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The Properties of Solvents

Y. Marcus

The Hebrew University of Jerusalem, Israel

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The Properties of Solvents

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Volume 4

The Properties of Solvents

Y Marcus

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Series Preface

There are many aspects of solution chemistry. This is apparent from the wide range of topics which have been discussed during recent International Conferences on Solution Chemistry and International Symposia on Solubility Phenomena. The Wiley Series in Solution Chemistry was launched to fill the need to present authoritative, comprehensive and upto-date accounts of these many aspects. Internationally recognized experts from research or teaching institutions in various countries have been invited to contribute to the Series.

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Volumes in the Series are important reading for chemists, physicists, chemical engineers and technologists as well as environmental scientists in academic and industrial institutions.

May 1996

Peter Fogg

Preface

I would like to thank Dr Peter Fogg for encouraging me to participate in this series edited by him on Solution Chemistry. This is the subject towards which my research has gravitated in the last two decades, dealing mainly with solvation phenomena. Since solution chemistry is carried out in solvents, it is necessary to be very familiar with their properties in order to understand what is going on.

As will become apparent, it is expedient to continue with the following excerpts from the preface to a previous book of mine, *Ion Solvation*, published in 1985:

'During my work of research on chemical interacting systems, I seem to succumb every eight years or so to the urge to sit down and write a book. The first effort, *Ion Exchange and Solvent Extraction of Metal Complexes* (with [the late] Aviezer Steven Kertes) was published in 1969, the second one, *Introduction to Liquid State Chemistry*, was published in 1977, and here is the third one.'

Since 1985, another book, *Ion Properties*, was published in 1997, so that the eight year interval has not been kept, but to amend this, the present book is offered. To quote further:

'My main purpose does not change.... I use this opportunity to locate gaps in our knowledge, and either fill these with new research while the book is being written or do this to the best of my ability in the course of time. Many new research ideas have thus come to me from my attempts to present current factual knowledge and theoretical interpretation in an organized form.... The scope of university research nowadays, I regret to record, is not conducive to the carrying out of extensive and systematic sets of measurements of high accuracy on the properties of chemical systems. Both from the standpoint of student interest and from that of the necessary financial support, work on systems that are not of immediate practical importance, but which could become so in time, is not encouraged. Still, as pointed out in the final chapter of this book, the applications of [solvents] in many fields of chemistry and other disciplines depends on the availability of reliable data on such systems. Furthermore, theories, models, and interpretations require adequate data to operate on, in order to be tested and to provide the insight on the interactions and processes that is being sought. I have therefore

endeavored in this book to present as many reliable data as seem to be relevant, without trying to be exhaustive, and to provide these with appropriate annotations. . . . I hope that the long lists of references [following] the extensive tables do not detract too much from the readability of the book. I preferred to have the tables right at the place where the data are discussed or where they can be employed by the reader as an illustration to the points discussed, rather than have them relegated to appendixes.'

Is it necessary to justify further the writing of the present book?

The data collected and shown are from secondary sources—where they have previously been critically evaluated and selected—whenever warranted, but more recent primary sources in research journals have been used to supplement the former or to supersede them if deemed necessary. Access to the primary sources has been through the abstracts up to 1996. The selection of the solvents for which the data are included in this book (the List) is discussed in the Introduction. I am solely responsible for such choices, regarding solvents and data, as have been made. I will be grateful for indications of errors, oversights, and further useful data that may be brought to my attention. Some of the tables are confined to those solvents from the List for which the relevant data have been reported. However, for most of the more extensive tables, many blank spaces have been left, and in some cases entire rows of data have been left blank. This was done with the hope of calling attention to the lack of reliable data, and the expectation that some of these blanks may be filled within the useful lifetime of this book (and its author).

Y. Marcus
Jerusalem,
June 1998

List of Symbols

A	surface area of a molecule
A_{vdW}	van der Waals surface area
A, B, C	constants in the Antoine equation
AN	(Gutmann–Mayer) acceptor number
a	activity
a	diameter of ion (distance of closest approach)
a, b	constants in the van der Waals equation
B	(Koppel–Palm) donicity scale
B	second virial coefficient
$b\epsilon$	non-linear dielectric effect
C_p	constant pressure molar heat capacity
C_v	constant volume molar heat capacity
c	(volume) concentration (moles per dm^{-3} of solution)
c	specific heat (constant pressure)
c	speed of light, $2.997\,92 \times 10^8 \text{ m s}^{-1}$
cmc	critical micelle concentration
D	debye unit of dipole moment, $3.335\,64 \times 10^{-3} \text{ C}\cdot\text{m}$
D	(self) diffusion coefficient
DN	(Gutmann) donor number
D_s	(Persson) softness parameter
d	density
d_c	critical density
E	electric field strength
E°	standard electrode potential
$E_{1/2}$	polarographic half-wave potential
E_{conf}	configurational energy
E_T^N	normalized (Dimroth–Reichardt) polarity index
$E_T(30)$	(Dimroth–Reichardt) polarity index
ΔE_η	activation energy for viscous flow
F	Faraday's constant, $96\,485 \text{ C mol}^{-1}$
f	fugacity

f	rational activity coefficient
f	ultrasound frequency
ΔG^*	solvation Gibbs free energy
$\Delta_r G^\circ$	standard Gibbs free energy change for the reaction specified by subscript r
ΔG^\ddagger	activation (Gibbs free) energy
ΔG_A	standard Gibbs free energy for (gas phase) proton dissociation
g	(Kirkwood) dipole orientation correlation parameter
$g(r)$	pair correlation function
ΔH^*	solvation enthalpy
ΔH°	standard enthalpy change
ΔH^\ddagger	enthalpy of activation
$\Delta_v H$	enthalpy of vaporization
h	Planck's constant, $6.626 \times 10^{-34} \text{ J s}^{-1}$
I	ionic strength
IDLH	concentration presenting immediate danger to life or health
K	equilibrium constant
K_H	Henry's law constant (for gas solubility)
$\text{p}K_a$	negative of logarithm of acid dissociation constant in aqueous solution
$\text{p}K_b$	negative of logarithm of base dissociation constant in aqueous solution
$\text{p}K_{\text{BH}^+}$	negative of logarithm of protonation constant in aqueous solution
$\text{p}K_S$	negative of logarithm of autoprotolysis constant
k	reaction rate constant
k_B	Boltzmann's constant, $1.3807 \times 10^{-23} \text{ J K}^{-1}$
k_P	packing factor
LD_{50}	lethal dose for 50% of the animals tested
M	(relative) molar mass
m	molality (moles per kg solvent)
N_{Av}	Avogadro's number, $6.0221 \times 10^{23} \text{ mol}^{-1}$
n_S	number of solvent molecules
n_D	refractive index at the sodium D-line
P	external (ambient) pressure
P	polarization
P	1-octanol/water partition constant
P°	standard pressure of 0.1 MPa
PA	proton affinity
P_C	critical pressure
PEL	permissible exposure limit
P_i	internal pressure
p	(saturation) vapor pressure
Q	equilibrium quotient

R	gas constant, $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$
R_D	molar refractivity at the sodium D-line
r	radius
r	distance from center of particle
ΔS^*	solvation entropy
ΔS°	standard entropy change
ΔS^\ddagger	entropy of activation
S_F	(molar) entropy of fusion
S_N1	monomolecular nucleophilic substitution reaction
S_N2	bimolecular nucleophilic substitution reaction
s	molar solubility
T	absolute temperature
T_0	ideal glass transition temperature
T_b	(normal, absolute) temperature of boiling
T_C	critical temperature
T_g	(absolute) glass transition temperature
T_m	(absolute) temperature of melting
T_r	reduced temperature, T/T_C
T_i	triple point
t_b	(normal) boiling point (in $^\circ\text{C}$)
t_m	melting temperature (in $^\circ\text{C}$)
$\Delta_v U$	vaporization energy
u	ion mobility
$u(r)$	pair potential
$u^{LJ}(r)$	Lennard–Jones pair potential
ΔV^*	solvation volume
ΔV°	standard volume change
ΔV^\ddagger	volume of activation
V^E	(excess) molar volume of mixing
V_L	(Leahy) intrinsic volume
V_{vdW}	van der Waals volume
V_X	(McGowan) intrinsic volume
w	mass (weight) fraction
XYZ	generalized solvent-dependent variable
x	mole fraction
Y	(Grunwald–Winstein) solvent polarity parameter
γ	packing fraction
Z	(Kosower) polarity index
Z_C	critical compressibility factor
z	(algebraic) charge of ion
$[]$	concentration of the enclosed species
α	polarizability

α	number of solvent molecules sorbed per phenyl group in polystyrene
α	(Kamlet–Taft) hydrogen bond donation ability
α	ultrasound absorption coefficient
α_P	isobaric expansibility
β	(Kamlet–Taft) electron pair donation ability
γ	Ostwald coefficient (for gas solubility)
γ_{\pm}	mean ionic activity coefficient
${}_w\gamma_s$	transfer activity coefficient from solvent w to solvent s
δ	(Hildebrand) solubility parameter
δ	NMR chemical shift
δ	(Kamlet–Taft) polarizability parameter
ε	(negative of the) depth of the potential well
ε	relative permittivity (dielectric constant)
ε_0	permittivity of free space, $8.8542 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$
ε_0	static, low frequency, relative permittivity
ε_{∞}	relative permittivity at very high ('infinite') frequency
η	(dynamic) viscosity
κ	specific conductance
κ_S	isentropic, adiabatic compressibility
κ_T	isothermal compressibility
λ	equivalent conductivity
λ	thermal conductivity, $\text{W K}^{-1} \text{ m}^{-1}$
λ_c	critical wavelength
μ	dipole moment
μ	(Marcus) softness parameter
ν	wavenumber
ξ	correlation length
π	group contribution to the 1-octanol/water partition constant
π^*	(Kamlet–Taft) polarity/polarizability parameter
ρ	number density
σ	surface tension
σ	collision diameter of molecules
τ	(orientational) relaxation time
Φ	fluidity
ϕ	volume fraction in actual mixture
φ	volume fraction when volume change on mixing is disregarded
χ	molar volume diamagnetic susceptibility
χ	(Flory–Huggins) interaction parameter
ω	electric field frequency

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CHAPTER 1

Introduction

1 A SURVEY OF USEFUL SOLVENTS

Solvents are substances that are liquid under the conditions of application and in which other substances can dissolve, and from which they can be recovered unchanged on removal of the solvent. So many substances conform to this definition—practically all those that can be liquefied under some conditions—that it is not very helpful, unless the word ‘application’ is stressed, meaning that the solvents and the solutions in them ought to be applicable for some purpose. In the present context, therefore, materials that can be liquefied only under extreme conditions of temperature and pressure will not be considered extensively. This excludes, for instance, molten salts and slags on the one hand and ‘permanent’ gases on the other, unless they have found some use as ‘supercritical solvents’. Then, again, binary or multi-component liquid mixtures are not dealt with here, although they can be very useful as solvents, since this would have expanded the size of this book enormously. This still leaves a host of organic and many inorganic substances that are liquid at or near ambient conditions, which could be considered to be solvents under the present definition. Of these, a limited number are selected, in order for this book to be useful and handy, rather than trying in vain to be comprehensive and encyclopedic.

The solvents that are included in the extensive compilations of physical and chemical properties shown in this book (the List, referred to as such in this book) have been selected so as to cover the major classes of solvents, and bring several examples of each class. The properties of solvents that have not been included, but that belong to these classes, in particular isomers or higher members of homologous series, can often be inferred from the reported data at least to some extent. One criterion according to which solvents have been selected for inclusion in the List is that most of their physical and chemical properties, among those considered here, should be known. In particular, those chemical properties pertaining to their ability to solvate solutes are stressed as criteria for inclusion, since this book is a part of a series on Solution Chemistry. This solvating ability

can be characterized by so-called solvatochromic parameters or similar indices of solvation ability, and some, at least, of the most commonly used of these parameters, ought to be known for inclusion of the solvent in the List.

Water, being the most abundant, extensively employed, and a very useful solvent, has always been accorded very wide attention by chemists of all sub-disciplines who have been studying solutions. As an antithesis, the keyword 'non-aqueous' has figured in the titles of many treatments of other solvents. Inorganic solvents have long been considered to be the typical 'non-aqueous solvents', as is manifested in the titles of several books dealing almost exclusively with them, written or edited in the fifties and early sixties by authors such as (Audrieth and Kleinberg 1953; Sisler 1961; Waddington 1965). Only little attention was accorded at the time to organic non-aqueous solvents. In the last few decades, however, this tendency has reversed completely, and a large number of organic, in particular dipolar aprotic, solvents have been dealt with extensively in this context of 'non-aqueous solvents', almost to the exclusion of the traditional inorganic ones, as, for instance, in the books edited by (Coetzee and Ritchie 1969; Lagowski 1966–1978; Covington and Jones 1968). However, the older compilations of physical properties of organic substances (International Critical Tables 1926–1930; Landolt–Börnstein Tables 1959 and Timmermann's compilation) do not include most of the now commonly used dipolar aprotic solvents, the relevant data being found only in more recent works, e.g., (Riddick, Bunger and Sakano 1986 and the DIPPR compilation 1997). Then, again, in many books with extensive data, solvents used for electrolytes or ions, polar solvents, whether protic or not, are not always considered together with those used for non-polar commercial materials, such as paints, polymers, etc., or for pharmaceuticals and industrial processes. Here, both kinds are accorded the appropriate space.

A classification scheme for solvents needs, therefore, to reflect to some extent the uses for which the solvents are put. Many classification schemes have been proposed, and a single major property, that may form the basis for the usefulness of solvents for certain applications, can often be employed in order to classify solvents. On the other hand, a few selected properties may advantageously be used to form the basis for the classification. Various solvent classification schemes have been presented (Reichardt 1988) and a common solvent classification scheme is:

- (i) non-polar solvents (such as hexane and tetrachloromethane),
- (ii) solvents of low polarity (such as toluene and chloroform),
- (iii) aprotic dipolar solvents (such as acetone and N,N-dimethylformamide),
- (iv) protic and protogenic solvents (such as ethanol and nitromethane),
- (v) basic solvents (such as pyridine and 1,2-diaminoethane), and
- (vi) acidic solvents (such as 3-methylphenol and butanoic acid).

Some other classification schemes shown below (that differ from the one above only in minor details or in the terminology) are as follows. One classification, (Kolthoff 1974) and (Reichardt 1988), called *A* below, is according to the

polarity, described by the relative permittivity (dielectric constant) ϵ , the dipole moment μ (in 10^{-30} C·m), and the hydrogen bond donation ability E_T^N (see Chapter 4). Another suggested classification (Parker), called *B* below, stresses the acidity and basicity (relative to water) of the solvents. A third one, (Chastrette 1974, 1979), called *C* below, stresses the hydrogen bonding and electron pair donation abilities, the polarity, and the extent of self-association. As stated above, the differences among these schemes are mainly semantic ones and are of no real consequence.

Solvent classification scheme *A*.

Designation	ϵ	μ	E_T^N	Examples
apolar aprotic	< 15	< 8.3	0.0–0.3	hydrocarbons, halogen substituted hydrocarbons, tertiary amines
weakly polar aprotic	< 15	< 8.3		ethers, esters, pyridine, primary and secondary amines
dipolar aprotic	> 15	> 8.3	0.3–0.5	ketones, nitriles, nitro-compounds, N,N-disubstituted amides, sulfoxides
protic			0.5–1.0	water, alcohols, mono- or unsubstituted amides, carboxylic acids, ammonia

Solvent classification scheme *B*.

Solvent designation	Relative acidity/basicity	Examples
protic–neutral	fairly strong as either	H ₂ O, CH ₃ OH, (CH ₃) ₃ COH, C ₆ H ₅ OH
protogenic	more acid than water	H ₂ SO ₄ , HCOOH
protophilic	more basic than water	NH ₃ , HCONH ₂ , H ₂ NC ₂ H ₄ NH ₂
aprotic, protophilic	more basic and less acidic than water	HCON(CH ₃) ₂ , CH ₃ SOCH ₃ , C ₅ H ₅ N, (C ₂ H ₅) ₂ O, tetrahydrofuran
aprotic, protophobic	fairly weak as either	CH ₃ CN, CH ₃ COCH ₃ , CH ₃ NO ₂
aprotic, inert	fairly weak as either	C ₆ H ₁₄ , C ₆ H ₆ , ClC ₂ H ₄ Cl, CCl ₄

Solvent classification scheme *C*.

Solvent class	Examples
apolar, aprotic, electron pair donors	amines, ethers
slightly polar, aprotic, aromatic	chlorobenzene, anisole, acetophenone
apolar, aprotic, aromatic	benzene, substituted aromatic hydrocarbons
aprotic dipolar	nitromethane, acetonitrile, acetone, pyridine
highly polar aprotic	dimethyl sulfoxide, benzonitrile, nitrobenzene
highly polar, polarizable aprotic	sulfolane, hexamethyl phosphoramide
hydrogen bonding	alcohols, ether-alcohols, phenols
highly associated hydrogen bonding	water, ethylene glycol, formamide
miscellaneous	chloroform, carbon disulfide, aniline