \times 10^{-3}t$
	Ice	$916.9 - 0.1307t$
	Protein	1330
	Carbohydrate	$1599 - 0.3105t$

where $\lambda_1, \lambda_2, \dots$ are the intrinsic thermal conductivity values for each component in the food structural model, and x_1^v, x_2^v, \dots are the volumetric fractions of each component in the system. The series, parallel and ME models were applied, the mathematical formulation for each of these structural models being listed in Table I. The series model gives the highest thermal resistance to heat conduction, the parallel model gives the lowest and the ME model is intermediate.

The intrinsic thermal conductivity values³⁾ for glucose, sucrose, potato starch, gelatin, and egg albumin determined from the effective thermal conductivity in the unfrozen state by applying these three models are shown in Table II. It should be noted that the "intrinsic" thermal conductivity varies from model to model because the "intrinsic" value itself is dependent on the inherent structural model. Although the temperature-dependency of the "intrinsic" thermal conductivity is neglected in the present analysis, the predicted effective thermal conductivity from the model agrees well with the observed data as far as unfrozen samples were concerned.

By using these values for the intrinsic thermal conductivity, the effective thermal conductivity in the frozen state was analyzed again by applying the series, parallel and ME models. In the frozen state, a system is composed of three phases: the pure ice phase, unfrozen water phase, and solute phase. The thermal properties of a pure material necessary for calculating the effective thermal conductivity are listed in Table III.⁸⁾ With the ME model,

Table IV. Comparison between the Predicted and observed Values for the Effective Thermal Conductivity of a 38.3% Glucose Solution

Temperature	λ_{exp} ($\text{W m}^{-1} \text{K}^{-1}$)	%difference in predicted effective thermal conductivity			
		Series	ME 1	ME 2	Parallel
-20.5	0.895	-24	-2.1	24.9	41
-16.1	0.785	-19	1.4	26.2	42
-9.25	0.532	-1.3	7.5	18.7	27

Notes. ME 1: Maxwell-Eucken model with ice as the dispersed phase. ME 2: Maxwell-Eucken model with ice as the continuous phase.

only two phases are allowable in the system. In this case, the unfrozen water phase and the solute phase were combined and presumed to form a thick solution phase, the effective thermal conductivity of which was determined from the ME model of the unfrozen sample. The ME model was then repeatedly applied to the frozen system. With the ME model in the frozen state, there are two choices in the model formulation depending on which phase has been chosen as the dispersed phase: the pure ice phase (ME1 model) or thick solution phase (ME2 model).

Results

Prediction of the effective thermal conductivity of low-molecular-carbohydrates

The ice fraction for the glucose and sucrose solutions were determined from the phase diagram expressed by the following equation¹⁰⁾:

$$\ln X_w + \ln \gamma_w = (-\Delta H_f/R)(1/T - 1/T_f) \quad (2)$$

where X_w is the molar fraction of water, γ_w is the activity coefficient of water, ΔH_f is the heat of fusion of water (6003 J/mol), R is the gas constant, T is the temperature (K) under consideration, and T_f is the freezing temperature (K) of water. Chandrasekaran and King¹¹⁾ have applied Margules' equation for the activity coefficient of water as follows:

$$\ln \gamma_w = -(\alpha'/T)(1 - X_w)^2 \quad (3)$$

Parameter α' was determined to be 836 and 1800 (K) for the glucose and sucrose solutions, respectively, and Eqs. (2) and (3) gave the phase diagram and the temperature dependency of the ice fraction as described before.¹⁰⁾

Table IV shows a comparison of the effective thermal conductivity between the predicted and the observed results for a frozen 38.3% glucose solution. Among the four models tested, the ME1 model gave the best result, while the parallel model gave the worst.

Figure 1 shows a comparison of the measured effective thermal conductivity and that predicted by the ME1 model for glucose solutions at various concentrations. The prediction is in a good agreement with the experimental results for the samples from -20 to 20°C. Figure 2 shows similar results for the sucrose solutions, the ME1 model again giving the best prediction, although some deviation is apparent with the 41.8% sample.

Prediction of the effective thermal conductivity of gels containing high-molecular-weight materials

The ice fraction for polysaccharides and proteins was determined by the DSC method³⁾ and can be expressed by the following equation:

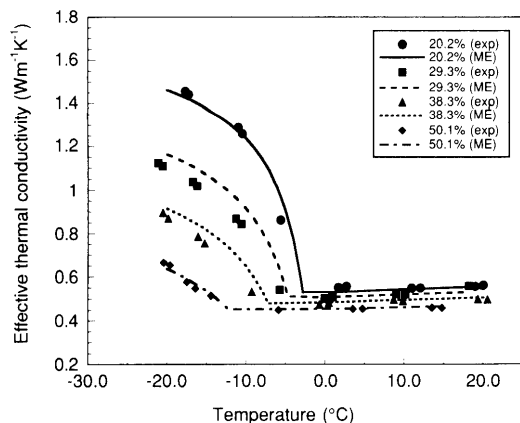


Fig. 1. Comparison of the Measured Effective Thermal Conductivity and the Value Predicted by the MEI Model for Glucose Solutions.

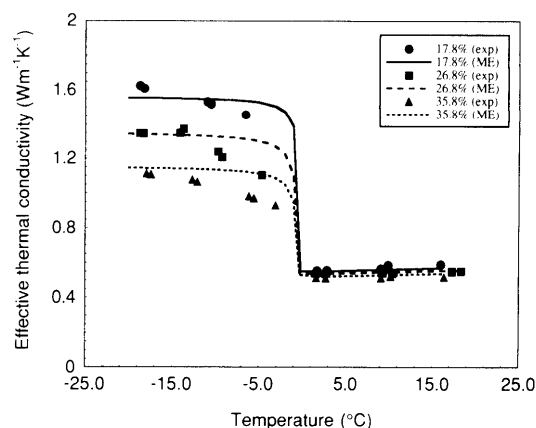


Fig. 3. Comparison of the Measured Effective Thermal Conductivity and the Value Predicted by the MEI Model for Potato Starch Gels.

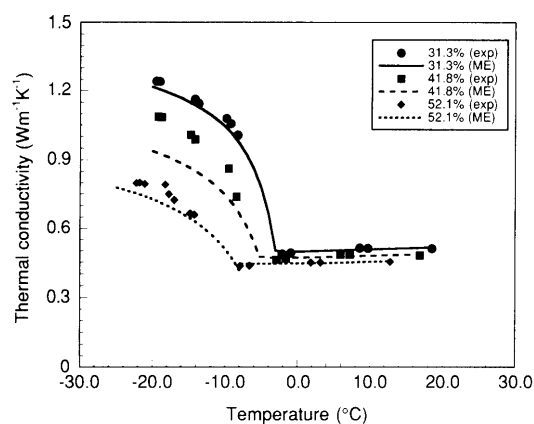


Fig. 2. Comparison of the Measured Effective Thermal Conductivity and the Value Predicted by the MEI Model for Sucrose Solutions.

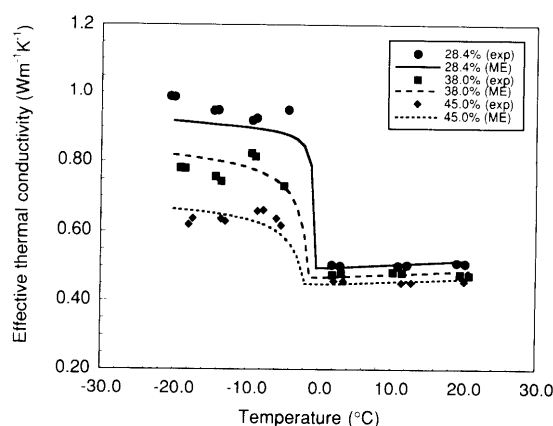


Fig. 4. Comparison of the Measured Effective Thermal Conductivity and the Value Predicted by the MEI Model for Gelatin Gels.

$$x_i = (x_w - x_b)(1 - t_f/t) \quad (4)$$

where x_i is the ice fraction (wt%), x_w is the water content (wt%) before freezing, x_b is the bound water content (wt%) determined from optimal curve fitting,³⁾ t_f is the initial freezing point (°C), and t is the temperature under consideration (°C). The parameters in Eq. (4), t_f and x_b , were determined and are expressed as follows:

$$t_{f(\text{potato starch})} = -0.00849x_s + 2.53 \times 10^{-5}x_s^2 \quad (5)$$

$$t_{f(\text{gelatin})} = -0.00831x_s + 7.75 \times 10^{-4}x_s^2 - 3.40 \times 10^{-5}x_s^3 \quad (6)$$

$$t_{f(\text{egg albumin})} = -0.0238x_s - 8.93 \times 10^{-4}x_s^2 \quad (7)$$

$$x_{b(\text{potato starch})} = 0.00939x_s - 1.43 \times 10^{-4}x_s^2 \quad (8)$$

$$x_{b(\text{gelatin})} = 0.00647x_s + 5.47 \times 10^{-7}x_s^2 \quad (9)$$

$$x_{b(\text{egg albumin})} = 0.00217x_s - 4.19 \times 10^{-6}x_s^2$$

where x_s is the solid content (wt%).

By using the ice fraction described by Eqs. (4)–(9), the effective thermal conductivity was calculated from the structural models. A comparison of the experimentally determined effective thermal conductivity of gels containing gelatinized potato starch and the figure predicted with the theoretical model is shown in Fig. 3. The value predicted by the MEI model is in a good agreement with the experimental data for temperatures well below the freezing point. This prediction, however, produces a relatively large

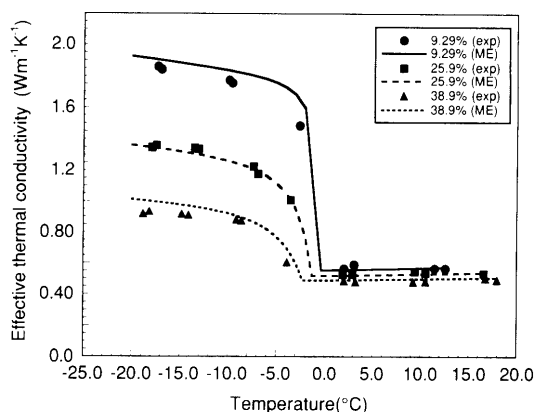


Fig. 5. Comparison of the Measured Effective Thermal Conductivity and the Value Predicted by the MEI Model for Egg Albumin Gels.

discrepancy in the temperature range just below freezing point for the gels with high concentrations.

Figure 4 shows a comparison of the observed effective thermal conductivity of gelatin gels and the value predicted by the MEI model, which again proved to be the best predictor over the other three series, parallel and ME2 models. The predicted effective thermal conductivity of egg albumin gels also indicates that the MEI model gives the best prediction among the four models tested and is shown in Fig. 5.

Discussion

Lentz⁴) has applied the ME1 model for evaluating the effective thermal conductivity of a frozen gelatin gel of 6 to 20% concentration at temperatures ranging from -10 to -30°C . The model gave a value in good agreement with the experimental results in some cases, but not all, probably because of the error in estimating the ice fraction. Barrera and Zaritzky⁵) and Renaud *et al.*⁶) have also applied the ME1 model for evaluating the effective thermal conductivity of frozen beef liver⁵) and of food gels⁶) containing gelatin, egg albumin, starch, and sucrose. In these investigations, however, the effective thermal conductivity of each frozen sample was measured by the transient method, which can involve the effect of temperature-dependent latent heat in the measurements for the frozen sample. In addition, the ice fraction was estimated either by a cryoscopic decrease model⁵) or by the ideal solution theory based on Raoult's law.⁶) The ideal solution theory was firstly applied by Heldman⁷) to analyze the ice fraction in food. This theory is applicable only to a dilute solution of low-molecular-weight materials and has a limitation in the definition of the apparent molecular weight when high-molecular-weight materials are involved. Experimental results have shown that the ideal solution theory is not applicable to a glucose and sucrose system with a concentration higher than 20–30 wt%.¹⁰)

Pham and Willex⁹) carried out a thorough investigation on the effective thermal conductivity of frozen fresh lamb meat, offal, and fat measured by the steady-state method with guarded hot-plate apparatus combined with the ice fraction estimated from the initial freezing point data. In their theoretical analysis, they compared the parallel, series, ME, and Levy models, and chose the Levy model as the best predictor. In their analysis with the ME model, however, they assumed ice to be in the continuous phase (ME2 model), so that they might have needed to add more resistance in their heat transfer model *via* the Levy model, which modifies the ME model by adjusting the volume fraction of the dispersed phase.

Murakami and Okos⁸) have applied the parallel-perpendicular model, a linear combination of the series and parallel model, to evaluate the effective thermal conductivity of frozen red fish. In this model, the relative contribution of the series heat-conduction mechanism to the parallel heat-conduction mechanism might have functioned as a fitting parameter, which is difficult to determine on a

rigorous theoretical basis.

In the present paper, the effective thermal conductivity values for glucose, sucrose, potato starch, gelatin, and egg albumin solutions in the frozen state were mathematically analyzed at various concentrations from -20 to 20°C , based on the measured data for the ice fraction of the same sample that was used for measurement of the effective thermal conductivity. As a result, the ME1 model with pure ice as the dispersed phase proved to be the best model in all the cases tested, suggesting the wide applicability of the ME1 model for predicting the effective thermal conductivity of frozen food. This result was rather unexpected because a dendritic ice structure grows from the surface to the inside in a direction parallel to the heat flow in a freezing process with ice crystal growth.¹²) Therefore, the ice structure in frozen food is presumed to be interconnected to some extent. This ice structure might not be strong enough as a whole to be considered as the dispersed phase from the aspect of heat conduction.

Establishing a systematic description of the effective thermal conductivity of food materials in the frozen state is also helpful for analyzing the ice structure formed in frozen food,¹²) which will be important to the analysis and control of such freeze-related operations as freeze-drying, freeze concentration, and freeze texturization.

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