COLLIGATIVE PROPERTIES OF FOODS

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Summary

The analysis of food behavior as a system affected by its own composition and external conditions is interesting for the analysis and design of preservation processes. The description of food as an aqueous solution and the application of fundamental chemical thermodynamic concepts to this type of solution allow the understanding of certain food properties related to composition, as in the colligative properties. These properties, based on the fundamentals of phase equilibrium, comprise the depression of freezing

point, elevation of boiling point, and osmotic pressure. The magnitude of such properties is affected by the quali- and quantitative composition of food, which in turn modifies the behavior of food during processes, such as in freezing, vaporization, osmotic dehydration, and membrane applications, among others. For this reason, it is important to know the theoretical concepts that can aid in understanding the colligative properties, as well as the application of these concepts to practical aspects of processes, such as those already mentioned.

1. Introduction

Most food systems can be studied as aqueous solutions. Therefore, it is possible to describe their thermodynamic behavior through the theoretical concepts applied to the ideal, as well as to real solutions. Such behavior mainly depends on the type, quantity, and interaction of the non-volatile solute or solutes contained in the food, in relation to the most important solvent in food, water. At first, solute-water interactions in foods affect certain properties, such as vapor pressure, chemical potential, and activity coefficients, but these in turn act on other properties, among which, the so-called colligative properties (i.e., freezing point depression, elevation of boiling point, and modification of osmotic pressure).

Such colligative properties are of interest to food engineers for the design and analysis of dehydration processes (e.g., concentration and osmotic dehydration), and freezing, and change magnitude according to the type of food and solute or solutes present within. In this way, the thermodynamic description of foods, and particularly the analysis of their colligative properties, is important and, in principle, can be determined based on the theoretical concepts describing solution behavior, which may or may not be ideal. For this reason, before studying in detail the above- mentioned properties it is recommended that one have a general view of what an ideal solution is, including a thermodynamic description.

2. Ideal Solutions

A two-component ideal solution can be defined as one in which the total pressure (P) of the gaseous phase generated from this is

$$P = X_1 P_1 + X_2 P_2 \tag{1}$$

where X_1 and X_2 are the mol fraction of components 1 and 2 of the mixture, with n_1 and n_2 as the moles of each to a total of n moles $(n = n_1 + n_2)$. In the case of binary mixtures of liquids, the ideal behavior is complied with, since a greater similarity exists between the chemical structures of both compounds.

According to Equation (1), it is obvious that Raoult's law describes the denominated partial pressure of each component $i(\overline{P_i})$ of the gaseous phase in equilibrium with the liquid phase:

$$\overline{P_i} = X_i P_i \tag{2}$$

where P_i is the vapor pressure of pure component i at temperature T.

On the other hand, if it appears that equilibrium between the solution and the gaseous phase generated exists, and if the latter behaves as a perfect gas, then it is possible to apply the chemical potential concept described in the topic Thermodynamics in Food Engineering (TFE):

$$\mu_{i(sol)} = \mu_{i(g)} = \mu_{i(g)}^{\circ} + RT \ln \overline{P_i} \tag{3}$$

which represents the chemical potential equality of the component, i, in the solution

$\left(\mu_{i(sol)} \right)$ and the vapor $\left(\mu_{i(g)} \right)$ thereby released, in terms of the standard chemical potential of the vapor $\left(\mu_{i(g)}^{\circ} \right)$ and of the component's partial pressure.

A combination of Equations (2) and (3) to define the chemical potential of component i in the solution leads to

$$\mu_{i(sol)} = \left[\mu_{i(g)}^{\circ} + RT \ln P_i \right] + RT \ln X_i \tag{4}$$

In this equation, the term $\left[\mu_{i(g)}^{\circ} + RT \ln P_i \right]$ is a constant at each temperature and represents the chemical potential of i as a pure liquid $\left(\mu_{i(1)}' \right)$. Hence,

$$\mu_{i(sol)} = \mu_{i(1)}' + RT \ln X_i \tag{5}$$

This equation is used to describe the solution behavior in terms of the concentration of each component. Additionally, if the solution participates in processes in which the pressure is maintained near 1 atm and pressure changes are very small, then the chemical potential of component i as a pure liquid will tend to equal the potential of component i in liquid form, and under standard conditions (1 atm of pressure), this means: $\mu_{i(1)}' = \mu_{i(1)}^{\circ}$. Thus, Equation (5) becomes

$$\mu_{i(sol)} = \mu_{i(1)}^{\circ} + RT \ln X_i \tag{6}$$

This equation is applied to the denominated truly ideal solution, and is particularly important in describing the behavior of many foods.

2.1. Thermodynamic Properties of Truly Ideal Solutions

If every component in a mixture behaves according to Equation (6), in all the

composition and temperature ranges considered, then the total free energy of the solution can be obtained:

$$G = \sum \mu_{i(sol)} n_i \qquad (7)$$

This expression is the result of integrating Equation (89), presented in TFE. If one mol of solution is considered, the molar free energy would be $G = \sum \mu_{i(sol)} (n_i/n)$ or $G = \sum \mu_{i(sol)} X_i$.

On the other hand, if the mixing process forms a solution, the free energy change resulting from this process should equal the difference found in the free energy of the solution minus that of all the isolate components in the liquid phase. Hence,

$$\Delta G_{mix} = \sum \mu_{i(sol)} X_i - \sum \mu_{i(1)}^{\circ} X_i \qquad (8)$$

Combining Equation (6) and (8) yields the free energy change in the mixture per each mol of solution, as a function of its composition:

$$\Delta G_{mix} = RT \sum X_i \ln X_i \qquad (9)$$

Regarding entropy of the mixture conducted at constant pressure; it can be calculated using Equation (68) from TFE:

$$\Delta S_{mix} = -\left(\delta \Delta G_{mix} / \delta T \right)_P \qquad (10)$$

This equation combined with Equation (9) generates the definition for ideal entropy as $\Delta S_{mix} = -R \sum X_i \ln X_i$.

Additionally, entropy change in the mixture, if an ideal solution is formed, can be calculated using Equation (64) from TFE:

$$\Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} \qquad (11)$$

This equation can be expressed as,

$$\Delta H_{mix} = RT \sum X_i \ln X_i - RT \sum X_i \ln X_i = 0 \qquad (12)$$

which indicates that in the formation of an ideal solution (if heat is not absorbed or released), there is no enthalpy change.

If Equation (69) from TFE is used to calculate the volume change in the formation of an ideal solution (at constant temperature), it can be demonstrated that such change is zero:

$$\Delta V_{mix} = \left(\delta \Delta G_{mix} / \delta P\right)_T = \left(\delta RT \sum X_i \ln X_i / \delta P\right)_T = 0 \tag{13}$$

Equations (9), (10), (12), and (13) describe the denominated thermodynamic properties of truly ideal solutions, and are the basis for defining those corresponding to real solutions.

2.2 Ideal Solid-liquid Solutions

It is important to analyze the behavior of liquid solutions in food engineering, but even more important is the analysis of solids in liquid solutions, since they describe the behavior of most foods. In many cases, it is feasible to consider solutions as ideal and binary, in which one of the solutes predominates in the food. This dominant solute is called a compound (2) and the water (or solvent) is called a component (1). Under equilibrium conditions, this binary solution can be expressed in terms of the chemical potential using Equation (6):

$$\mu_{2(s)}^{\circ} = \mu_{2(sol)}^{\circ} = \mu_{2(1)}^{\circ} + RT \ln X_2 \tag{14}$$

In this equation $\mu_{2(s)}^{\circ}$ and $\mu_{2(1)}^{\circ}$ represent the standard chemical potential of the solute in solid and liquid form, respectively, and the difference between them is denominated as free-energy change during melting (fusion). Hence,

$$-\Delta G_{fus}^{\circ} = \mu_{2(s)}^{\circ} - \mu_{2(1)}^{\circ} = RT \ln X_2 \tag{15}$$

If Equation (15) and the Gibbs-Helmotz expression are combined to evaluate the free energy changes as a function of temperature in the formation process of solid-liquid solutions, then

$$\left(\delta \ln X_2 / \delta T\right)_P = \Delta H_{fus}^{\circ} / RT^2 \tag{16}$$

In this expression, the term ΔH_{fus}° represents the molar fusion heat of the solid. On the other hand, if the solute forms a homogeneous solution with the solvent, and the solubility of the former is 1 at the melting point of the solid $\left(T_{fus}\right)$, then Equation (16) can be integrated between T_{fus} and T to generate the relationship of solute solubility as a function of temperature. Thus,

$$\ln X_2 = \left(\Delta H_{fus}^{\circ} / R\right)\left[\left(1/T_{fus}\right) - \left(1/T\right)\right] \tag{17}$$

This equation is useful in calculating the solubility of a solute in a liquid when the values of the fusion heat and fusion point are known.

Together with the description made before, it is important to recognize that in most

cases, the liquid fraction of any food behaves as a truly ideal solid-liquid solution, mainly due to the reason that such a fraction is a diluted solution. It can be said that the behavior of this type of solution follows the Raoult law mentioned previously.

3. Colligative Properties

Depression of freezing point, elevation of boiling point, and osmotic pressure of a solution are called colligative properties. In the case of diluted solutions, these properties linearly depend on the concentration of the solutes present. All the properties are interdependent, and since ideal solutions depend on the number of molecules present, if the molar concentration of the solution is measured, then any colligative property can be calculated. The parameter that serves to relate such properties is the activity of the solvent, which in the case of foods is called water activity (a_w).
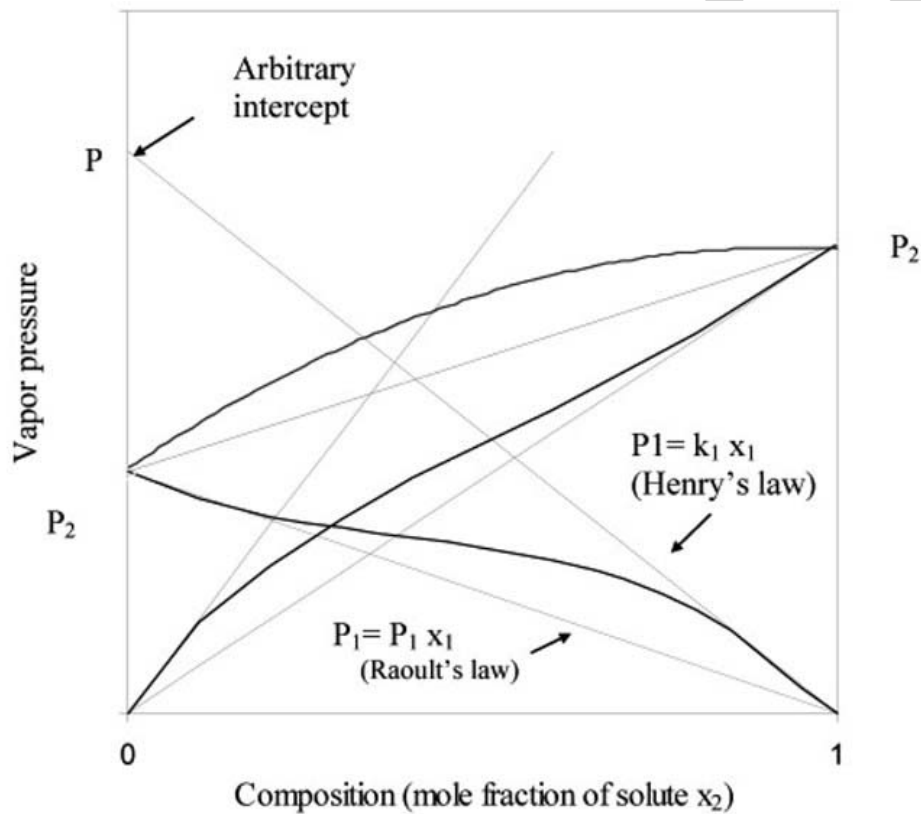

Figure 1. Vapor pressure of the components and total vapor pressure of a liquid mixture that deviates positively from Raoult's law (schematic). Water ethanol mixtures deviate from Raoult's law in this manner.

To understand the concepts related to colligative properties, two fundamental laws for solutions should be recalled, Raoult's law and Henry's law. The Raoult law, presented in Equation (2), indicates that the vapor pressure of the solvent is directly proportional to the molar fraction. Also, this law (graphically represented in Figure 1) can be approximately applied to many solutions and applied exactly to those diluted (i.e., ideal solutions). It is clear from Equation (2) that if the molar fraction of a solvent is known, its vapor pressure can be easily calculated.

On the other hand, Henry's law, which is experimentally obtained, indicates that the vapor pressure of the solute $\left(P_{(s)}\right)$ is proportional to the molar fraction of the solute $\left(X_{(s)}\right)$. However, the proportionality constant is not generally the vapor pressure of the pure solute, but a term experimentally determined, known as Henry's constant $\left(k_{(s)}\right)$. Henry's law is represented in Figure 1 and expressed as
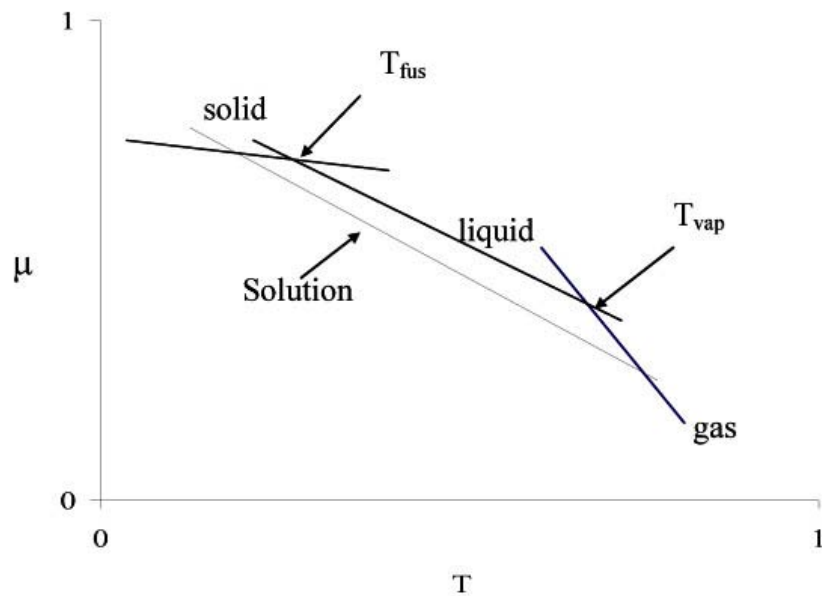
$$P_{(s)} = k_{(s)}\, X_{(s)} \tag{18}$$

Figure 2. Effect of added solute on the chemical potential of a liquid solvent, as a function of temperature. The freezing point is depressed and the boiling point is elevated.

If the solution is described by Raoult's law, for example, the solute is non-volatile and does not form a solution with the solvent when the latter is frozen, then the solute's presence will cause a decrease in the chemical potential of the solvent during a heating process (according to Equation 6). However, it would not affect the solid and gas phases. This effect is presented in Figure 2. The result of a reduction in the chemical potential of the liquid phase causes a reduction in the freezing point and an elevation in the boiling point of the solvent. Such depression and elevation represents the colligative properties.

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Biographical Sketches

Jorge Welti-Chanes was born in Puebla, City, Mexico; he obtained his B.S. in Biochemical Engineering (1976) and Master of Science in Food Engineering (1979) at the Instituto Tecnologico y de Estudios Superiores de Monterrey (ITESM) in his birth country. In 1979 he moved to Spain to obtain a Ph.D. degree in Chemical Sciences, with a major in Food Technology, from the Universidad de Valencia. He has been professor at the ITESM and, since 1977, at the University of the Américas-Puebla (UDLA). At UDLA, he has taught at undergraduate and graduate levels in the Departments of Chemical and Food Engineering and of Chemistry and Biology. He was Head of the department for one year, and then Dean of the Engineering Scholl (1986-1988). He was Academic Vice-President of UDLA (1988-2002) and currently is Professor and Researcher at the last institution and Visiting Research Scholar at Texas Christian University. His research areas are focused mainly on food and biological polymers, candy technology food drying, water activity, minimal processing of foods and biological materials, process

simulation and emerging technologies. He has been coordinator of diverse international research projects and advisor of different industries within the mentioned research areas. He was the World President of the International Association of Food and Engineering (1997-2000). Dr. Welti-Chanes is author of more than 140 scientific publications in refereed journals and books, and more than 150 presentations at international meetings. He is author or coeditor of the books: *Food Preservation by Moisture Control*, *Inventario de Alimentos de Humedad Intermedia Tradicionales de Iberoamérica*, *Engineering and Food for the 21st Century*, *Transport Phenomena in Food Engineering*, and *Harvesting, Handling, and Preservation of Fruits and Vegetables by Combined Methods at Rural and Village Levels (Technical Manual of FAO)*. He is a member of Editorial Boards for different journals and book-series, and an evaluator of research projects in Argentina, Chile, Uruguay, Venezuela, Mexico, and USA. He is advisor for different food enterprises in areas such as processing, quality assurance, and process optimization. Also, he has advised different universities in Mexico and Latin-America in Strategic Planning of Educational Processes.

María S. Tapia is Titular Professor in the Faculty of Science at Central University of Venezuela, Caracas, and was previously Chair of the Institute of Food Science and Technology (Instituto de Ciencia y Tecnología de Alimentos). She is Visiting Professor at the Universidad de las Américas, Puebla, México, and has been Visiting Scientist at the Center for Food Safety and Quality Enhancement at the University of Georgia, USA. She received her B.S. in Biology and has a Master of Science from Michigan State University. She has coordinated, both nationally and internationally, research projects in the following organizations: Consejo Nacional de Investigaciones Científicas y Tecnológicas de Venezuela (CONICIT); Agency for International Development (AID-CDR Program USA-Israel-Venezuela); Organization of American States (Multinational Project in Biotechnology and Food); Commission of the European Communities (R&D Program Life Sciences and Technologies for Developing Countries, National Coordinator as Associate Contractor); and Program of Science and Technology for Development (CYTED) as National Coordinator of Projects XI-1, XI-2 and XI-3, and International Coordinator of Project CYTED XI-15 (1999-2002) "Tecnologías Emergentes para la Conservación de Alimentos de Interés para Iberoamérica". She is Correspondent from Venezuela for Newsline, newsletter de (IUFoST) International Union of Food Science and Technologists. Her areas of research include the study of microbiology and microbiological stability during processing and storage of fruit products, and development of innovative technologies for fruit preservation based on the hurdle effect. She has published more than 50 scientific papers and book chapters, and has been advisor for 35 undergraduate theses and 11 Master's theses. She has been invited speaker to 21 international symposia and congresses. She is co-editor of the books: *Inventario de Alimentos de Humedad Intermedia Tradicionales de Iberoamérica; Handling, and Preservation of Fruits and Vegetables by Combined Methods at Rural and Village Levels (Technical Manual of FAO), Minimal Processing of Fruit and Vegetables. Fundamental Aspects and Applications, and Novel Food Processing Technologies.*

Stella M. Alzamora received her B.S. in Industrial Chemistry and her Ph.D. in Chemistry at the University of Buenos Aires (UBA), Argentina, where she is now Professor of Food Technology and Director of the Master in Science and Technology of the Industrialization of Foods. She is responsible for the Food Technology Programme of UBA and Principal Researcher of the National Council of Scientific and Technical Research. She was Head of the Industry Department in the Exact and Natural Sciences School (UBA) from 1991-1999. In 1993, she received the Konex Award, granted to 100 personalities of Science and Technique. Her research areas include innovative technologies for food preservation (mainly fruits) based on the hurdle effect, microbiological and physicochemical stability, quantitative microbiology and structural changes in vegetable tissues, and their relationship with mechanical properties. She is visiting professor at the University of the Americas, Puebla, Mexico; and vice president of ALACCTA (Asociación Latinoamericana y del CARIBE de Ciencia y Tecnología de Alimentos) 2000-2002. She has presented more than 150 research papers at national and international meetings, and published more than 75 scientific works in international journals and 17 chapters in books; in addition, she has edited 4 books. She is part of the editorial board of various journals and a Research Proposals referee for the national councils of Argentina, Chile, and Uruguay. She has advised various universities in Argentina on Food Science and Engineering educational curricula.

Enrique Palou is a Professor and Head of the Departamento de Ingeniería Química y Alimentos at Universidad de las Américas-Puebla in Mexico. Professor Palou is co-author of Nonthermal Preservation of Foods (Marcel Dekker, Inc.). The author or co-author of more than 30 scientific publications, Dr. Palou

received his Ph.D. (1998) in Engineering Science from Washington State University, and M.Sc. degree (1992) in Food Engineering from the Universidad de las Américas-Puebla, Mexico. He has presented more than 50 technical conferences at international meetings. Dr. Palou has taught Food Chemistry and Food Engineering since 1992. His research interests include predictive microbiology and innovative fruit processing technologies. The Sistema Nacional de Investigadores from Mexico honored him as Investigador Nacional Nivel I (National Researcher) in 1998. He is also a member of Institute of Food Technologies (IFT), American Society for Engineering Education (ASEE), International Association of Milk and Environmentals Sanitarians (IAMFES), and the Honor Society of Phi Kappa Phi. Currently, he is Treasurer of the International Association for Engineering and Food (IAEF) as well as for the Eighth International Congress on Engineering and Food (ICEF-8) to be held in Puebla, Mexico April, 2000.

Aurelio López-Malo is a Professor in the Departamento de Ingeniería Química y Alimentos at Universidad de las Américas-Puebla in Mexico. He is author and/or co-author of more than 100 scientific publications and co-editor of *Minimal Processed Fruits and Vegetables* (2000, Aspen Publishers, Inc.). He has made more than 150 technical contributions to several international conferences, symposia, and meetings. Aurelio received his Ph.D. in Food Science from Universidad de Buenos Aires, Argentina. His research interests include predictive microbiology, antimicrobials from natural resources and innovative fruit processing technologies. He was honored as Investigador Nacional Nivel II (National Researcher) in 1998 by Sistema Nacional de Investigadores from Mexico. He is also a member of the Institute of Food Technologies and International Association for Food Protection, and currently is part of the Journal of Food Protection editorial board.

Fidel T. Vergara-Balderas was born in Puebla City, Mexico; he obtained his B.S. in Food Engineering (1977) from the Universidad de las Américas A.C. (Mexico) and Master in Food Science (1980) from the Instituto Tecnológico y de Estudios Superiores de Monterrey, ITESM (Mexico). He was professor at ITESM, and since 1981, he has been professor and researcher at the Universidad de las Américas, Puebla (Mexico) where he teaches several courses in the Department of Chemical and Food Engineering. He was head of this department for 3 years (1996-1999). He is co-author of several scientific publications and presentations, and has offered consulting services and courses within the Food Industry in Mexico.