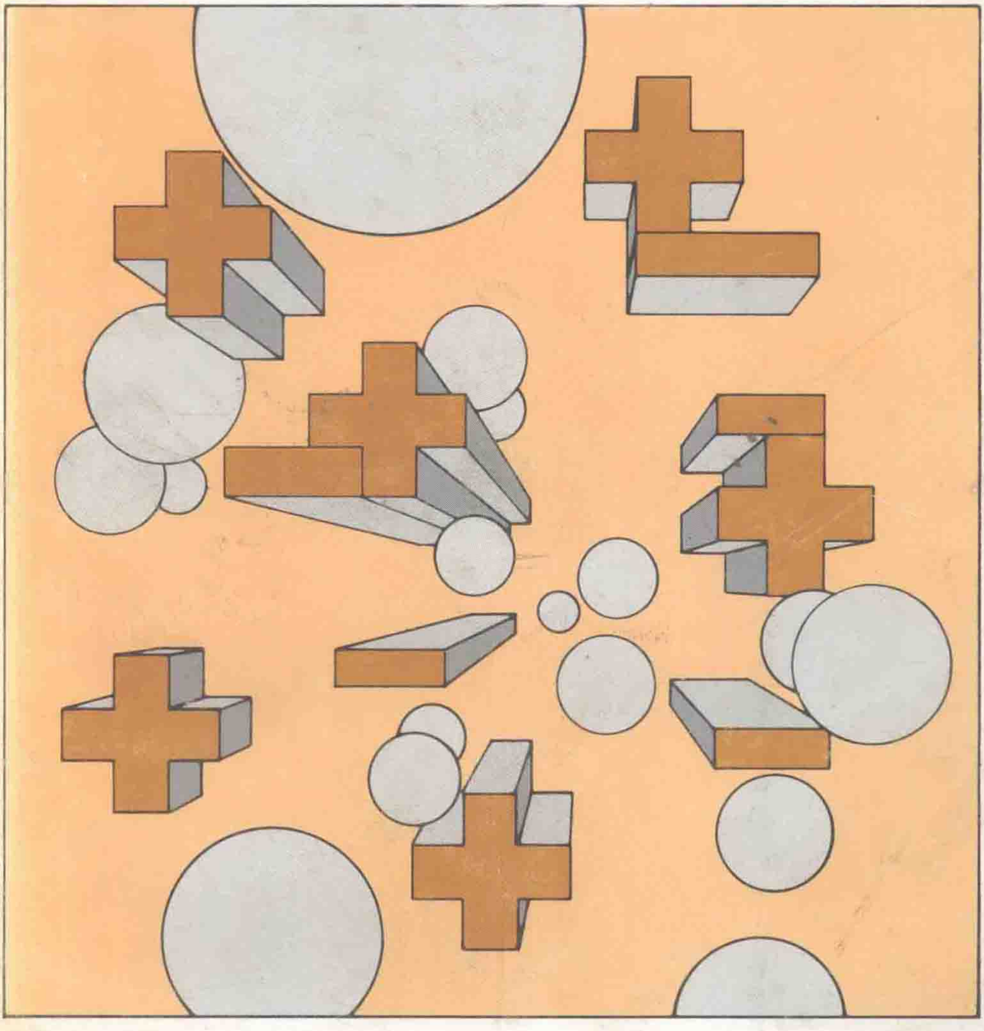
Thermodynamic Behavior of Electrolytes in Mixed Solvents—II

William F. Furter



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Thermodynamic Behavior of Electrolytes in Mixed Solvents—II

William F. Furter, EDITOR
Royal Military College of Canada

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Thermodynamic Behavior of Electrolytes in Mixed Solvents—II

Advances in Chemistry Series

M. Joan Comstock, *Series Editor*

FOREWORD

Advances in Chemistry Series was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the Advances in Chemistry Series maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

This is the second volume in a series dealing with the fundamental phenomena (and their applications) occurring when an electrolyte is dissolved in a mixed solvent, that is, in a solvent consisting of two (or more) liquid components. The first volume, ADVANCES IN CHEMISTRY SERIES 155, was published in 1976. Twenty-two chapters in the present volume represent contributions from nine different countries: the United States; Canada; Britain; Japan; Australia; France; India; Italy; and the Netherlands.

The various thermodynamic and physicochemical effects reported are often quite complex. The liquid phase continues to yield its mysteries with reluctance. A system composed of an electrolyte and a single-component solvent is complex enough; when the solvent consists of two or more components an additional range of complexity unfolds. This is largely the result of the greatly increased number of permutations and combinations possible in the interactions that may occur among the species present, both ionic and molecular, along with the usual tendency for these interactions to be composition dependent. Although much of the research represented here is basic, the potential for industrial application is immense; ranging, for instance, from applications in separating processes such as extractive distillation and liquid extraction, to electrochemical power sources such as fuel cells and batteries.

Some of the content deserves particular attention by industry at the present time. The first chapter by D. F. Othmer, 1978 winner of both the SCI Perkin Medal and the ACS Murphree Award, stresses the energy-saving potential of solvent or liquid–liquid extraction over more energy-consuming alternatives. Electrolytes often are used in such processing as complexing agents added to enhance interphase mass transfer of a solute species between two immiscible liquid phases. The three chapters dirctly following the one by Dr. Othmer examine the effects of nonvolatile electrolytes on the equilibrium vapor composition of mixed-solvent systems. Again there is a potential for major energy saving, this time in the replacement of generally high concentrations of liquid separating agent recirculated within conventional extractive distillation processes with much lower concentrations of a dissolved salt or other nonvolatile electrolyte as the separating agent.

The remaining eighteen chapters address a wide range of electrolyte effects on the liquid-phase properties of mixed-solvent systems, including such diverse but interrelated topics as solvation and liquid structure;

solubilities; activity coefficients; dissociation constants; distribution coefficients; free energies; viscosities; entropy; transfer functions; stability constants; acidity functions; enthalpies of solution; electrostatic theory; conductances; standard potentials; dielectric constants; various computational techniques; and related properties and behavior. A better understanding of such phenomena in this type of system must be obtained if efficient chemical engineering process design is to be achieved in systems where they are encountered.

Finally I would like to acknowledge the expert work of Joan Comstock and Candace Deren of the ACS Books Department in the production of this book and its predecessor.

Royal Military College of Canada
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March 22, 1979

WILLIAM F. FURTER

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Extraction of Concentrated Solutions

Refining of Sugar and Recovery of Acetic Acid from Wood-Pulping Liquors

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Separation of materials takes much of the energy used by chemical industry. Extraction often requires the least. An entirely water-miscible solvent may be immiscible with an aqueous solution that has a high concentration of a solid and may even extract another component therefrom. Thus, water-soluble acetone (alone or containing water-soluble ethanol) extracts impurities from raw sugar syrups or molasses (above 50% solids), refines sugar at less cost—especially in terms of energy, gives higher yields of sugar, and recovers valuable impurities that otherwise would be wasted. Acetone extracts acetic acid out of concentrated waste liquors obtained from semichemical or kraft-pulping processes after their acidification with sulfuric acid and is several times as efficient as conventional solvents. Operational profits may range from $15 to $20/ton of pulp produced.

Energy—as scarce and expensive as it is becoming—is used in the largest amounts in the process industries to separate the components of many diversified raw materials or feedstocks of most industries. It is used in the next largest amounts to separate the intermediates resulting from treatments with other materials for chemical or physical change or convenience. Finally, it is used in the least amounts to purify (i.e., separate) the products. Thus, the success of the chemical engineer in reducing these major requirements of energy—as its cost increases—will be of the greatest importance in maintaining the present selling prices of all resulting products—from pharmaceuticals to paper or pig iron and from acetic acid to zinc.

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The development of separation techniques is also a fascinating exercise in problem solving for the chemical engineer, in which his skill and experience are very important on the bottom line—i.e., in the energy cost as well as the dollar cost of the finished product. Also, the units of energy required in the separation processes now, more than ever before, translate into very important percentages of the dollar sum.

To separate solutions of both liquids and of solids in a liquid (particularly water), two methods usually are considered first: (1) vaporization—i.e., evaporation or distillation—to utilize the different relative volatilities of the components, either normally or accentuated by another liquid in azeotropic or extractive distillation and (2) liquid–liquid extraction to take advantage of the relative preferential solubility of one component in an added liquid.

A priori it would seem that liquid–liquid extraction with the almost negligible energy costs associated with the transfer of one material in a liquid solution (preferentially from one solvent to another) would be always more economical than vaporization in terms of energy. However, since the added solvent usually has to be separated subsequently from both the extract layer and the raffinate layer by distillation, these thermal costs for the overall separation may be substantial.

Processes using a great deal much less energy than conventional processes have been developed through pilot plant stages for the separation from an aqueous solution of important industrial materials, one of which is present as a very concentrated or saturated solution of a solid, which remains in the raffinate, while the other is extracted therefrom by an added solvent. Advantage is taken of the greatly lessened mutual solubility of the extracting solvent and of the water in the concentrated solution. The dissolved solid in the concentrated aqueous solution increases the relative solubility of the component dissolved in, and to be extracted by, the solvent compared with that in the water and at the same time reduces greatly the solubility of the solvent in the aqueous phase.

Two examples illustrate the many places in industry where other, quite different methods of separation are used conventionally to separate such concentrated solutions. Large amounts of energy are used now; valuable materials are lost or destroyed when a smaller amount of one material or group of materials is separated from the larger amount of another material or group of materials.

Sugar and Molasses

About 100 million tons world wide of sugar per year (more than half from cane, the balance mainly from beets) must be separated from five to ten times as much water and refined by more or less complete separation from a dozen impurities that are present in varying amounts. Juice expressed from sugar cane in the tropics is concentrated; sugar is crystallized therefrom and is shipped as "raw" (about 97% sucrose) to be refined to above 99% in the country of its use. Most of the molasses remaining as mother liquor after crystallizing out the raw sugar also is shipped from the point of origin (*1*).

The refining of raw sugar by solvent extraction costs less in energy and materials and can be done in a plant that is much less expensive to operate than a conventional plant (*2*).

When refining by solvent extraction, the cane juice can be concentrated to 60% or higher total solids, impurities can be dissolved out to give a pure syrup for shipment, or a pure sugar may be crystallized therefrom. If, alternatively, raw syrup instead of raw sugar is shipped (at the lower cost for handling a liquid in tankers), it can be refined by solvent extraction after delivery. Either operation will give a refined sugar or syrup at a much lower cost, particularly in energy requirements.

Conventional Cane Sugar Refining. Raw sugar as it is unloaded from the ships, besides containing 85–97% sucrose, also contains a small amount of water, suspended materials, invert sugars (glucose), and other organic chemicals such as aconitic acid, sugar cane fats and waxes, chlorophyl, various vitamins, and other constituents of the original sugar cane plant that have come with the juice. Soluble impurities are present in a thin aqueous film on the crystal surfaces of saturated sugar–molasses mixture.

The raw sugar is melted—i.e., dissolved in water—then refined in a sequence of evaporations and crystallizations with intermediate operations for removing and destroying minor impurities. By treatment with materials to adsorb the impurities, the sugar is crystallized from the purified solution and removed from the final mother liquid (molasses), which contains all of the impurities that were not adsorbed. These impurities—including potentially valuable wax, vitamins, and aconitic acid—if not wasted substantially in the molasses are lost on the adsorbent solid, with considerable expense in destruction or removal.

Such refining of raw sugar cane is done on a tremendous scale; most of it in this country is done in a dozen huge plants, one of which may spend $200,000 to refine 2,000 tons per day, of which $20,000 per day may be for fuel. Thus, all standard refining methods are expensive because of:

(a) the large heat cost in evaporating the water used to dissolve or to melt the raw sugar, as well as the water that is added in subsequent washing steps;

(b) revivification cost of the solid adsorbing agent, such as bone black, carbon black, or various ion-exchange resins, and the loss by discard of these adsorbed materials and ultimately the loss or discard of the adsorbent itself;

(c) complete loss of the value of all impurities except those sold as part of the final unseparable dregs, the ultimate molasses;

(d) mechanical and other losses (inversion) of the sugar during the numerous steps;

(e) the large size of and investment in the plant owing to the numerous steps and the considerable equipment required;

(f) the large requirements of water, principally for cooling; and

(g) the removal of pollution possibilities in various aqueous discharges from the refinery.

Refining of Raw Sugar by Washing with Solvent. To identify the impurities, raw sugar crystals of a carefully selected size, hence with a readily calculable surface area per unit weight, had their thin surface layer dissolved sequentially by several washings with nearly saturated sugar syrups of very high purity. Almost all impurities dissolved in the first washings, and these impurities were almost entirely in a film on the surface of the crystals. After very slight dissolution of the crystal surfaces themselves, most of the grain was almost pure sucrose. Thus, it appeared that a nonaqueous solvent, herein called the first solvent, which would dissolve off and separate the impurities from the crystals, would save the high cost of the classic melting or complete dissolution and the subsequent evaporation of water, crystallization of sugar, and removal of impurities in a low value liquid residue—molasses.

Previously reported experiments showed that the most desirable first solvents have the same number of oxygen and carbon atoms in the molecule. Such compounds are completely water soluble and also are good solvents for the impurities. (Solvents with molecules that contain chlorine, nitrogen, or atoms other than carbon hydrogen, and oxygen are not useful.) Thus, methanol and acetic acid are good, and the low boiling point of methanol is an advantage (3).

From 0.1 to 8% water in the first solvent aids this extraction. More water improves the efficiency of the solvent but decreases its selectivity—i.e., the solubility of many impurities is increased considerably, but so is the solubility of sugar. Thus, the water reduces the yield of refined sugar but increases its purity.

A higher temperature of washing, up to the solvent's boiling point, increases the removal of impurities in the least time. The temperature must not be high enough to carmelize the sugar. Good washing is secured in 1–2 hr with an equal weight of methanol just below its boiling point of 65°C. Higher temperatures require a pressure operation, which greatly reduces the time required.

With glacial acetic acid, temperatures up to its boiling point, 118°C, may be used. This higher washing temperature—without pressure—removes impurities in less time than methanol, and at temperatures between 105° and 110°C, the raw sugar is refined in 45–90 min.

Almost complete recovery of the solvent is essential, and higher boiling solvents makes this easier, but all but about 1% of the methanol may be recovered in a suitable closed system. Methanol is distilled readily for its recovery from water and from aqueous sugar solutions. Distillation of acetic acid, if used as a solvent, removes water also from the dissolved impurities and leaves a first molasses. (Other methods of separation of the solvent may be used.)

A very small amount of surface-active agent improves the rate of washing—i.e., reduces the time. A sucrose ester of a fatty acid, such as sebacic, in amounts of 0.001–0.01% of raw sugar, reduces the time necessary for extraction by 25–30%. This stays in the extract layer.

Sugar refined by washing with methanol is a very light straw color. Acetic acid gives a refined sugar with a much lighter color and lower ash. This indicates that the acidic as well as the solvent nature of acetic acid is important. Hence, a very small amount of sulfuric acid was added to methanol when this was used to give a pH of about 1.25. This step eliminated most of the color in the refined sugar, increased its purity by 0.1–0.25%, and reduced its ash content from 0.12–0.15% to 0.05–0.1%. This acidification also reduced the total free and combined aconitic acid from 0.05–0.15% to 0.01–0.02%. Aconitic acid was related directly to remaining color and, to a lesser degree, to the remaining ash. Thus, addition of sulfuric acid to spring the aconitic acid present at a pH of 1.25–1.3 gave a purity of 99.8% sucrose, improved color, and a washing time of less than 30 min at a temperature of 30°–40°C (3).

This washing by a completely water-soluble solvent does not remove all of the water in the raw sugar: the solubility of water in methanol and vice-versa is depressed by this complete saturation with sugar and the salting out of impurities.

The centrifuged and washed crystals of highly refined sugar immediately gave above 99% of the sucrose of the raw sugar. However, 1 or 2% of this came back as recycle from subsequent solvent extractions; these extractions would be on a very small scale because almost all of the sucrose content was produced as refined sugar in the first step.

Solvent Extraction of Sugar Solution Coming from the Washing of Raw Sugar. The solvent or extract layer from the washing of impurities from the raw crystals was settled to remove dirt and other small solid particles. The solvent was evaporated for immediate recycle, leaving behind a first molasses.

Equally as economical as the washing of impurities off of the raw sugar crystals, in terms of thermal energy and other costs, is the liquid–liquid extraction of impurities from concentrated sugar solutions (including molasses) by a solvent that is entirely soluble in water. Again, the high concentration of the sugar salts-out the impurities and prevents the mutual miscibility of the water in the sugar solution with the solvent, which, by itself, is completely miscible in all proportions with pure water.

In this way, constituents of the first molasses produced by solvent washing of raw sugar crystals can be separated by a second solvent. Preferably it is one that removes the less water-soluble impurities—oils, fats, waxes, aconitic acid, chlorophyl, etc.—from the sucrose and invert sugar. Hydrocarbons and chlorinated hydrocarbons, ethers, higher alcohols, and ketones have disadvantages as a solvent—e.g., they often form relatively stable emulsions.

Acetone was first rejected because of its complete miscibility with water but was found to be the best on all counts when it was used with solutions above 50% total solids because of the salting-out effect. Thus, the first molasses, diluted to 75% total solids, can be extracted in a counter-current extractor with one-half as much acetone by volume. The partition coefficient for aconitic acid may be over 4 to 1 in favor of acetone. The acetone extract layer contains a little water, and when the acetone is distilled off, a semisolid residue is left.

Analysis of this residue showed only about 4% sucrose, 6% inverts, and 17.4% total acids. Most of this (15.7%) was obtained as aconitic acid by leaching with hot water and subsequent crystallization. The residue was oils, waxes, and chlorophyl and could be separated by other solvent extractions; the sucrose and inverts were left to be processed for their sugar content by combining them with the raffinate from the extraction of the first molasses. The first molasses also was evaporated to strip off acetone and to concentrate the syrup further to a grain formation. The raw sugar obtained was about 98% sucrose and was recycled to join the original raw sugar feed, of which it represented approximately 1.3%. The extract layer was a small amount of light-colored molasses, low in sucrose and high in invert sugars; analysis showed it to contain five to ten times as much of several vitamins as conventional blackstrap molasses.

Solvent Extraction of Conventional Sugar Solutions. Sugar syrup made by directly concentrating cane juice or the blackstrap molasses that results after the crystallization of sugar therefrom can be refined also (2) by acetone extraction to remove the nonsugar constituents of oils, fats, waxes, chlorophyll, acids, etc. When total solids in the syrups are about 50%, the acetone forms a second layer that contains a larger percentage of the impurities than the first layer. The mutual solubility of acetone with the syrup decreases at high temperatures and this improves the extraction. Since the viscosity of the syrup is reduced greatly at higher temperatures, the rate of extraction is greatly increased. Other entirely water-soluble liquids were tried—e.g., methanol, ethanol, and glacial acetic acid. By themselves they usually go into solution, then remove the water to precipitate crystals (very small) and to give a solution and a solid phase at equilibrium. However, when mixed with appropriate amounts of acetone, they also give two liquid phases and can be used to refine sugar syrups.

Thus, as first indicated, the salting-out effect on impurities of concentrated sugar solutions will allow the refining of a sugar syrup by simple evaporation of a sugar juice expressed from cane to a total solids content of more than 50% and subsequent extraction with acetone, either at the point of production or at a refinery to which the raw syrup is shipped in tankers. A refined syrup or sugar then can be made mode cheaply than by present methods.

As another example, after a reaction process, acetic acid remained in a 60% sucrose solution. Water-miscible acetone was used to extract the acetic acid, and the partition coefficient between the two layers (gram acetic per gram acetone/gram acetic per gram sugar solution) was over 5 compared with less than 1.0 for solvents conventionally used to extract acetic acid from industrial solutions. This example shows again the great ability of the high concentration of the dissolved solid to prevent the normal miscibility of water and acetone and to salt-out the acetic acid from the aqueous solution into the extracting solvent.

Acetic Acid

Acetic acid is produced industrially by the oxidation or other degradation of many organic materials, and it is involved as a solvent or reagent in the synthesis of many important compounds. Having the same ratio of oxygen to carbon atoms as does the carbon monoxide molecule, it is often an intermediate in many oxidation processes, both chemical and bacterial. Formic acid, which has the same ratio of oxygen to carbon as does carbon dioxide, was produced also but in lesser amounts because of its comparative instability. Numerous chemical reactions leave acetic acid or its salts in the spent aqueous solutions, together with a high concentration of other liquids or solids. The decomposition of lignocellulose by any process gives acetic acid and usually formic acid or their salts. For example, destructive distillation gives charcoal as the principal product, pulping gives cellulose for paper, alkaline fusion gives oxalates, and bacterial action gives numerous materials. Often large amounts of other solids are present also in the aqueous solution of acetic acid or its particular salt, depending on the raw material used. All of these may involve large amounts of other solids, which may salt-out the acetic acid (and formic acid if it is present) in an extraction for their removal.