Review Paper

Thermodynamic Characteristics of Solvents: A Review

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Abstract

In this review article some theories related with thermodynamic properties of solvents, and solvent mixtures are discussed.

Keywords: Thermodynamic properties, solvents, binary solvents.

Introduction

Recently, research on solvents and solutions has become a topic of interest because many of the solvents commonly used in laboratories and in the chemical industry are considered as unsafe for reasons of environmental protection. On the list of damaging chemicals, solvents rank highly because they are often used in huge amounts and because they are volatile liquids that are difficult to contain. Therefore, the introduction of cleaner technologies has become a major concern throughout both academia and industry. This includes the development of environmentally benign new solvents, sometimes called neoteric solvents (neoteric = recent, new, modern), consitituting a class of novel solvents with desirable, less hazardous, new properties. The term neoteric solvent covers supercritical fluids, ionic liquids, and also perfluorohydrocarbons (as used in fluorous biphasic systems).

For the development of a sustainable chemistry based on clean technologies, the best solvent would be no solvent at all. For this reason, considerable efforts have recently been made to design reactions that proceed under solvent-free conditions, using modern techniques such as reactions on solid mineral supports (alumina, silica, clays), solid-state reactions without any solvent, support, or catalyst between neat reactants, solid-liquid phase-transfer catalyzed and microwave-activated reactions, as well as gas-phase reactions. However, not all organic reactions can be carried out in the absence of a solvent; some organic reactions even proceed explosively in the solid state. Therefore, solvents will still be useful in mediating and moderating chemical reactions and e, the experimental and theoretical examination of the structure of liquids is among the most difficult tasks of physical chemistry¹.

Solvent Mixtures

Much of chemistry is carried out in solution hence solvents are necessary and widely employed requisite in chemical processes, both in industry and in the laboratory. A solvent is a substance that is a liquid at the temperature of application, which other substances can be dissolved in or mixed with to yield a homogeneous isotropic liquid. Water is the most widely used solvent because of its availability, low cost, non-toxicity and safety as well as its ability to dissolve a great variety of substances including electrolytes and polar organic substances. Certain substances are more soluble in polar organic solvents, which also have other properties that make them useful and desirable solvents. In many of these applications the solvents are employed in substantially pure form, as so called neat solvents, and many have various impurities removed before use².

For certain applications, however, neat solvents fall short of the mark as far as their dissolving power or other properties are concerned. It is then expedient to use solvent mixtures, which may range from binary mixtures involving two solvents to ternary (three solvents) or even higher multi-component mixtures. Some of the admixed substances may not be liquids at the temperature of applications hence mixtures involving them are not properly called solvent mixtures. Then again, the presence of a small amount of one liquid substance in a large excess of another at mole ratios or fraction of say, 1: 100, may have far reaching effects on the properties of the major component. Such dilute solutions are proper subjects for study and lead to important insight concerning their behavior, but are not ordinary called "Solvent Mixtures".

Mixed solvents are often used in chemistry to modify molecular environment in order to modulate processors such as chromatographic separation, organic synthesis, reaction kinetic and protein folding³. Physical properties of binary mixtures are often studied to get information about the mutual interaction between the solvent molecules.

Solvation of solute in a mixed binary system is another phenomenon, which depends on the mutual interaction of

solvents. It has been observed that the maximum energy of charge transfer (CT) transition in various solutes act as a reporter of solvation interaction reflecting solute-solvent and solvent-solvent interactions at the microscopic level⁴.

A number of theories have been developed for binary mixtures. These theories are based on either the radial distribution function or on the choice of some suitable physical model. Theories of perturbation type have been extended to the case of mixtures from the problems of pure liquids where it showed its successful application. Lennard Jones and Devonshire attempted first to evaluate the thermodynamic functions for a single component fluid in terms of intermolecular energy parameter. They used "free volume" or "cell" model.

I. Prigogine and S. Garikian extended the above model to the liquid mixtures Random mixing of components was their main assumption that can be used if the molecules have similar sizes. I.Prigogine and A.Belleman developed two fluid versions of the cell model. They got the result that while V^E was negative for mixtures of molecules of same size but they found large +ve VE for solutions with molecules having small difference in their molecular size. D. Cook and Languet-Higginsgave a new approach with his theory of conformal solution which is based on the principle of corresponding states as developed by Pitzer. He used a simple perturbation approach to show that the properties of mixtures could be obtained from the knowledge of intermolecular forces and the thermodynamic properties of the pure components.

A more successful approach is due to Flory, who also made use of certain features of cell theory and assumes an empirical equation for the dependence of energy on volume. Flory and coworkers have developed a statistical mechanical theory for predicting the excess functions of binary mixtures from the equation of state, properties of pure liquids alongwith adjustable parameters. This theory was developed originally for non-polar liquids only however, use of adjustable parameters makes it applicable to components whose molecules interact in a specific manner. This is the only theory that can be applied to mixtures of realistic interest in which the component molecules may differ considerably in size and shape.

D.Patterson and G.Delamas combined both Prigogine and Flory theories and presented a general, unified theory from which one is able to identify various contributions such as free volume, interaction, internal pressure, etc. in the excess thermodynamic quantities. Recently, A.J.Trezczanowicz and G.C.Benzon⁵, Heintz and co-workers⁶⁻⁷ described the thermodynamic properties of associated mixtures using, association. The thermodynamic properties were expressed as the sum of chemical term described by an associated model and a physical contribution given by Flory equation of state theory. This model is known as extended real associated solution (ERAS) model.

Ion-Solvent and Ion-Ion Interactions

The thermo -physical properties of liquid systems are strictly related to the molecular interactions present in different binary liquid mixtures. The variation of these properties with composition gives us important data about intermolecular interactions and the structure. There is a wide range of possible interactions between the components of a mixture, such as hydrogen bonding, molecular associations, charge transfer, dipole-dipole and dipole-induced dipole interactions. As a consequence of these interactions, deviations occur from ideal behavior of dielectric constant and viscosity. These deviations can be defined by excess dielectric constants and viscosities.

The interaction between liquid-liquid and liquid-solid system are very important, because it help to understand the interactive forces working among them. Recently various workers studied the drug released mechanism in mixed solvent system. It is observed that a solid is soluble in one solvent and insoluble in another. But it is fairly soluble or extremely soluble in mixed solvent systems. Such behavior of organic compounds varies from compound to compound and it has to be studied in detail. These studies will also help us to understand the nature of ion-solvent forces which overcome the ion-ion forces holding together the crystals. If the compound is solid or ionic crystal, a solvent reduce the force which hold the ions together. A stage is reached when the cohesive forces are so weakened that the ions, which could only vibrate in solid state, acquire a new degree of freedom, i.e. the freedom of translation motion.

There are various models suggested for the interactions of ions in single solvent system. The Born model suggests a simple process for calculating the free energy, ΔG , of ion-solvent interaction.

When an ion is present in a polar solvent like water, the structure of water near ion is divided into three regions. In the primary or structure-enhanced region next to the ion, the water molecules are immobilized and oriented by the ionic field, they move as and where the ion moves. Then, there is a secondary or structure-broken region, in which the normal bulk structure of water is broken down to varying degrees. The in-between water molecules, however, do not partake of the translational motion of the ion. Finally, at sufficient distance from the ion, the water structure is unaffected by the ion and displays the tetrahedrally bonded network characteristic of bulk water.

The second model assumes that there is an interaction between ion and dipole of solvent. The solvent molecules interact in such a way that there is minimum interaction energy involved.

In this theory, the first contribution was considered to arise from the interaction between the ions and water molecules which are members of the primary solvent sheath. The second contribution is due to the interaction between a primary solvated ion and the surrounding solvent. A change in heat content due to the structure breaking around a primary solvated ion constitute the third contribution.

When a, non-electrolyte is added to the solvent system its solubility changes due to primary and secondary solvation. There are various examples which affect the solubility of non-electrolytes in presence of ions such as salting out of soap and manufacturing of dyes, detergents, emulsions, polymerization and the concentration of antibiotics and vitamins from aqueous solution, all depend in some parts of their manufacture upon salting in.

Ion-solvent interactions are only part of the story relating ions to its environment. When an ion looks out upon its surroundings, it sees not only solvent dipoles but also other ions. The mutual interactions between these ions constitute an essential part of the picture of an electrolytic solution. The ion-ion interactions are important, because they affect the equilibrium properties of ionic solutions and also because they interfere with the drift of ions, for instance, under an externally applied electric field.

The degree to which these interactions affect the properties of solutions will depend on the mean distance apart of the ions, i.e. on how densely the solution is populated with ions, because inter ionic fields are distance dependent. This ionic density will in turn depend on the nature of electrolyte i.e. on the extent to which the electrolyte gives rise to ions in solution. Solutions of most potential electrolytes in water generally contain only small concentration of ions and therefore, ion-ion interactions in these solutions are negligible; the ions are on the average too far apart. The behavior of such solutions is governed predominantly by the position of the equilibrium in the proton-transfer reaction between the potential electrolyte and water. In contrast, true electrolytes are completely dissociated into ions when the parent salts are dissolved in water. The resulting solution generally consists only of solvated ions and solvent molecules. The dependence of many of their properties on concentration is determined by interactions between ions and to understand these properties, one must understand ion-ion interaction.

The structure of Solvent

Water is a unique solvent in many senses. One of the most remarkable properties of water is the strong and steric solvent structure formed by the hydrogen bonding network. In particular, the solvent structure plays a very important role in the hydrophobic case. If the solute molecule is strongly hydrophobic, the water network around the hydrophobic solute tends to be stronger than of the bulk phase. It is called the hydrophobic hydration. In 1938, Butler et.al found that the dissolution entropy changes of non-polar solutes are negative and heat capacity changes are very large. In 1945, Frank and Evans interpreted this observation by the iceberg hydration model, which is the basic model of the hydrophobic hydration⁴.

In 1959, Kauzmann proposed the concept of hydrophobic interaction, and since ~1970, Ben-Naim has developed the concept of hydrophobic hydration. After that many observations and calculations of hydrophobic hydration have been reported. The solvent structure of water has been elucidated by x-ray diffraction⁸, neutron diffraction and several calculations. The hydrogen bond of water molecule can extend to four directions, and the solvent structure is tetrahedral like that of diamond.

Pure water is a polymer, (HO)_n, and the value of n is not known presently. Many theories have been proposed by several workers to deal with the structure of water. All these theories have been explained with theoretical models. Many models have been proposed for the structure of liquid water, but none has been completely verified experimentally. One of the models suggests that liquid water consists of ice-like clusters of water molecules in a labile equilibrium with free water molecules. According to continuum model, although a great majority of hydrogen bonds between water molecules in ice at 0°C remain unbroken, but when ice is melted, they distorted or bent at different angles.

The structural feature of liquid water depends primarily on its ability to participate in any number of hydrogen bonds by utilizing its two H-atoms and loan pair of electrons on oxygen. In many structures, water achieves its tetra-co-ordination. One of the structures which show this behavior is the ordinary form of ice that exists at 0°C and 1 atmospheric pressure. The ice lattice is open one, accounting lower density than the liquid water at the melting point. When ice melts, there still exists a high degree of H-bonding in the resulting liquid.

Frank and Wen considered the "flickering cluster concept". They described that the formation of H-bonds in liquid water is a co-operative phenomenon i.e. the bonds are not made and broken singly, but several at time thus producing a short lived clusters of highly hydrogen bonded regions surrounded by non-bonded molecules. This concept assumes that when bond is formed several will form and when one bond breaks, several will break. However, all these models prove themselves untenable for a complete description of the physico-chemical properties of water and an interpretation of its anomalies.

Liquid water consists both of bound ordered regions of a regular lattice and regions in which the water molecules are hydrogen-bonded in a random array; it is permeated by monomeric water and interspersed with random holes, lattice vacancies, and cages. There are chains and small polymers as well as bound, free and trapped water molecules. The currently accepted view of the structure of liquid water treats it as a dynamic three-dimensional hydrogen-bonded network, without a significant number of non-bonded water molecules, that retains several of the structural characteristics of ice (i.e. tetrahedral molecular packing with each water molecule hydrogen-bonded to four nearest neighbors), although the strict

tetrahedrality is lost. The H-O-H bond angle in vapor phase and in solid 9 is 104.35° and 19.8° respectively. High dielectric constants also support the flickering cluster concept.

In principle, other hydrogen-bonded solvents should possess similar complicated structures. However, whereas water has been thoroughly studied, the inner structures of other solvents are still less well known.

Alcohols are the compounds with polar character. The dipole-dipole type of Van der Waals forces is present. In addition to dipole-dipole forces, alcohols are hydrogen bonded and thus involves strong intermolecular interactions. The physico-chemical properties of aliphatic alcohols like methanol, ethanol etc. varies with variation in increasing chain length of alkyl group. Alcohols are the most well known solvents used to study the hydrophobic effects. Alcohols are highly applicable in pharmaceutical industries. In view of their simple molecular structure, increasing hydrophobic character, with increasing chain length and high solubility in polar solvents, most of their physical properties have been extensively studied.

Mixtures of water with aliphatic alcohols are of considerable interest from the viewpoint of the existence of some interaction, such as hydrogen bonding between water which contains an - OH group and can act as a donor- and alcohol molecules, which have one acidic H atom on the -OH group and can act as – acceptors.

The assumptions of forces of interaction between solvent and solute led, on the other hand, to the century-old principle that "like dissolve like", where the word "like" should not be too narrowly interpreted. In many cases, the presence of similar functional groups in the molecules suffices. When a chemical similarity is present the solution of the two components will usually have a structure similar to that of the pure materials (e.g. alcohol-water mixture).

However, rather than the "like dissolves like" rule, it is the intermolecular interaction between solvent and solute molecules that determines the mutual solubility. A compound A dissolves in a solvent B only when the intermolecular forces of attraction KAA $^{\rm and}_{\rm KBB}$ for the pure compounds can be overcome by the forces $_{\rm KAB}$ in solution.

Intermolecular forces are those which can occur between closed-shell molecules. These are also called Van der Waals forces, since van der Waals recognized them as the reason for the non-ideal behavior of real gases. Intermolecular forces are usually classified into two distinct categories. The first category comprises the so-called directional, induction, and dispersion forces, which are non-specific and cannot be completely saturated (just as Coulomb forces between ions cannot). The second group consists of hydrogen-bonding forces, and charge-transfer or electron-pair donor-acceptor forces. The latter groups

are specific, directional forces, which can be saturated and lead to stoichiometric molecular compounds. For the sake of completeness, in the following the Coulomb forces between ions and electrically neutral molecules (with permanent dipole moments) will be considered first, even though they do not belong to the intermolecular forces in the narrower sense.

The term solvation refers to the surroundings of each dissolved molecule or ion by a shell of more or less tightly bound solvent molecules. This solvent shell is the result of inter molecular forces between solute and solvent. For aqueous solutions the term used is hydration. Intermolecular interactions between solvent molecules and ions are particularly important in solutions of electrolytes, since ion exert specially strong forces on solvent molecules.

Since volume is an additive property, gross changes in the volume of a system can be assessed by comparing the volume of the system with those of its components. Moreover, volumetric data often lead to interpretations in terms of molecular interactions within the system. Volumetric data of drugs, lipids, bilayers, and membrane proteins can provide clues to the interactions occurring in cellular fluids. Recent literature on the volumetric properties of drugs and other materials of biological importance shows increasing interest by a number of workers in this area of study.

Anomalous physical properties of alcohol-water mixtures at room temperature have been studied extensively over the year. Different structures and mechanism for formation of those structures in alcohol-water solutions at low to high alcohol concentrations have been proposed ¹⁰⁻¹¹. Several experimental studies indicate that at low alcohol content, water structure is stronger than that in pure water. At higher alcohol concentration, however, the water structure breaks down and the characteristic chain like structure of pure alcohol predominates¹². At high water content, at infinitely dilute third component (an ion or a neutral solute) competes with the alcohol molecules to be properly "surrounded" by water structure. This is dictated by the relative interaction strengths between the solute and the solvent molecules of different species. As a result the structure forming and breaking ability of alcohol in water is modified in presence of an ion or a solute.

Moreover, specific interactions among these components may favour enriching of one component over the other in the first few solvation shells giving rise to what is known as preferential solvation. In such a situation one would like to ask the following question. First, will there be any preferential solvation and thus non-ideality in the absence of any solute-solvent and solvent-solvent specific interactions second, how solvent size disparity would affect the preferential solvation and thus the non-ideality, third, what are the effects of solute size on the non-ideality, fourth can one develop a theoretical formalism which will be simple and analytically tractable yet

capable of describing the liquid structure in these complex mixtures, at least qualitatively?

Recently Hemant Kashyap and Ranjit Biswas¹³ extended the mean spherical approximation (MSA) framework in order to investigate answer to these questions. They extended MSA formalism to study the solvent size ratio dependence of non-identity in Born-free energy of solvation of an infinitely dilute ion in two different types of binary mixtures at different mole fraction of the solvent components, mixtures containing associating (H-bonding) solvents, (ethanol and water) and those made-up of non-associating solvents (DMSO and acetonitrile). The D.M. of water is slightly larger than ethanol, but the size is considerably smaller. This assists water molecules to be perfectly chosen in the first solvation shell and hence the non-ideality is likely to be stronger.

Therefore, larger ions would be able to accommodate the larger solvent components leading to a more "homogeneous" solvation structure. This in turn, will render the non-ideality weaker. It is to be noted here that the preferential solvation in model binary mixtures have been studied earlier 14-15 and these studies indicated that specific interactions among the components are not crucial for giving rise to non-identity. The ethanol- water mixtures show greater non-ideality than DMSO- acetonitrile mixture by using MSA framework.

Literature Survey

N.Adeyinka et.al16 applied the reduced 3-suffix solubility equation to the characterization of solubility in the ethanolwater system. The reduced 3-suffix solubility equation was developed to predict the solubility of non-polar organic compounds in solvent mixtures. The equation was shown to be adequate for describing the solubility profiles of the compound tested in ethanol-water and other systems ¹⁷⁻¹⁸. For a binary solvent mixture, the experimental data needed are the solubility of the compound in each of the pure solvents and the solubility in mixture of solvent. The latter is needed to estimate the solutesolvent interaction constant C Much attention has been paid to the volumetric behavior of dilute aqueous alcohol solutions, where unique changes in many thermodynamic properties are observed ¹⁹. Since the alcohol molecule in water can be regarded as a "soluble alkane", the interesting volumetric behavior has been usually interpreted in terms of the groupwater interactions that are so called iceberg effect or hydrophobic hydration. On the other hand, little attention has been paid to the contributions of the hydrophilic group-water interactions to the volumetric properties. The large negative excess volume observed for aqueous monohydric alcohol system is not due to the hydrophobic effects, but mainly to geometrical factors and hydrophilic interactions²⁰.

Thermodynamic properties of binary mixtures of alkanols with polar and non-polar solvents have been described by a number of workers²¹⁻²² in terms of lattice model theories. In the chemical

industry, a knowledge of the thermodynamic properties of nonelectrolyte solutions are essential in the design involving chemical separations, heat transfer, mass transfer and fluid flow²³. The mixtures of binary non-electrolyte liquids have been studied from different perspective in recent years. Equilibrium and thermodynamic properties are studied very widely for a number of mixtures and statistical theories are developed to correlate these properties with intermolecular forces²⁴.

Physicochemical investigations of electrolyte solutions were aimed to have a better understanding of ionic interactions in different solvents. The active interest in the solution chemistry of electrolytes at low concentration region resulted into a primitive model of ions, interacting in a structureless dielectric medium, obeying Coulombs law. On the other hand anhydrous molten salts have also been extensively studied²⁵ with a view to their use as industrial solvents, electro-winning of metals, high energy-density storage batteries, nuclear reactors, disposal of wastes and vulcanology.

Mixed electrolytes are very important in that they are found in numerous processes in chemical industry. They occur in enormous quantities in water of the oceans and have an important role in the physiological process of body fluids and cell equilibria. Various types of interactions exist between the ions in solutions and of these ion-ion and ion-solvent interactions are of current interest in all the branches of chemistry. These interactions help in better understanding of the nature of solute and solvent i.e. whether the solute modifies or distorts the structure of solvent²⁶⁻²⁸.

Solute-solvent interaction studies have been a subject of active interest among physical chemists and mostly the inferences regarding these interactions are drawn from conductance, molar volume data and viscosity data together. Studies in mixed solvents are of considerable interest because peculiar results are obtained in most of the solvent systems. The volumetric, viscometric and acoustical properties of binary liquid-mixtures containing alcohols as a function of molecular size, shape and molecular association of alcohols have been reported²⁹⁻³⁰.

Most of the drugs are organic molecules with both hydrophobic and hydrophilic groups. These molecules often contain certain groups, which are responsible for their acidic, basic or amphoteric properties. Pharmacological properties³¹⁻³² of drugs is highly dependent on the solution behavior. These drug molecules show specific interactions with lipid molecules due to hydrophobic groups and electrostatic interactions due to hydrophilic groups. The processes of drug transport, protein-binding, anesthesia are but a few examples where drug and biomacromolecules appear to interact in an important and vitally significant manner. The mechanisms of these molecular processes, however, are not clearly understood.

Fundamental properties such as enthalpy, entropy and Gibb"s free energy represent the macroscopic state of the system as an average of numerous microscopic states at a given temperature and pressure. An interpretation of these macroscopic properties in terms of molecular phenomenon is generally difficult. Sometimes, higher derivatives of these properties can be interpreted more effectively in terms of molecular interactions. For example the partial molar volume, the pressure derivatives of partial molar, Gibb"s energy are useful parameters for interpreting solute-solvent interactions. Various concepts regarding molecular processes in solution, hydrophobic hydration³³, micellization and cosphere overlap during solute-solute interactions³⁴to a large extend, have been derived and interpreted from the partial molar volume data.

The physico-chemical properties play important role in interpreting the molecular interactions occurring among mixed components. As a result there has been renewed interest in the study of physico-chemical properties of liquid-liquid systems³⁵ ³⁷. One of the important ways to study molecular interactions in fluids is the use of thermodynamic properties. The first systematic attempt made in this direction was by Young³⁸, who collected a large amount of data on the thermodynamic and mechanical properties of liquid mixtures. The thermodynamic properties are the convenient parameter for interpreting solutesolvent interactions in the solution phase, which ultimately explain the excess properties using different interaction parameters. The excess thermodynamic properties of mixed system correspond to the difference between the actual property and the property if the system behaves ideally. These properties provide important information about the differences in the intermolecular forces operating among mixed components. The theoretical values of the excess functions depend critically on the assumption about the extent of their interactions, weak or strong, and size. The interactions between the molecules can be established from a study of characteristic departure from ideal behavior of some of the physical properties like density, viscosity, conductance and refractive index³⁹.

The present theories on liquid, acknowledge about molecular size, molecular structure and polarity are found to be inadequate to predict the properties of a mixture from the nature of its constituents. This is due to the non-availability of the data essential for understanding the nature of interactions among the constituents of the system. The physico-chemical properties involving excess thermodynamic functions has their relevance in carrying out engineering applications in the process industry and in the design of industrial separation processes. The current theories and their results expressed in terms of excess thermodynamic functions can be successfully checked and utilized if the experimental data for the excess functions are available. The data along with relevance information of the excess thermodynamic functions can be used for development of empirical correlation and also for the improvement of theoretical knowledge.

When a solute, polar or non-polar, dissolved in water, it may break water structure or preserve water structure through interactions. The equilibrium between non-bonded water and bonded water is disturbed due to the addition of a solute in water. Thus solutes or additives can be classified as water structure breakers or water structure makers. Ben and Neim have considered that water consists of distinct species of different densities both monomeric and polymeric forms. When a non-polar or partially polar solute is added to water, the added solute drives the equilibrium towards the species of highest density. Thus the free volume is made available for the accommodation of solute. This volume may be greater or less than that actually required by solute. The physical chemistry of drug molecules is a subject of study of recent origin and a number of researchers are looking for physical properties of several drugs. The first stage in this process is to study thermodynamic properties of drugs in aq. solution. Literature survey reveals that very few drug molecules are studied on this background.

Tarlok S. Banipal et.al⁴⁰. determined and reported density, viscosity and apparent molar volume of glycine, DL- α alanine in water and in aqueous solutions of each of potassium chloride, barium chloride, glucose and sucrose.

Ramkrishna Pramanik and Sanjib Bagchi⁴¹ have studied the solvation of ,6-diphenyl-4-(,4,6-triphenyl)-1-pyridinium phenolate in ethanol + octan-1-ol binary mixture. The results, indicating preferential solvation of the solute by ethanol, have been analyzed in terms of a suitable model to get information about solute-solvent and solvent-solvent interaction.

Conclusion

The present paper describes that the thermodynamic properties of liquid gets modified if the liquid mixture is used as solvent for electrolytes and non electrolytes.

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