

**Arieh Ben-Naim**

# **Solvation Thermodynamics**

# Solvation Thermodynamics

**Edward Leamington Nichols, William  
Suddards Franklin**

## **Solvation Thermodynamics:**

**Solvation Thermodynamics** Arieh Y. Ben-Naim, 2013-03-09 This book deals with a subject that has been studied since the beginning of physical chemistry. Despite the thousands of articles and scores of books devoted to solvation thermodynamics I feel that some fundamental and well established concepts underlying the traditional approach to this subject are not satisfactory and need revision. The main reason for this need is that solvation thermodynamics has traditionally been treated in the context of classical macroscopic thermodynamics alone. However solvation is inherently a molecular process dependent upon local rather than macroscopic properties of the system. Therefore the starting point should be based on statistical mechanical methods. For many years it has been believed that certain thermodynamic quantities such as the standard free energy or enthalpy or entropy of solution may be used as measures of the corresponding functions of solvation of a given solute in a given solvent. I first challenged this notion in a paper published in 1978 based on analysis at the molecular level. During the past ten years I have introduced several new quantities which in my opinion should replace the conventional measures of solvation thermodynamics. To avoid confusing the new quantities with those referred to conventionally in the literature as standard quantities of solvation I called these nonconventional generalized and local standard quantities and attempted to point out the advantages of these new quantities over the conventional ones.

**Solvation Thermodynamics** Professor of Physical Chemistry Arieh Ben-Naim, 2014-01-15 [Molecular Theory of Solutions](#) Arieh Ben-Naim, 2006-07-27 This book presents new and updated developments in the molecular theory of mixtures and solutions. It is based on the theory of Kirkwood and Buff which was published more than fifty years ago. This theory has been dormant for almost two decades. It has recently become a very powerful and general tool to analyze, study and understand any type of mixtures from the molecular or the microscopic point of view. The traditional approach to mixture has been for many years based on the study of excess thermodynamic quantities. This provides a kind of global information on the system. The new approach provides information on the local properties of the same system. Thus the new approach

supplements and enriches our information on mixtures and solutions. **Single-Ion Solvation** Philippe Hunenberger, Maria Reif, 2011-04-18 Ions are ubiquitous in chemical, technological, ecological and biological processes. Characterizing their role in these processes in the first place requires the evaluation of the thermodynamic parameters associated with the solvation of a given ion. However, due to the constraint of electroneutrality, the involvement of surface effects and the ambiguous connection between microscopic and macroscopic descriptions, the determination of single ion solvation properties via both experimental and theoretical approaches has turned out to be a very difficult and highly controversial problem. This unique book provides an up to date, compact and consistent account of the research field of single ion solvation thermodynamics that has over one hundred years of history and still remains largely unsolved. By reviewing the various approaches employed to date, establishing the relevant connections between single ion thermodynamics and electrochemistry, resolving conceptual

ambiguities and giving an exhaustive data compilation in the context of alkali and halide hydration this book provides a consistent synthesis in depth understanding and clarification of a large and sometimes very confusing research field The book is primarily aimed at researchers professors postgraduates graduates and industrial researchers concerned with processes involving ionic solvation properties these are ubiquitous eg in physical organic analytical chemistry electrochemistry biochemistry pharmacology geology and ecology Because of the concept definitions and data compilations it contains it is also a useful reference book to have in a university library Finally it may be of general interest to anyone wanting to learn more about ions and solvation Key features discusses both experimental and theoretical approaches and establishes the connection between them provides both an account of the past research covering over one hundred years and a discussion of current directions in particular on the theoretical side involves a comprehensive reference list of over 2000 citations employs a very consistent notation including table of symbols and unambiguous definitions of all introduced quantities provides a discussion and clarification of ambiguous concepts ie concepts that have not been defined clearly or have been defined differently by different authors leading to confusion in past literature encompasses an exhaustive data compilation in the restricted context of alkali and halide hydration along with recommended values after critical analysis of this literature data is illustrated by a number of synoptic colour figures that will help the reader to grasp the connections between different concepts in one single picture

### **Thermodynamics of Solvation** Gennadii Alekseevich Krestov,1991

Aimed at scientists interested in the structure and dynamics of aqueous electrolyte solutions this work examines the concept of the chemical nature of solutions It shows quantitatively in tabulations of thermodynamic data for metal ions and anions the role of solvents as chemical reagents

### **Fundamental Solvatochromic and Thermodynamic Studies of Complex**

**Chromatographic Media** Andrew James Dallas,1995    *Elementary Thermodynamics* John Parker,1891    Ionic Solvation

Gennadii Alekseevich Krestov,1994 This comprehensive widely read anthology presents cogent and provocativearticles from differing political perspectives on major issues in post World WarII America The fourth edition is considerably expanded to include newselections on the AIDS epidemic gay rights the women s movement and the Clinton Gore administration In addition to articles by leading historians theeditors have chosen first person accounts by participants in each of the issuesunder discussion from Martin Luther King Jr s Letter from the BirminghamJail to Al Gore s speech on environmentalism With lively introductions to eachsection providing a context for the articles this book helps students makesense of the tumultuous world of our time

### **Thermodynamics of Apolar Solvation in Mixed Aqueous Solvents** Prateek Pinakin

Shah,2008 Solubility of apolar molecules in aqueous media influences a number of natural and industrial processes Examples range from the bioavailability of small molecule pharmaceuticals to the fate of synthetic chemicals in the environment Apolar solvation also plays a role in biological processes such as protein folding Most theoretical investigations in the literature have focused on pure water as the solvent despite the fact that many natural and industrial systems include relatively high

concentrations of cosolvents Examples of common cosolvents include salts alcohols polyols and carbohydrates Despite the importance of mixed aqueous solvents little work has been done to understand apolar solvation in these mixtures Using molecular dynamics and statistical and classical thermodynamics this thesis provides a systematic and extensive theoretical study of apolar solvation thermodynamics over a wide range of temperatures pressures and cosolvent compositions up to 30 w w% and 60 w w% for the chosen cosolvents The transfer free energy enthalpy and entropy of methane and hard sphere solutes are calculated in binary water cosolvent water methanol ethanol sorbitol mixtures and a common molecular basis is shown to describe and predict the results across a broad range of solvent conditions From a classical thermodynamics perspective characteristic properties of water i e temperature of maximum density and temperature of minimum solubility are predicted by MD simulation to be suppressed to lower temperatures upon addition of either methanol or sorbitol as the cosolvent This behavior holds across a wide range of temperature pressure and cosolvent concentration By contrast apolar solute solubility is increased by addition of methanol but decreased by addition of sorbitol These findings are in conflict with traditional classification schemes such as structure making breaking and hydrophobic enhancement suppression and highlight the limitations of such heuristics for rationalizing cosolvent effects on solubility Exact statistical mechanical theories of mixtures such as Kirkwood Buff theory are also confirmed to be have limited predictive capability due to practical implementation issues that have been suggested previously in the literature From a molecular perspective it is shown that the distribution of void space is the dominant controlling factor that determines the sign and magnitude of the free energy of apolar solute dissolution in these water cosolvent mixtures This finding complements the literature for pure water and shows apolar solvation for small solutes is dominated by the work of cavity formation Additionally this thesis shows for the first time that the transfer free energy of apolar solutes from water to mixed aqueous solvents can be described by a common dependence on solvent packing fraction This dependence is independent of temperature pressure and the cosolvent identity The results also provide a clear molecular scale explanation for anomalous behaviors observed in simulation and experiment for apolar solvation in methanol water mixtures specifically a minimum in apolar solute solubility is observed as a function of methanol concentration Such solubility minima are shown to be due solely to the non monotonic dependence of packing fraction on solvent composition under isobaric conditions This unusual behavior is due to competing effects between changes in the average molecular density and changes in the bulk density as solvent composition is changed at fixed temperature and pressure This highlights that it is unnecessary to invoke arguments regarding alterations in hydrogen bond network structures or the stability of hydrogen bonded systems in order to explain any of these anomalous or characteristic solvation properties of water or mixed aqueous solvents Rather the attractive interactions between solvent molecules primarily determine the bulk density at a given temperature and pressure and small apolar solute solubility is then determined by the efficiency with which solvent molecules pack i e purely steric considerations at that bulk density Motivated by these findings

a thermodynamic cycle approach is proposed that separates the overall transfer process at constant temperature and pressure into two steps. The first step captures primarily the effects of changing solvent-solute interactions via changes in the solvent chemical composition. It occurs at fixed mass density to experimentally approximate fixed packing fraction. The second step is an expansion or compression of the binary cosolvent water mixture to achieve the same pressure as the initial state point for the cycle. In such a manner the effects of density changes with pressure i.e. the equation of state EoS are quantified. Transfer free energies and enthalpies for methane across a range of solvents are captured qualitatively and semi-quantitatively using only the EoS step. The EoS step alone is able to quantitatively describe entropies of transfer further emphasizing the dominant role of cavity formation and void distributions in apolar solvation across a range of solvents. Extension of this thermodynamic cycle approach to analyze protein unfolding is briefly presented and illustrates a number of additional challenges for accurately capturing solvation thermodynamics of proteins in mixed aqueous solvents.

A

Text-book of Physics: Properties of matter. 11th ed. 1927 John Henry Poynting, Sir Joseph John Thomson, 1913

An

**Outline of the Theory of Solution and Its Results** John Livingston Rutgers Morgan, 1897    **A handbook of physics and chemistry, by H.E. Corbin and A.M. Stewart** Herbert Ernest Corbin, 1899    Thermodynamics and Chemistry, by F. H. MacDougall Frank Henry Macdougall, 1921    *Thermodynamics of the Steam-engine and Other Heat-engines* Cecil Hobart Peabody, 1898    *Physics of the Ether* S. Tolver Preston, 1875    **Lecture Notes on Physics** Charles Bird (B.A., F.R.A.S.), 1880    Contributions to Molecular Physics in the domain of radiant heat. A series of memoirs published in the 'Philosophical Transactions' and 'Philosophical Magazine,' with additions John Tyndall, 1872    **Lessons in Elementary Practical Physics** Balfour Stewart, William Winson Haldane Gee, 1887    *The Elements of Physics: Electricity and magnetism* Edward Leamington Nichols, William Suddards Franklin, 1896    Elementary physics and chemistry, by R.A. Gregory and A.T. Simmons. 3 stages Sir Richard Gregory, 1900

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