PHYSICAL CHEMISTRY
of
NONAQUEOUS SOLUTIONS

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Department of Physical Chemistry

PROLOGUE

Why NONAQUEOUS SOLUTIONS ?

The variety of properties of non-aqueous solvents that makes it possible to successfully solve many problems of modern chemistry. This largely explains the extremely wide use of a rich arsenal of non-aqueous, primarily organic solvents in today's daily practice.

The main tasks of studying the discipline is to teach students:

To know the main properties of most popular nonaqueous solvents, methods of their purification, and their toxic properties;

To be able to classify any solvent using quantitative parameters (descriptors);

To determine the pH values in nonaqueous solutions, to create buffer solutions in organic solvents;

To determine and explain the transport properties of ions in non-aqueous solvents;

To predict the properties of solutions of electrolytes and non-electrolytes in solvents of different chemical nature by using educational and scientific literature;

To correctly choose the necessary solvent for modifying the properties of organic and inorganic substances (solubility, thermodynamic reactivity, rate of chemical reactions);

To rationally choose the solvent necessary for carrying out one or another analytical operation, in particular, in titrimetric analysis and extraction

INTRODUCTION

Why SOLUTIONS ?

Why LIQUIDS ?

Over 90% of all studied chemical reactions occur in the liquid phase

Aristoteles

Ta hygra meikta malista ton somaton

(there are primarily liquids that react)

Corpora non agunt nisi fluida ??

(substances do not react unless they are liquid)

$$\left|\Delta H_{\mathrm{m}}^{0}\right| < \left|\Delta H_{\mathrm{v}}^{0}\right|$$

$$pV = RT$$

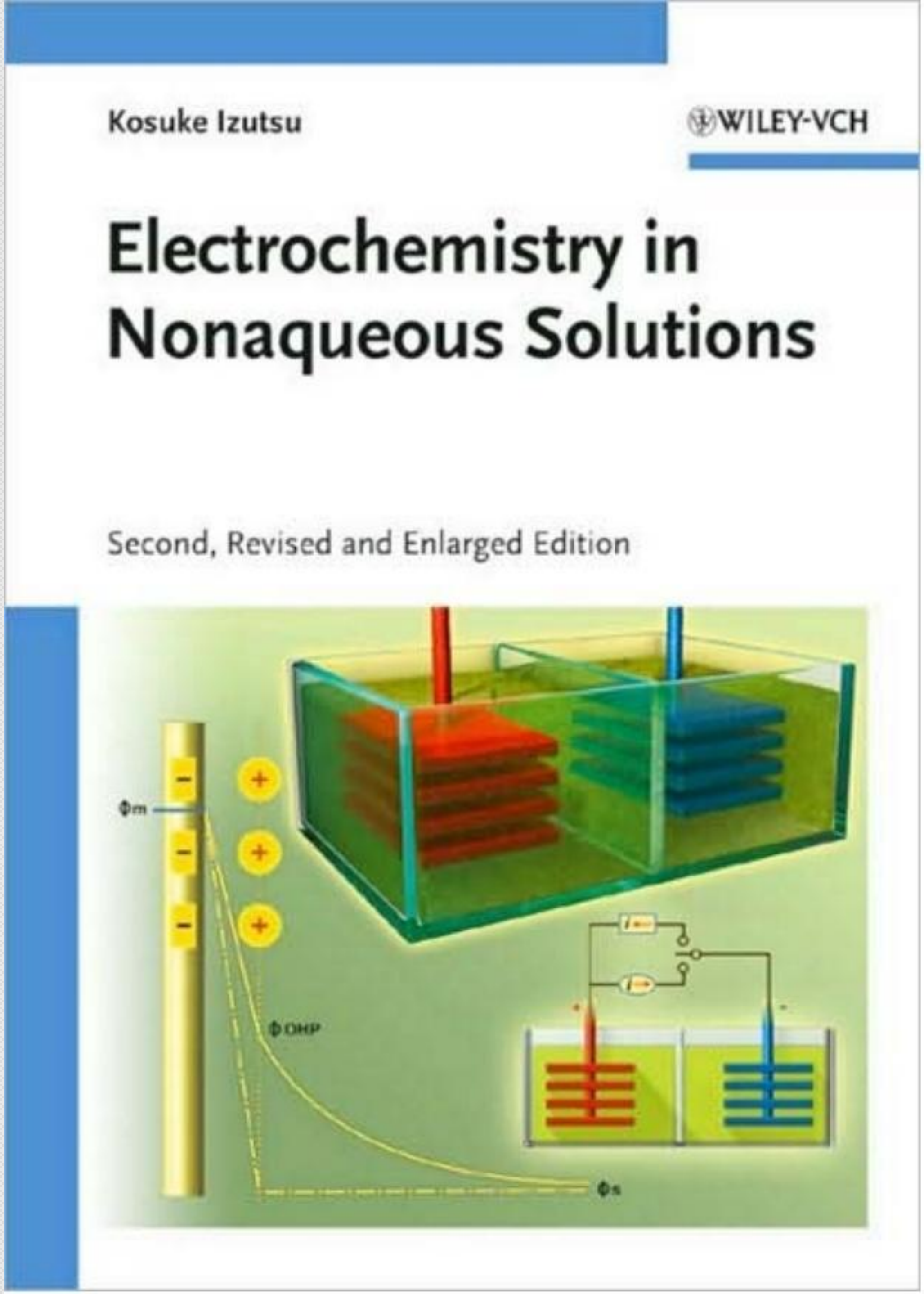
$$(p + \frac{\alpha}{V^2})(V - b) = RT$$

Solution and **dissolution**

Why are non-aqueous solvents needed for technology and scientific research? What are their advantages over water?

1. For increasing the solubility of poorly water-soluble compounds.
2. To shift the equilibrium state.
3. To accelerate the chemical reactions.
4. As liquid media in organic synthesis including polymerization.
5. As liquid media in colloidal synthesis.
6. In extraction.
7. For re-crystallization.
8. In chemical analysis – Titration in organic solvents.
9. In liquid-phase chromatography.

10. In photophysical processes (light emission).
11. In electrochemistry.
12. In metallurgy.
13. In UV-visible, infrared, and NMR spectroscopy.
14. For studying free radicals.
15. For studying complex formations between metal ions and ligands.



Kosuke Izutsu

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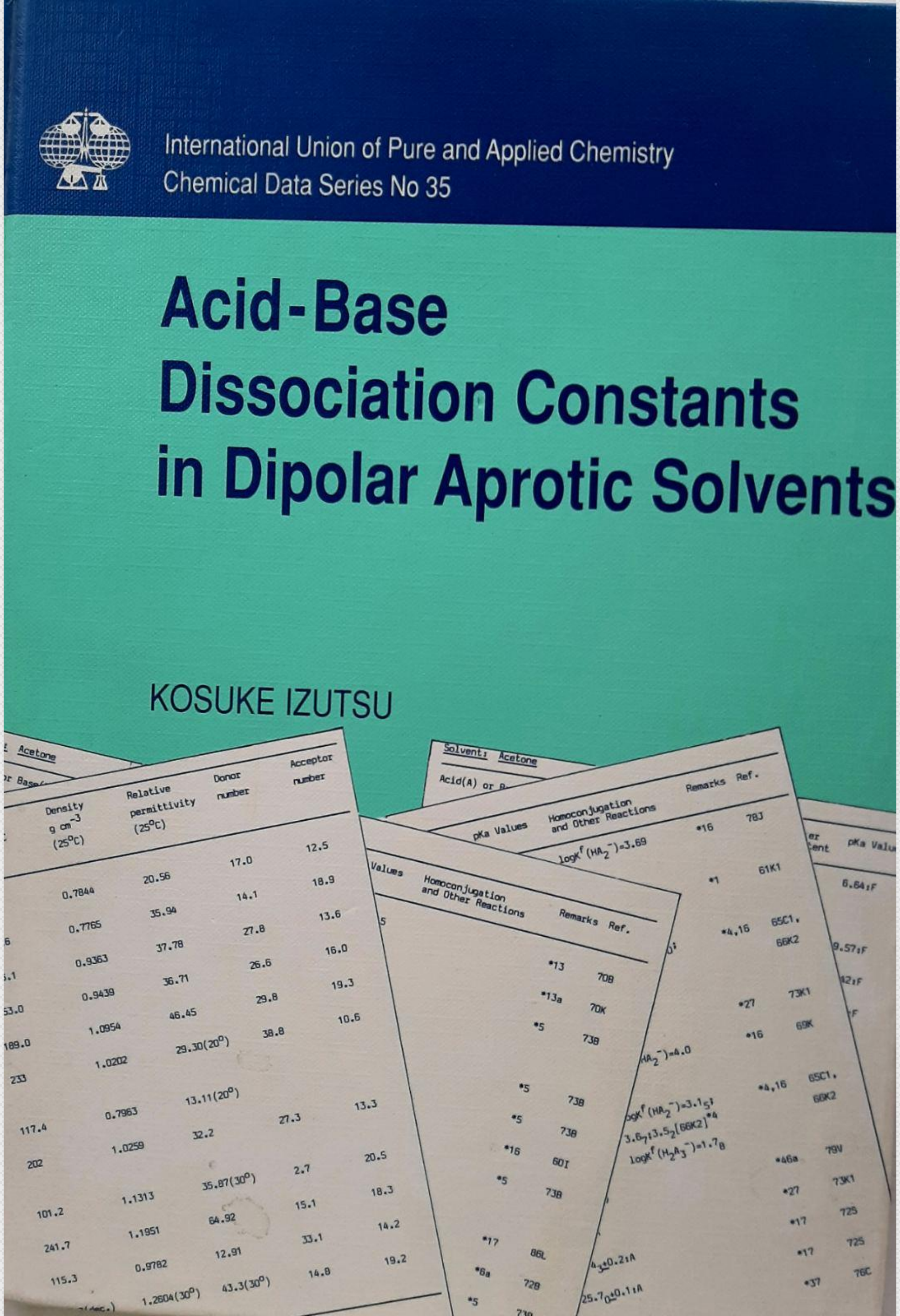
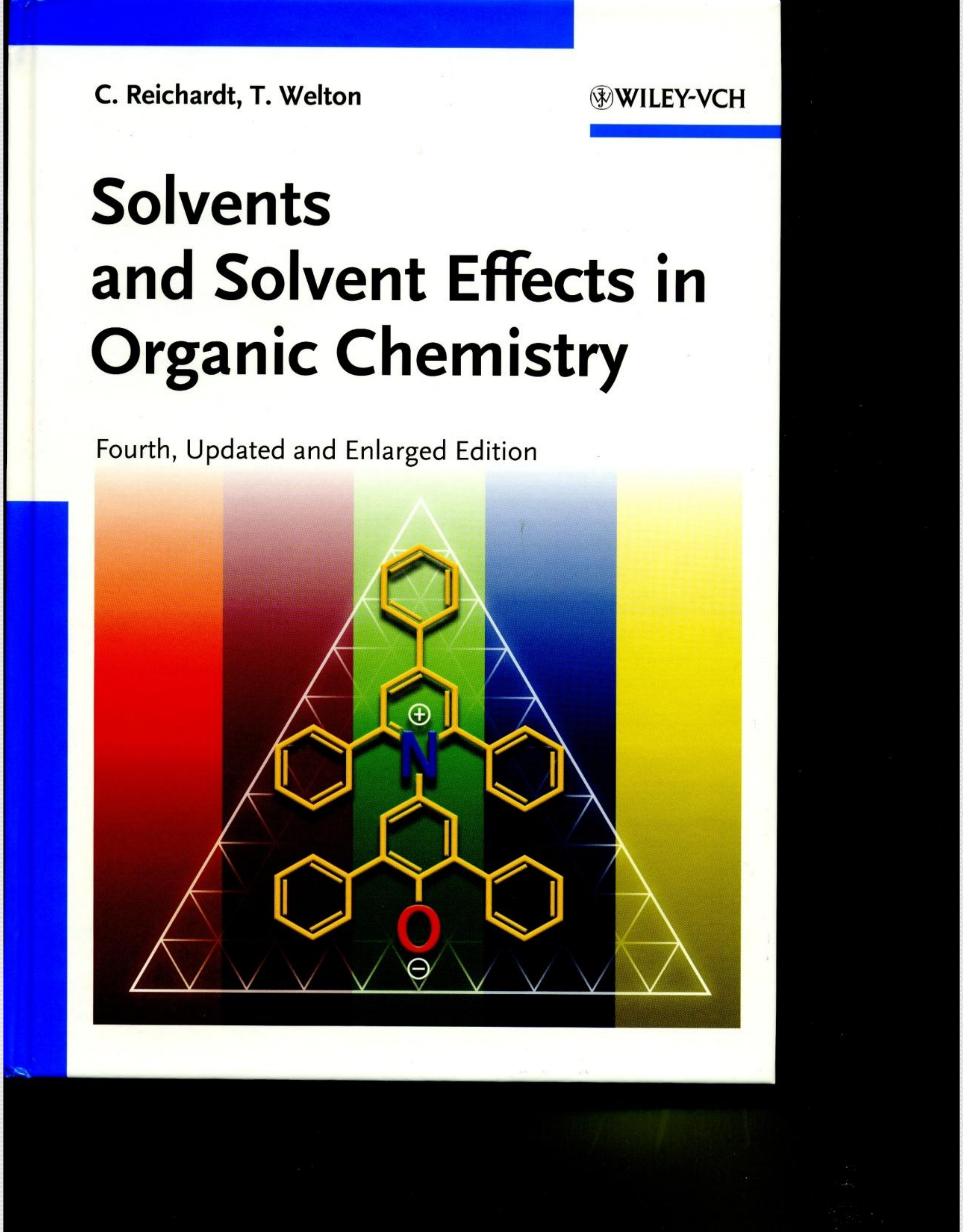


International Union of Pure and Applied Chemistry
Chemical Data Series No 35

Acid-Base Dissociation Constants in Dipolar Aprotic Solvents

KOSUKE IZUTSU



C. Reichardt, T. Welton

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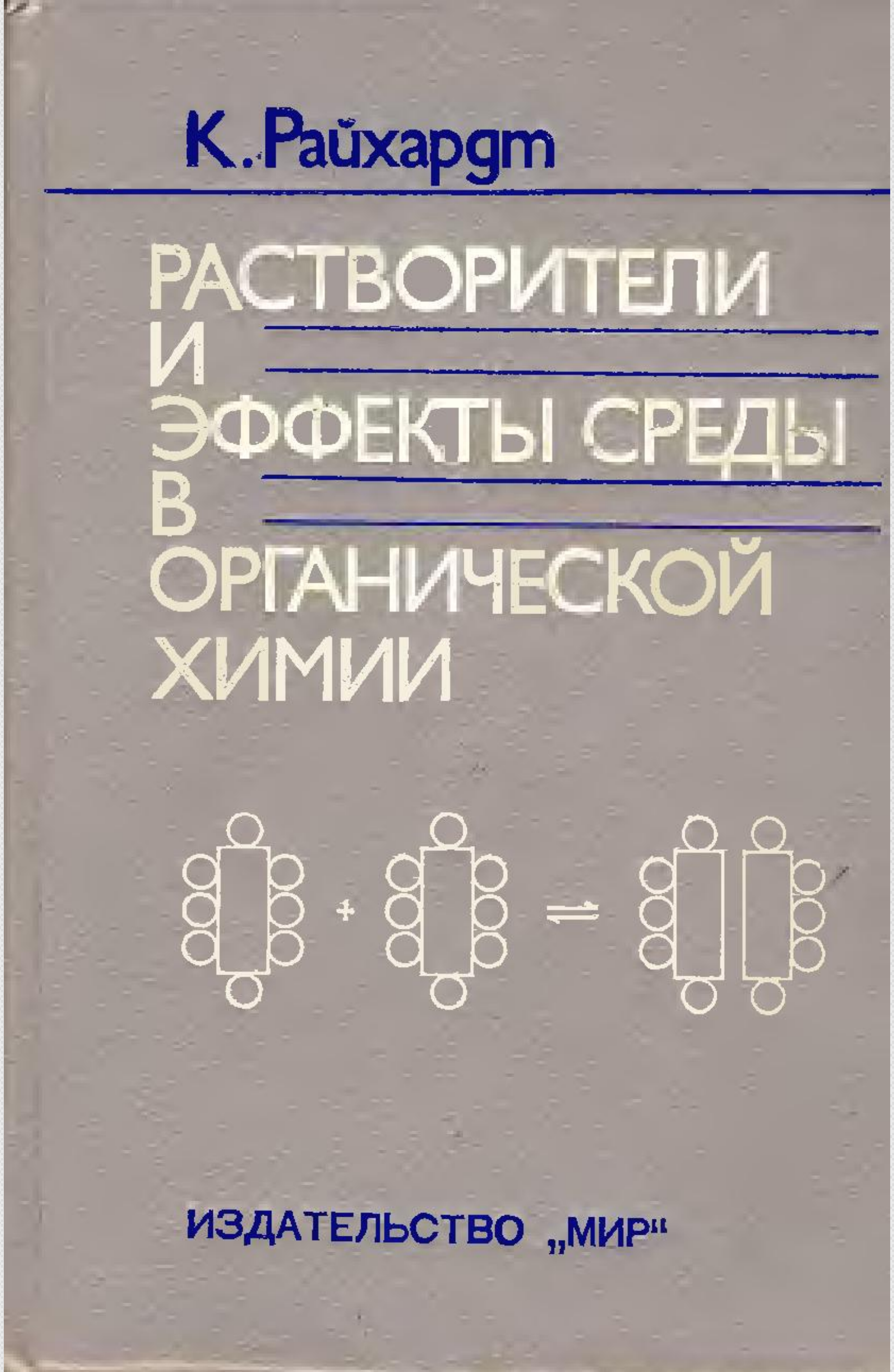
Solvents and Solvent Effects in Organic Chemistry

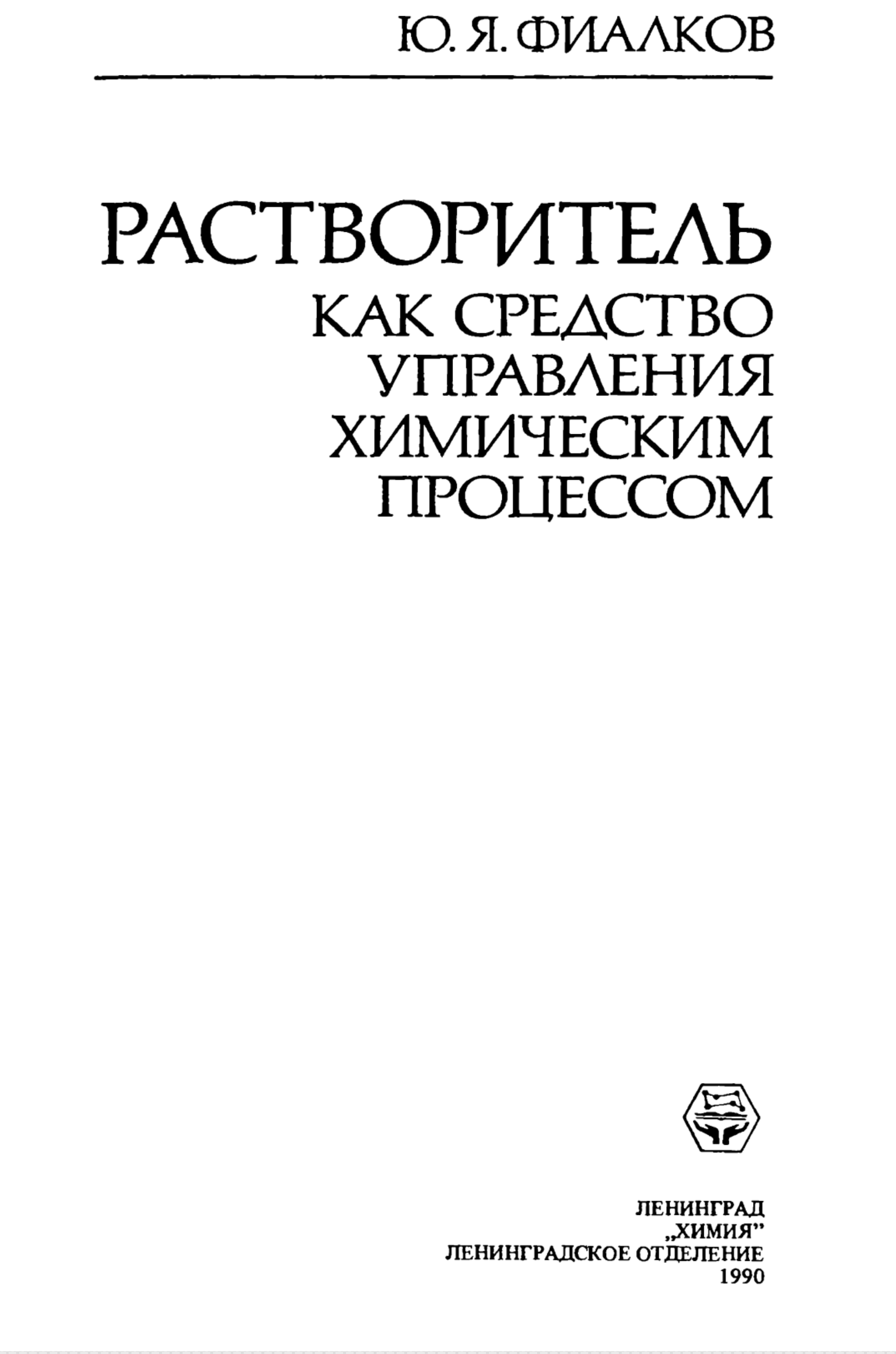
Fourth, Updated and Enlarged Edition



К. Райхардт

РАСТВОРИТЕЛИ
И
ЭФФЕКТЫ СРЕДЫ
В
ОРГАНИЧЕСКОЙ
ХИМИИ

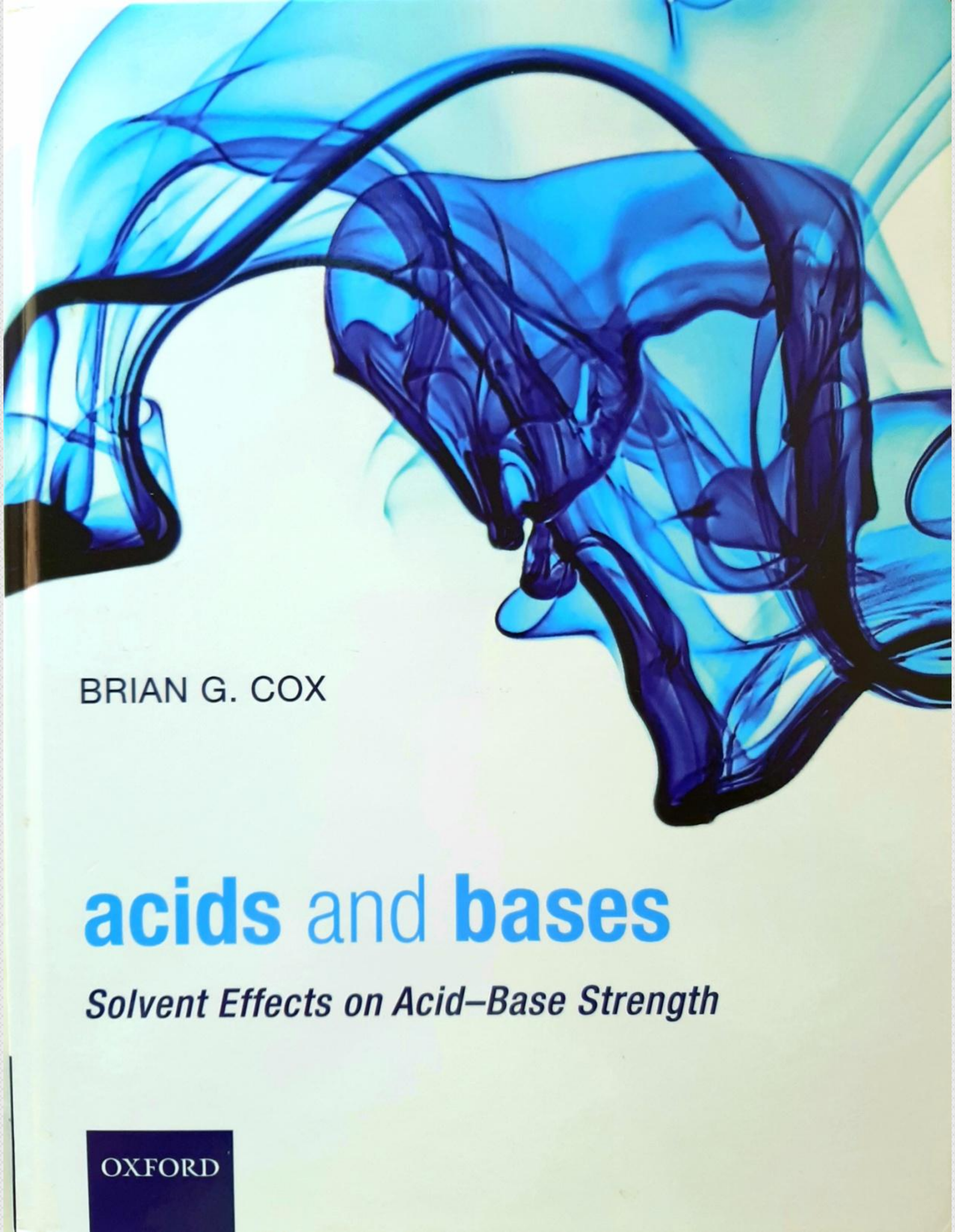
ИЗДАТЕЛЬСТВО „МИР“



Ю. Я. ФИАЛКОВ

РАСТВОРИТЕЛЬ
КАК СРЕДСТВО УПРАВЛЕНИЯ ХИМИЧЕСКИМ ПРОЦЕССОМ

ЛЕНИНГРАД
„ХИМИЯ"
ЛЕНИНГРАДСКОЕ ОТДЕЛЕНИЕ
1990



BRIAN G. COX

acids and bases

Solvent Effects on Acid–Base Strength

OXFORD

CONTENTS

- Introduction

  The characterization of the principal physico-chemical properties and the classification of nonaqueous solvents
- The influence of the solvents on the electronic absorption spectra. Solvatochromism
- The purification of solvents and precautions on working with them
- Electrolytes in solution. Association and dissociation processes
- Transport properties of ions in nonaqueous solvents
- Electrochemical cells and red-ox processes in nonaqueous media
- The influence of the solvents on the rates of chemical reactions
- Protolytic equilibria
- Solvation of electrolytes.
- Solvation and solubility of nonelectrolytes
- Distribution between phases.
- Comparison of equilibrium constants in different solvents
- Utilizing of organic solvents in chemical analysis

G. A. Krestov:

«Solvation is understood as the whole sum of energy and structural changes occurring in the system during the transition under given conditions of atomic and molecular particles (atoms, molecules, ions, radicals) [from vacuum] into the liquid phase of the solvent, leading to the formation of a solution of a certain chemical structure and a given composition (exceptions are changes accompanied by the breaking of chemical bonds in the atomic-molecular objects themselves and solvent molecules)».

The thermodynamics of solution and solvation of various compounds in organic solvents, the regularities of the influence of the nature of the solvent on the equilibrium and kinetics of reactions began to be studied more than a century ago by many scientists. The Kharkov chemists who worked at the Imperial Kharkov University in the 19th and in the first post-revolutionary years also contributed to this field of knowledge (P. D. Khrushchov, V. F. Timofeev, I. P. Osipov, G. E. Timofeev, G. E. Mukhin and others).

These traditions were continued and developed by N. A. Izmailov (1907–1961), who created the world famous school of physical chemistry of non-aqueous solutions. Separate areas of research were further developed by the students of N.A. Izmailov A.M. Shkodin, V.V. Aleksandrov, V.D. Bezugly, E.F. Ivanova and others.

N. A. Izmailov

Chapter 1. THE CHARACTERIZATION OF THE PRINCIPAL PHYSICO-CHEMICAL PROPERTIES

AND THE CLASSIFICATION OF NONAQUEOUS SOLVENTS

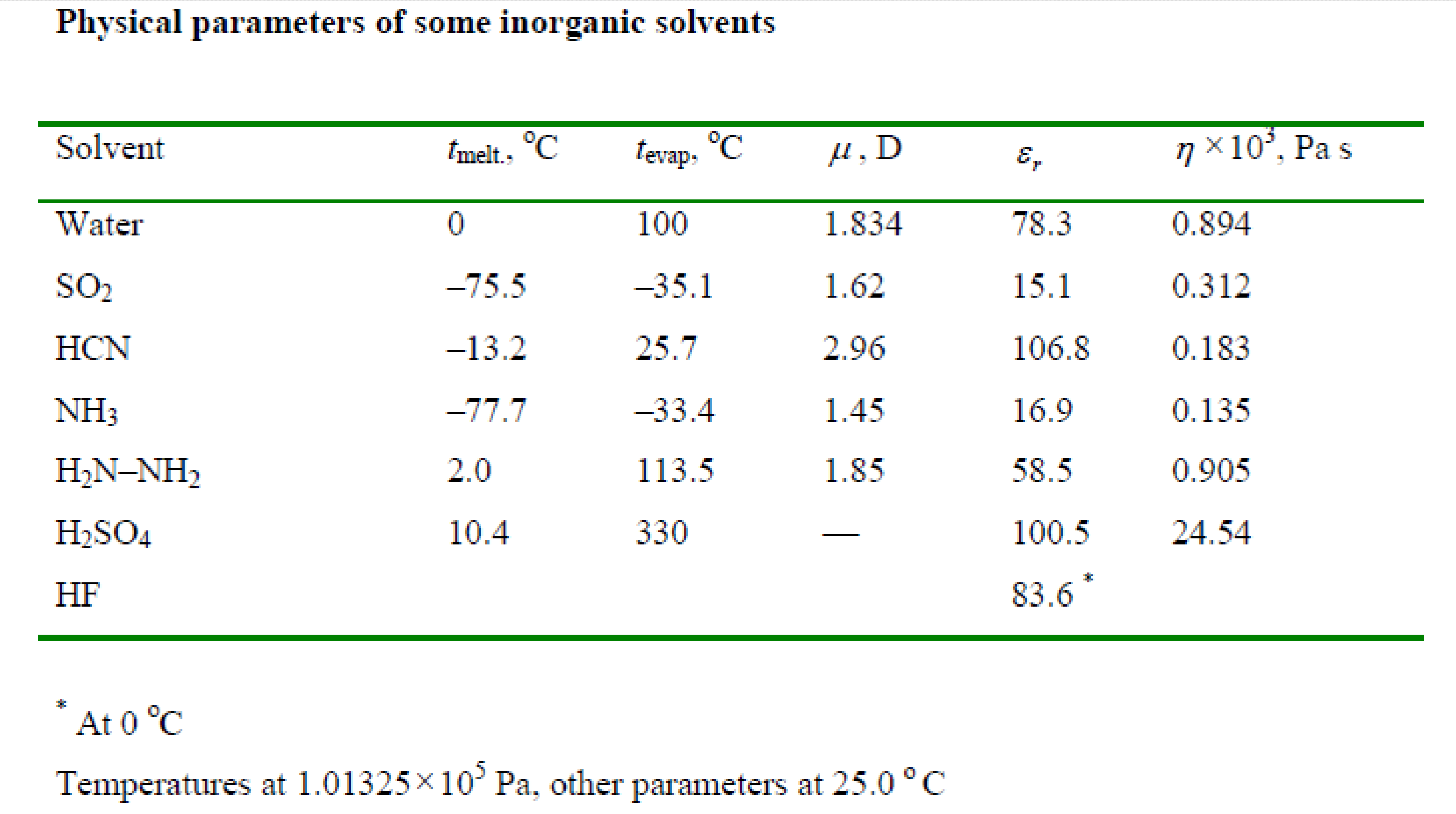
$$U = -\frac{1}{4\pi\varepsilon_0\varepsilon_\mathrm{r}} \times \frac{z^2e^2}{r}$$

ε_r - relative permittivity

$$F = \eta\left|\frac{du}{dx}s\right|$$

η - dynamic viscosity

Dielectric constant	$\varepsilon_0 = 8.8542 \times 10^{-12}$ F м$^{-1}$; (1 F = C^2 J^{-1} = C V^{-1})
Proton charge	$e = 1.602 \times 10^{-19}$ C
Avogadro number	$N_A = 6.022 \times 10^{23}$ mole^{-1}
Faraday constant	$F = 96\,487$ C mole^{-1}
Plank constant	$h = 6.6256 \times 10^{-34}$ J s
Gas constant	$R = 8.3143$ J mole^{-1} K^{-1}
Boltzmann constant	$k_\mathrm{B} = R\,(N_A)^{-1} = 1.38054 \times 10^{-23}$ J K^{-1}
Velocity of light	2.997925×10^8 m s^{-1}

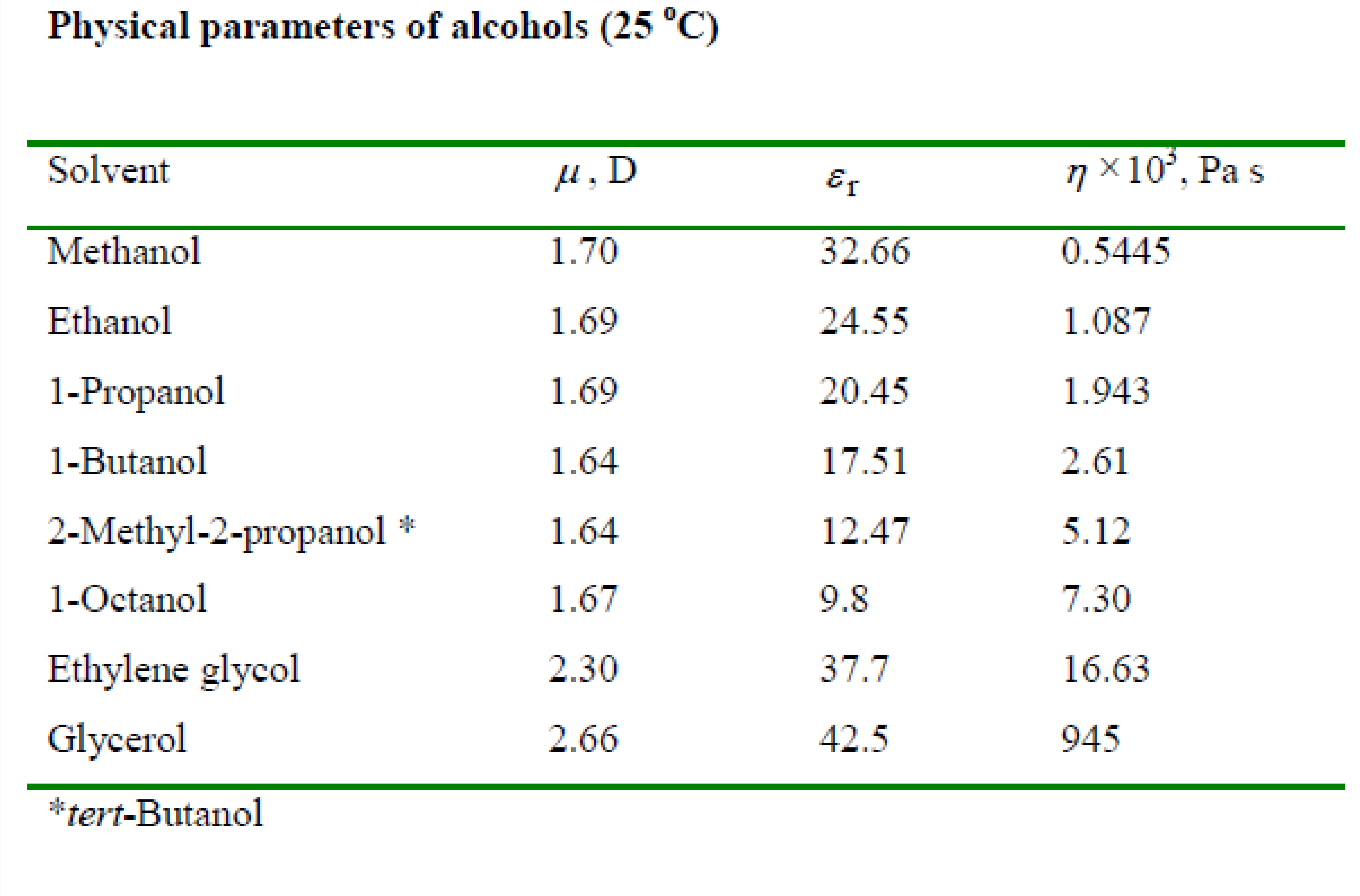


Physical parameters of some inorganic solvents

Solvent	$t_{\text{melt.}}$, °C	t_{evap}, °C	μ, D	ε_r	$\eta \times 10^3$, Pa s
Water	0	100	1.834	78.3	0.894
SO_2	–75.5	–35.1	1.62	15.1	0.312
HCN	–13.2	25.7	2.96	106.8	0.183
NH_3	–77.7	–33.4	1.45	16.9	0.135
$H_2N{-}NH_2$	2.0	113.5	1.85	58.5	0.905
H_2SO_4	10.4	330	—	100.5	24.54
HF				83.6 *	

* At 0 °C

Temperatures at 1.01325×10^5 Pa, other parameters at 25.0 °C

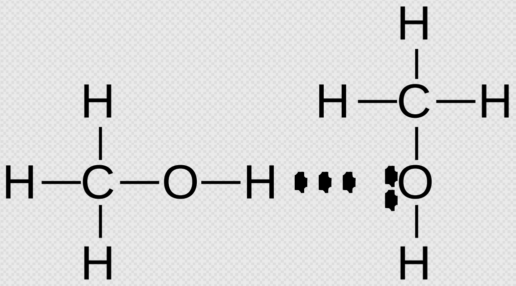
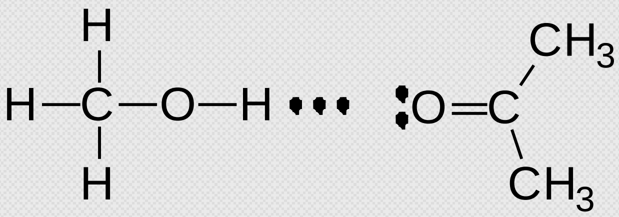


Physical parameters of alcohols (25 °C)

Solvent	μ, D	ε_r	$\eta \times 10^3$, Pa s
Methanol	1.70	32.66	0.5445
Ethanol	1.69	24.55	1.087
1-Propanol	1.69	20.45	1.943
1-Butanol	1.64	17.51	2.61
2-Methyl-2-propanol *	1.64	12.47	5.12
1-Octanol	1.67	9.8	7.30
Ethylene glycol	2.30	37.7	16.63
Glycerol	2.66	42.5	945

**tert*-Butanol

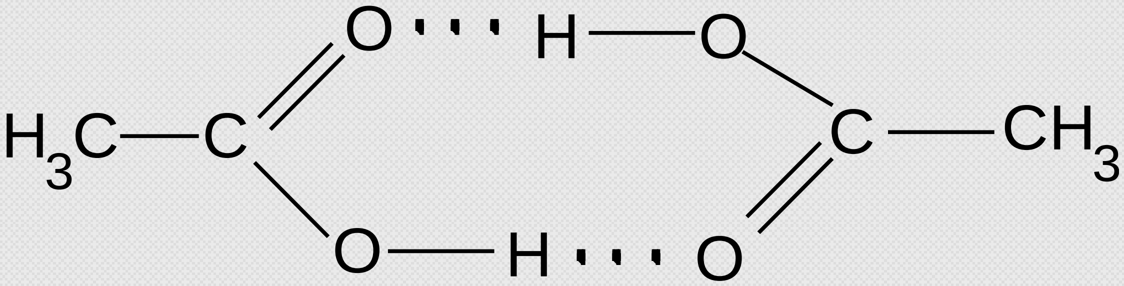
Hydrogen bonds and hydrogen bond donor-solvents (**HBD-solvents**)

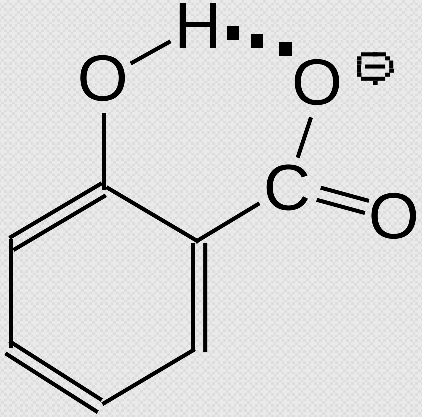
Hydrogen bond, or H-bond is the second bond, formed by a H atom that is already covalently bound with another atom:

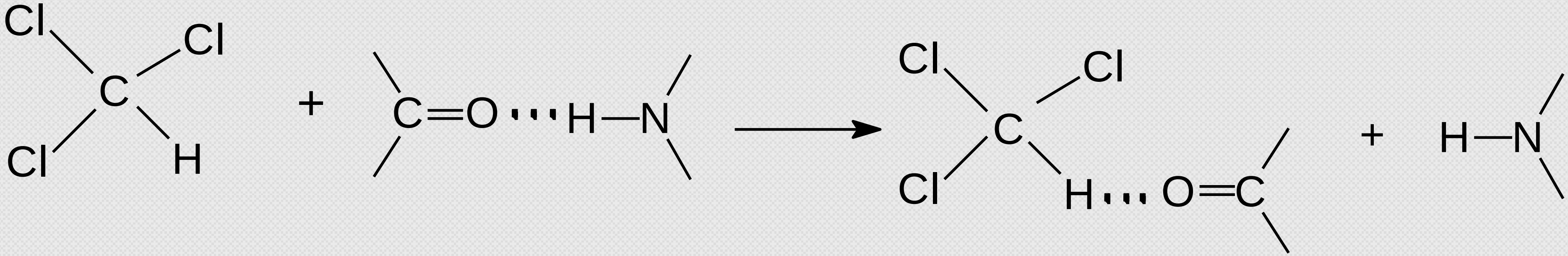
$$R{-}X{-}H \; + \; :Y{-}R' \rightleftharpoons R{-}X{-}H \cdots :Y{-}R'$$

Intermolecular H-bond:



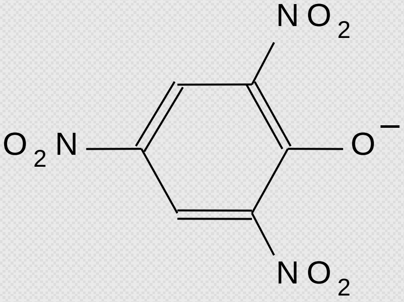
Intramolecular H-bond:

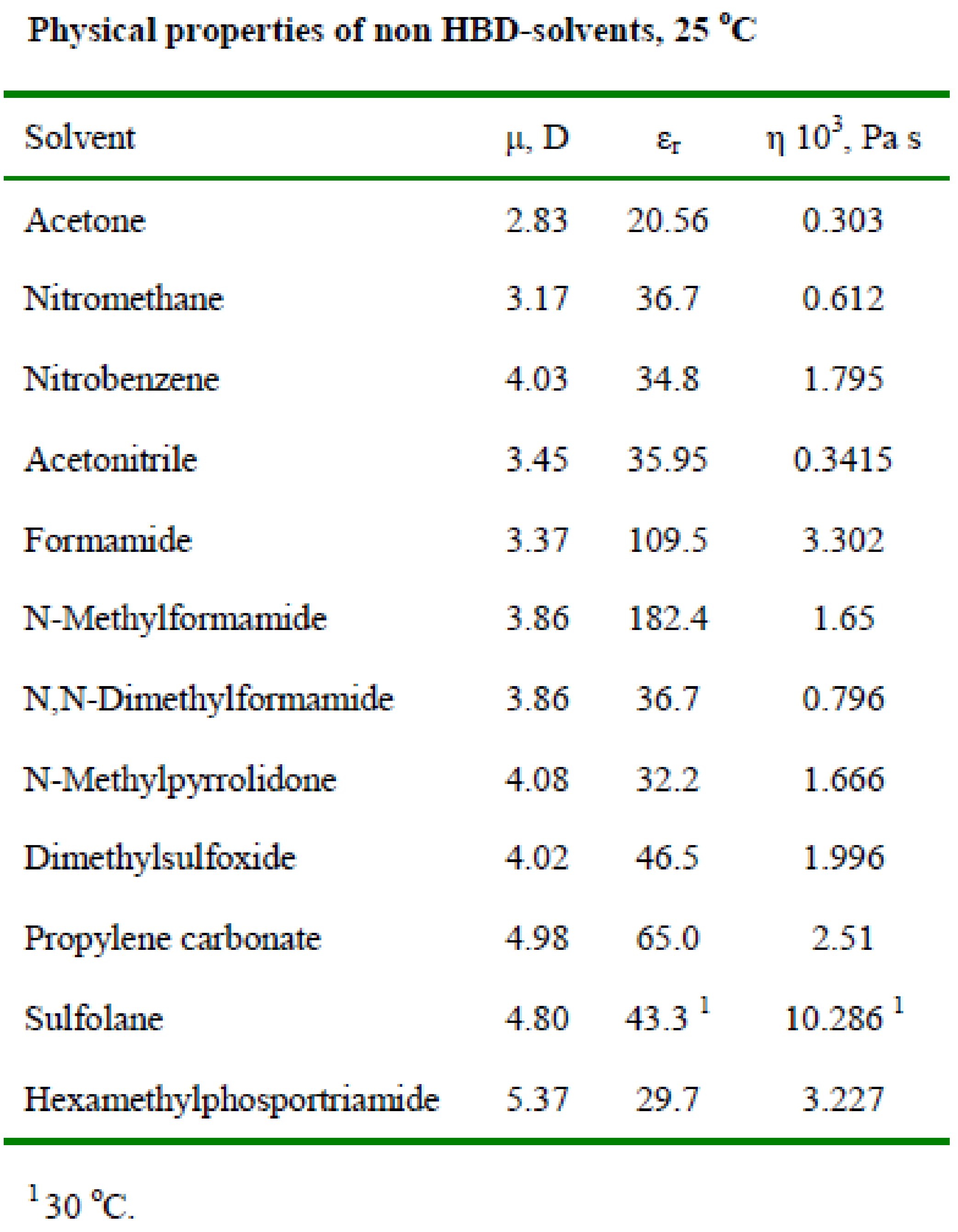




In alcohols: $R-O-H\cdots F^{\ominus}$

Non hydrogen bond donor-solvents: here small anions (F^-; HO^-; $R–COO^-$) are poorly solvated. Contrary to it, large anions with delocalized charge are well solvated: I^-, I_3^-, ClO_4^-, SCN^-, $C_6H_2(NO_2)_3O^-$, $B(C_6H_5)_4^-$

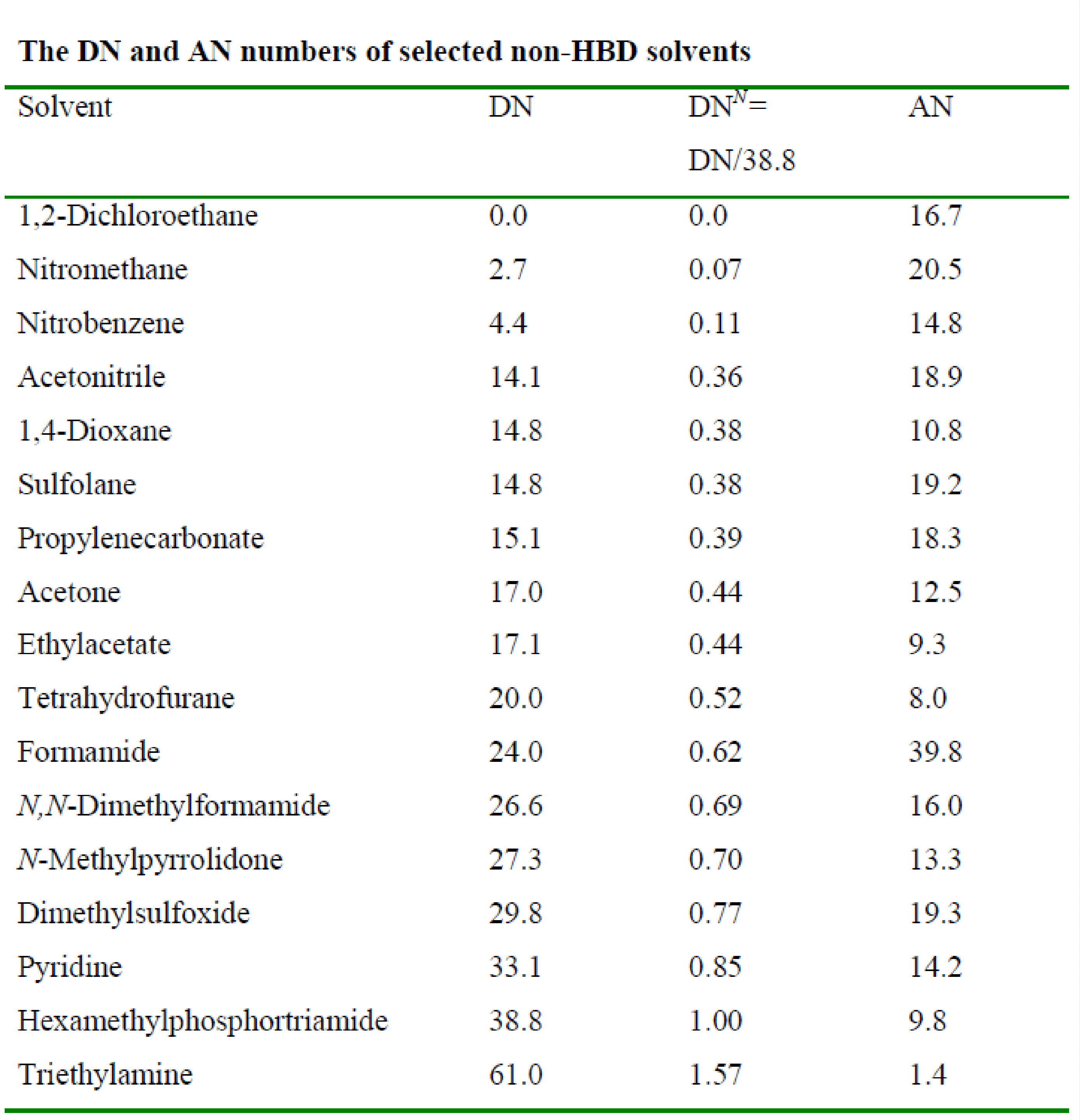




Physical properties of non HBD-solvents, 25 °C

Solvent	μ, D	ε_r	$\eta\ 10^3$, Pa s
Acetone	2.83	20.56	0.303
Nitromethane	3.17	36.7	0.612
Nitrobenzene	4.03	34.8	1.795
Acetonitrile	3.45	35.95	0.3415
Formamide	3.37	109.5	3.302
N-Methylformamide	3.86	182.4	1.65
N,N-Dimethylformamide	3.86	36.7	0.796
N-Methylpyrrolidone	4.08	32.2	1.666
Dimethylsulfoxide	4.02	46.5	1.996
Propylene carbonate	4.98	65.0	2.51
Sulfolane	4.80	43.3 [1]	10.286 [1]
Hexamethylphosportriamide	5.37	29.7	3.227

[1] 30 °C.



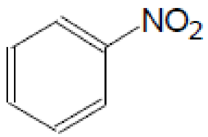
The DN and AN numbers of selected non-HBD solvents

Solvent	DN	$DN^N = DN/38.8$	AN
1,2-Dichloroethane	0.0	0.0	16.7
Nitromethane	2.7	0.07	20.5
Nitrobenzene	4.4	0.11	14.8
Acetonitrile	14.1	0.36	18.9
1,4-Dioxane	14.8	0.38	10.8
Sulfolane	14.8	0.38	19.2
Propylenecarbonate	15.1	0.39	18.3
Acetone	17.0	0.44	12.5
Ethylacetate	17.1	0.44	9.3
Tetrahydrofurane	20.0	0.52	8.0
Formamide	24.0	0.62	39.8
N,N-Dimethylformamide	26.6	0.69	16.0
N-Methylpyrrolidone	27.3	0.70	13.3
Dimethylsulfoxide	29.8	0.77	19.3
Pyridine	33.1	0.85	14.2
Hexamethylphosphortriamide	38.8	1.00	9.8
Triethylamine	61.0	1.57	1.4

Polar non HBD-solvents

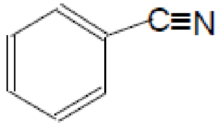
Nitromethane H_3C-NO_2

Nitrobenzene

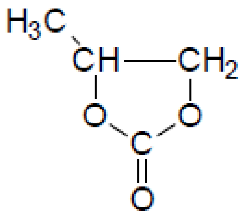


Acetonitrile $H_3C-C\equiv N$

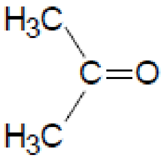
Benzonitrile



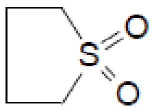
Propylenecarbonate (4-methyl-1,3-dioxolane-2-one)



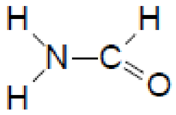
Acetone



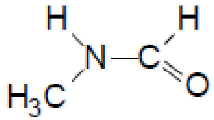
Sulfolane



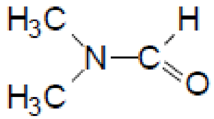
Formamide



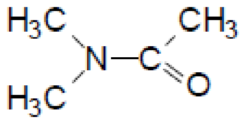
N-Methylformamide



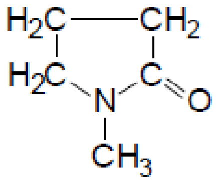
N,N-Dimethylformamide



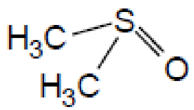
N,N-Dimethylacetamide



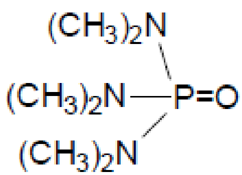
N-Methylpyrrolidone



Dimethylsulfoxide



Hexamethylphosphortriamide



Physical parameters of acidic, basic, and low-polar solvents (25 °C)

Solvent	μ, D	ε_r	$\eta \times 10^3$, Pa s
Acidic:			
Formic acid	1.77	56.1	1.621
Acetic acid	1.73	6.2	1.13
Basic:			
Ethylenediamine	1.90	12.9	1.54
Pyridine	2.37	12.3	0.884
"Inert" (low-polar):			
1,2-Dichloroethane		10.36	
Trichloromethane	1.12	4.89	0.540
Ethylacetate		6.02	
1,4-Dioxane		2.21	
Benzene		2.27	
n-Hexane		1.88	

Cohesion and cohesive pressure (**плотность энергии когезии**):

$$c = \frac{\Delta H_v - RT}{V_m}$$

V_m – molar volume; ΔH_v – enthalpy of vaporization.

Hildebrand solubility parameter: $\delta = c^{1/2}$

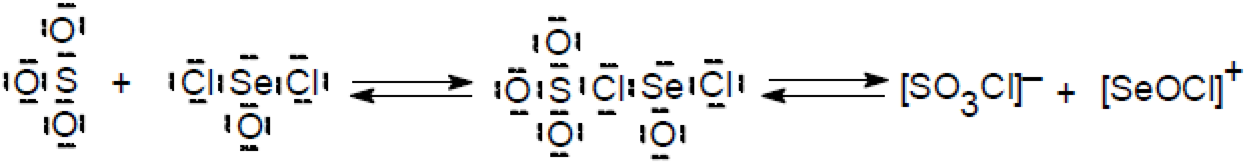
Internal pressure (**внутреннее давление**):

$$\pi = \left(\frac{\partial U}{\partial V_m}\right)_T$$

The values of the internal cohesion and internal pressure at 20 °C

Solvent	c, MPa	π, MPa
1,4-Dioxane	402	499
CCl_4	312	345
Benzene	357	379
Acetone	398	337
Acetonitrile	590	379
Ethanol	703	291
Methanol	887	285
H_2O (25 °C)	**2302**	151

Lewis acids (aprotic acids): $AlCl_3$, $FeCl_3$, $SnCl_4$, $SbCl_5$, metal cations and some other ions and molecules.



Gutmann’s Donor Numbers, DN:

$$\mathrm{D{:}} + \mathrm{SbCl_5} \rightleftharpoons \mathrm{D{:}SbCl_5};\quad \mathrm{DN} = -\Delta H^{\circ}_{\mathrm{D-SbCl_5}}\ \text{(kcal/mol)}$$

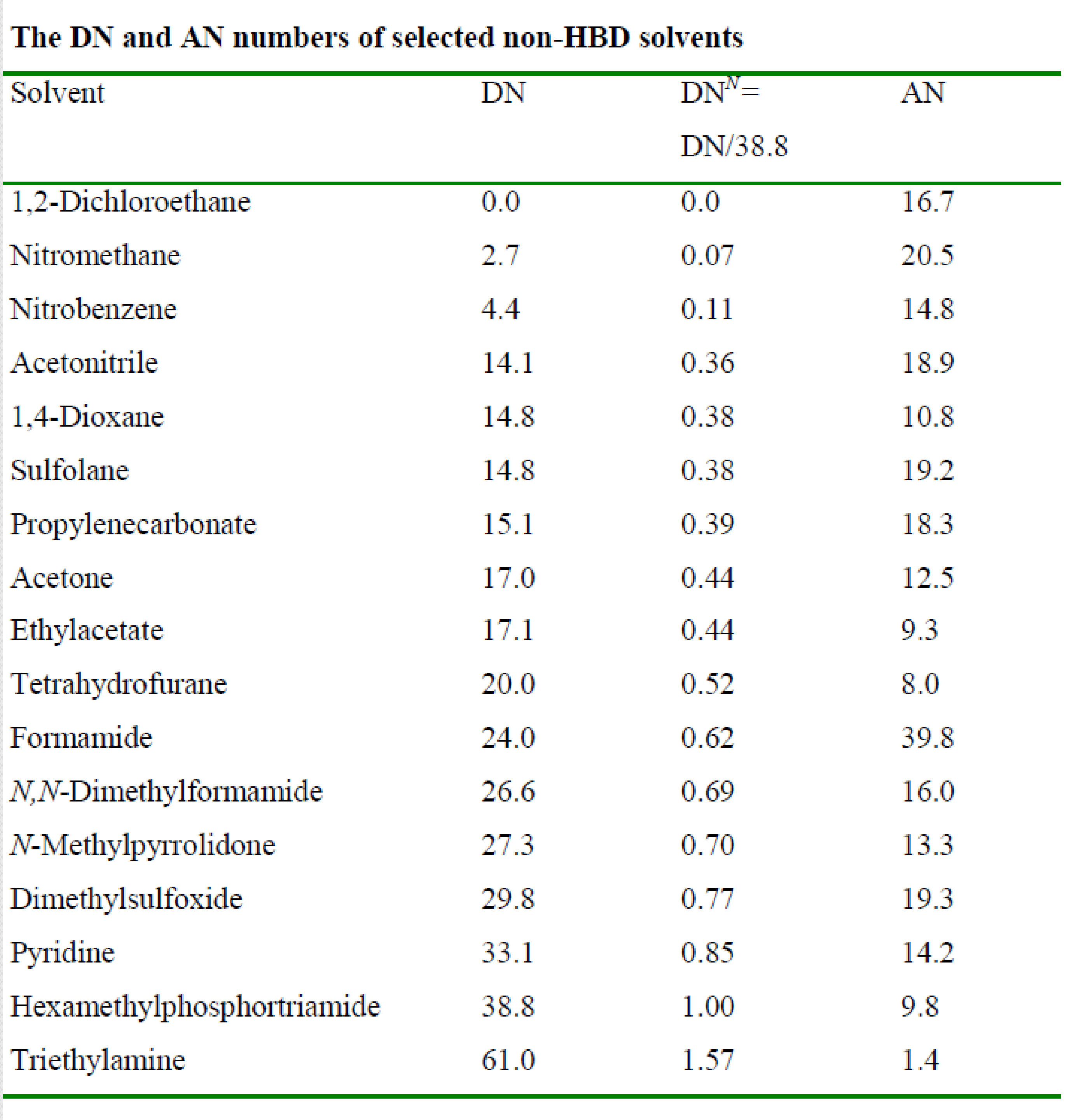
(in 1,2-dichloroethane)

In water: hydrolysis of $SbCl_5$.

Acceptor Number, AN:

AN is proportional to the chemical shift of ^{31}P in the NMR spectra of $(C_2H_5)_3P{=}O$; AN is a non-dimensional quantity and is estimated in respect to *n*-hexane.

The chemical shift ^{31}P for $(C_2H_5)_3PO{:}SbCl_5$ formation in 1,2-dichloroethane is equated to 100.



The DN and AN numbers of selected non-HBD solvents

Solvent	DN	$DN^N = DN/38.8$	AN
1,2-Dichloroethane	0.0	0.0	16.7
Nitromethane	2.7	0.07	20.5
Nitrobenzene	4.4	0.11	14.8
Acetonitrile	14.1	0.36	18.9
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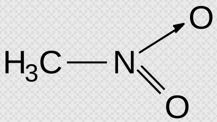
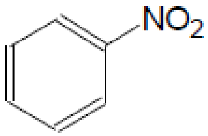


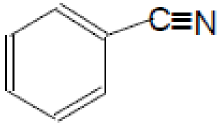
Nitromethane $H_3C{-}NO_2$

Nitrobenzene

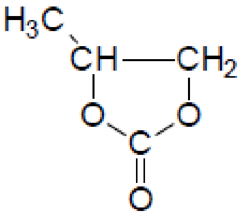


Acetonitrile $H_3C{-}C{\equiv}N$

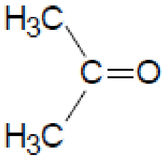
Benzonitrile



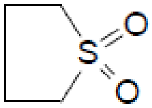
Propylenecarbonate (4-methyl-1,3-dioxolane-2-one)



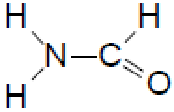
Acetone



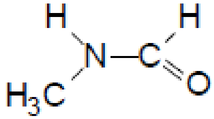
Sulfolane



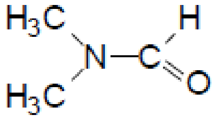
Formamide



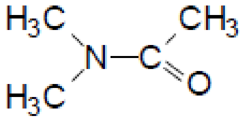
N-Methylformamide



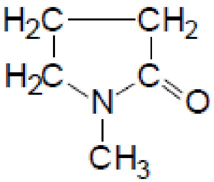
N,*N*-Dimethylformamide



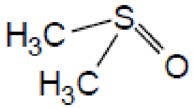
N,*N*-Dimethylacetamide



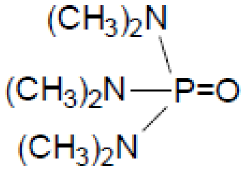
N-Methylpyrrolidone



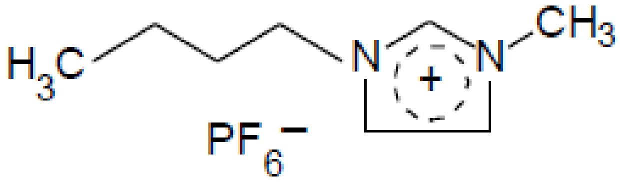
Dimethylsulfoxide



Hexamethylphosphortriamide



“Green solvents” – Room Temperature Ionic Liquids



$[\mathrm{bmim}]^+[\mathrm{PF}_6]^-$, $t_{\mathrm{melt}} = 12$ °C.

Negligible vapor pressure, incombustibility, high thermostability, wide electrochemical window

$\mathrm{C_2H_5NH_3^+NO_3^-}$: $t_{\mathrm{melt}} = 13–14$ °C.

(P. Walden, 1914).

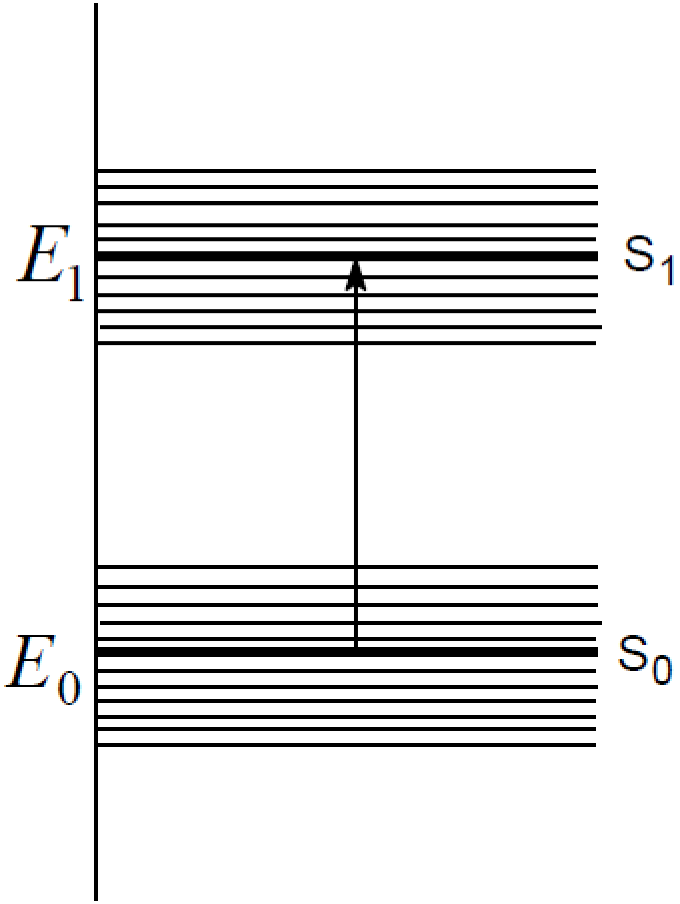
Chapter 2. THE INFLUENCE OF THE SOLVENTS ON THE ELECTRONIC ABSORPTION SPECTRA. SOLVATOCHROMISM

Energy of the quant:

$$E = h\nu$$

$h = 6.6256 \times 10^{-34}$ J s,

ν is frequency of electromagnetic vibrations ($\nu\lambda = c$).



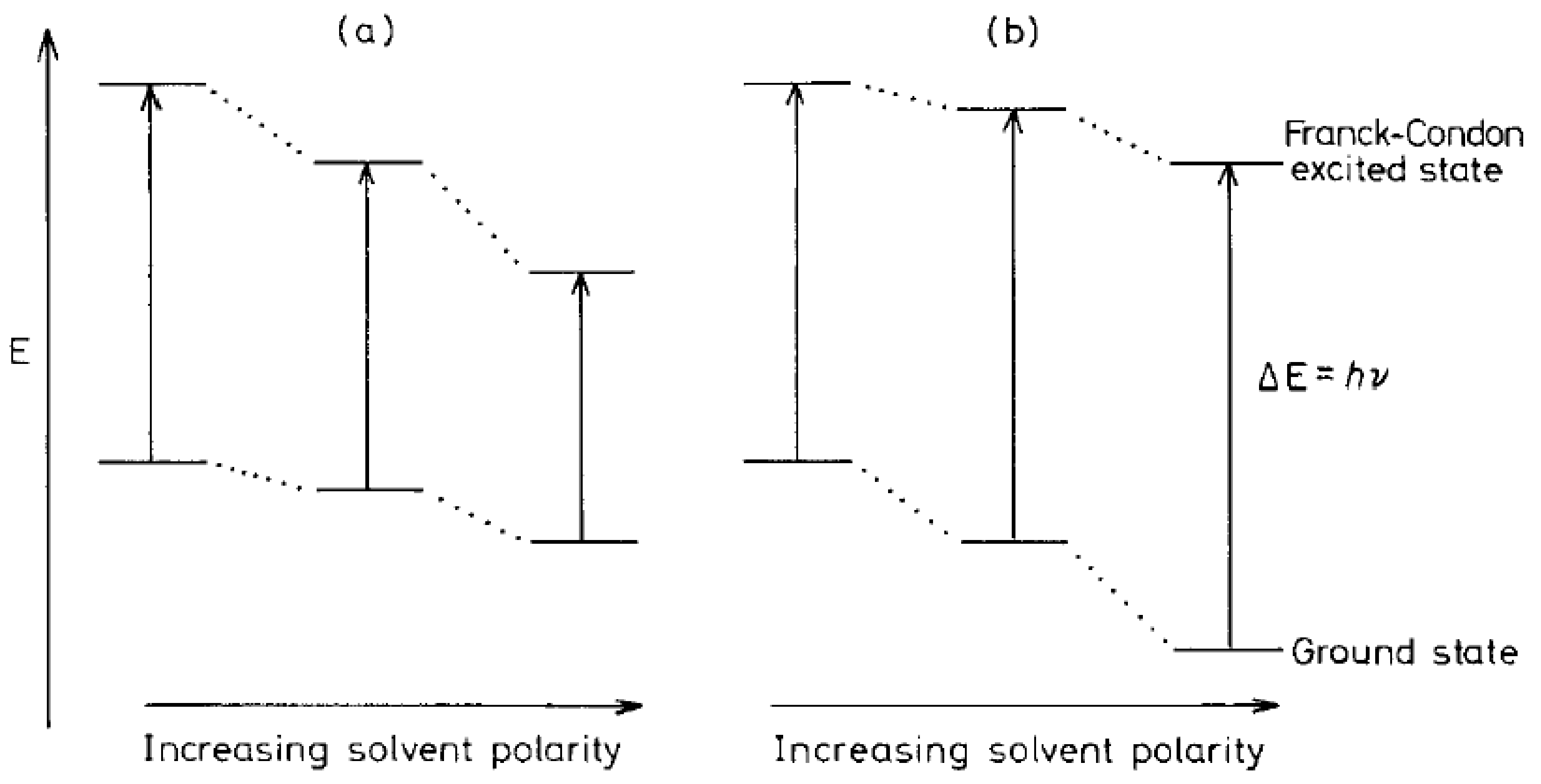
$$E_1 - E_0 = h\nu$$

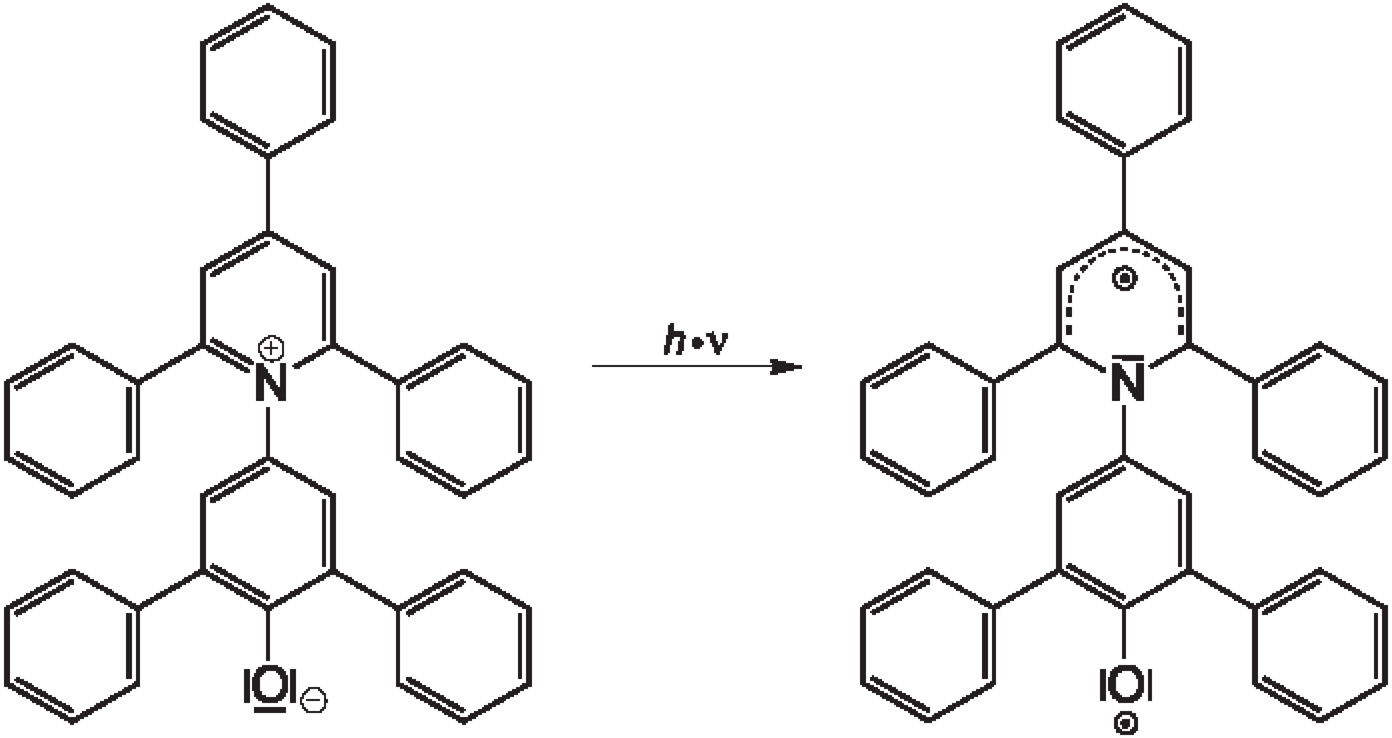
Absorption of a quant of light is an intramolecular process

Franck (1926) – Condon (1928) principle: the time of vibration of molecules is of order of magnitude of 10^{-12} s, while the time necessary for electronic transition is of the order of 10^{-15} s.

Influence of the solvent:
positive (a) and negative (b) solvatochromism

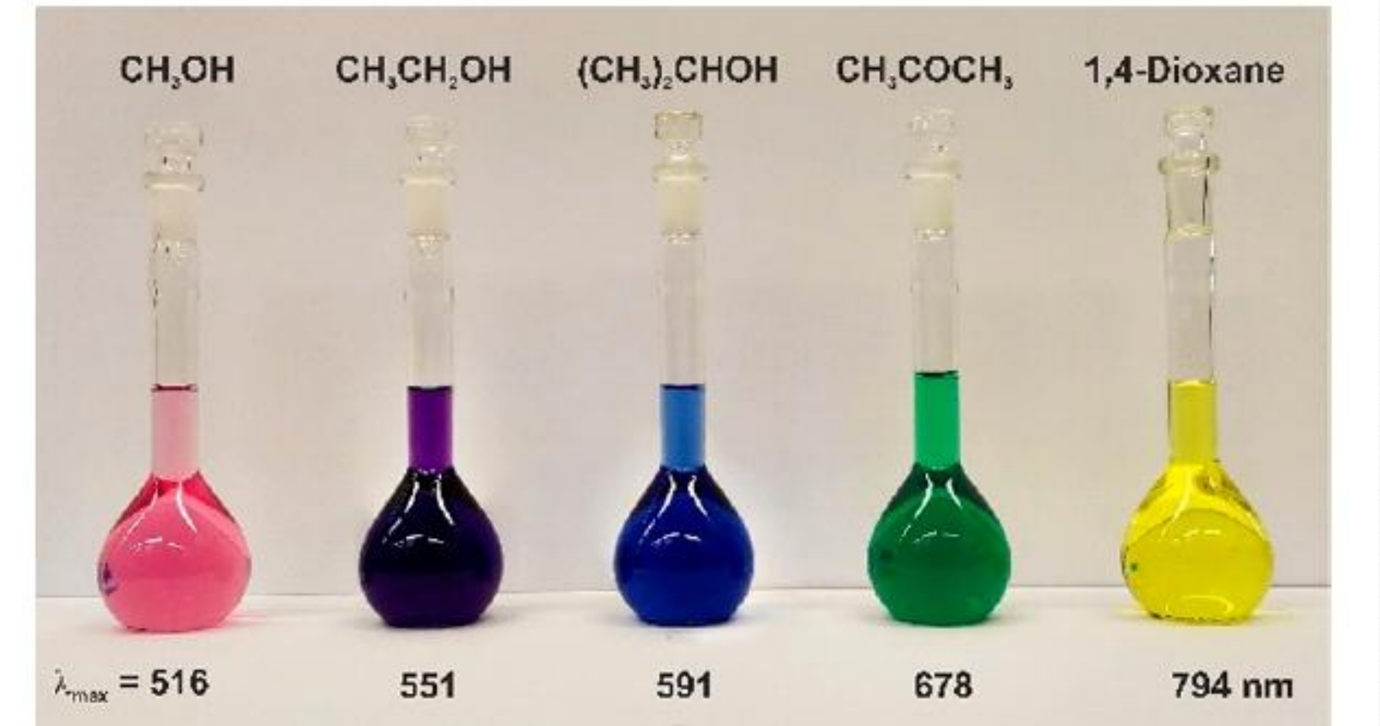
$\mu_g < \mu_e$ $\mu_g > \mu_e$





Solvent	$(C_6H_5)_2O$[a]	$C_6H_5OCH_3$	CH_3COCH_3	i-$C_5H_{11}OH$	C_2H_5OH	CH_3OH	H_2O[a]
λ_{max}/nm	810	771	677	583	550	516	453
Solution colour	–	yellow	green	blue	violet	red	–
Solvent polarity	⟶						

[a] Solubility very low.



(C. Reichardt, J. Org. Chem. 2022)

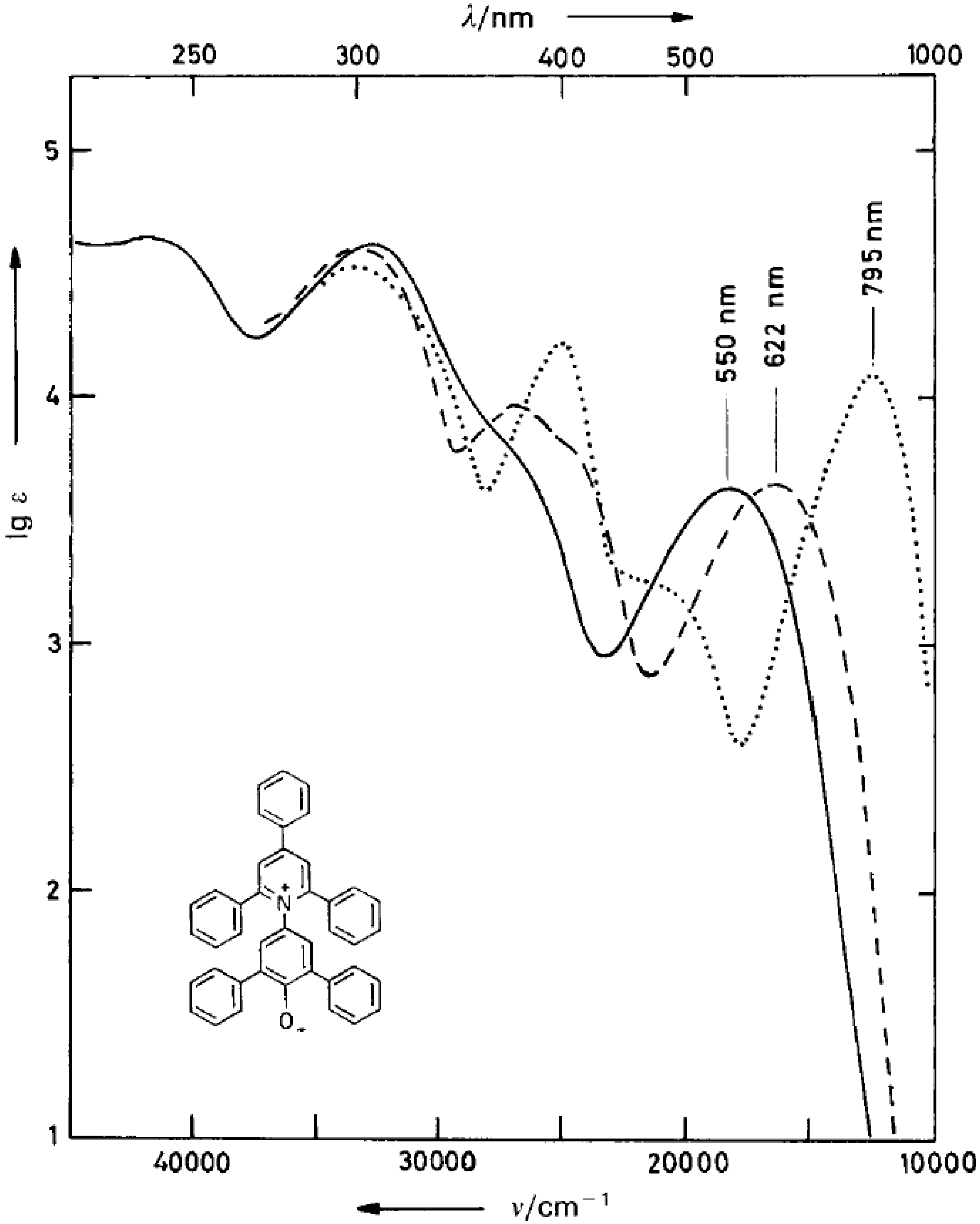
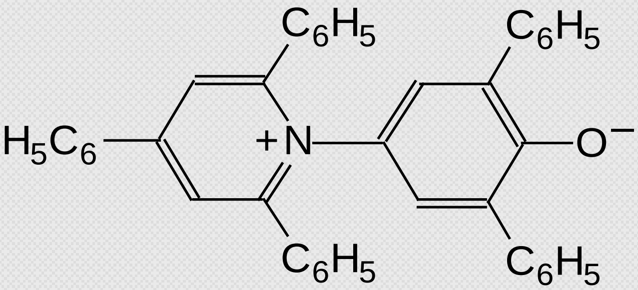


Fig. 6-2. UV/Vis absorption spectrum of 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate in ethanol (——), acetonitrile (- - - -), and 1,4-dioxane (· · · · ·) at 25 °C [10, 29].

Reichardt’s solvatochromic parameter



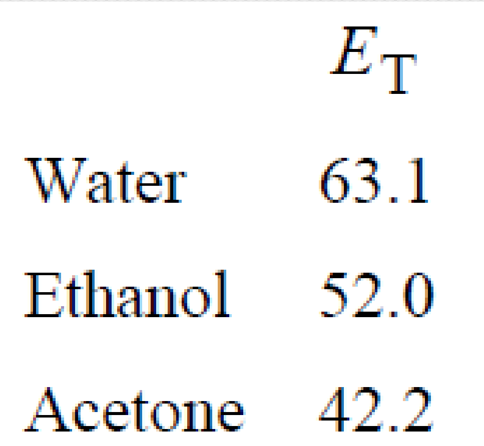
Dipole moment ca. 15 D in the ground state; and -6 D in the exited state

$$E_{\mathrm{T}} = hc\tilde{\nu}N_{\mathrm{A}} = 28591 \times \frac{1}{\lambda}(\mathrm{kcal\ /\ mole})$$

$\tilde{\nu}$ is wave number, cm^{-1}

λ is wave length, nm

$$\boxed{E_{\mathrm{T}}^{\mathrm{N}} = \frac{E_{\mathrm{T}}(30) - 30.7}{32.4}}$$



	E_{T}
Water	63.1
Ethanol	52.0
Acetone	42.2

Solvent descriptors

Solvent	E_T^N	AN	ε_r
Water	1.000	54.8	78.4
$C_2H_5NH_3^+NO_3^-$	0.954	—	—
Methanol	0.762	41.5	32.66
$bmim^+PF_6^-$	0.667	—	≈ 10
Ethanol	0.654	37.1	24.55
1-Butanol	0.586	32.2	17.51
Nitromethane	0.481	20.5	35.87
Propylenecarbonate	0.472	18.3	64.92
Acetonitrile	0.460	18.9	35.94
Dimethylsulfoxide	0.444	19.3	46.45
N,N-Dimethylformamide	0.404	16.0	36.71
2-Methyl-2-propanol (tert-butanol), 30 °C	0.364	27.1	12.47
Acetone	0.355	12.5	20.56
Nitrobenzene	0.324	14.8	34.78
Hexamethylphosphortriamide	0.315	9.8	29.30
Trichloromethane (chloroform)	0.259	23.1	3.8
Ethylacetate	0.228	9.3	5.9
1,4-Dioxane	0.164	10.8	2.21
Benzene	0.111	8.2	2.27
Tetrachloromethane	0.052	8.6	2.24
Triethylamine	0.043	1.4	2.42
n-Hexane	0.009	0.0	1.88
Tetramethylsilane	0.000	—	—
Gas phase	(–.111)	—	1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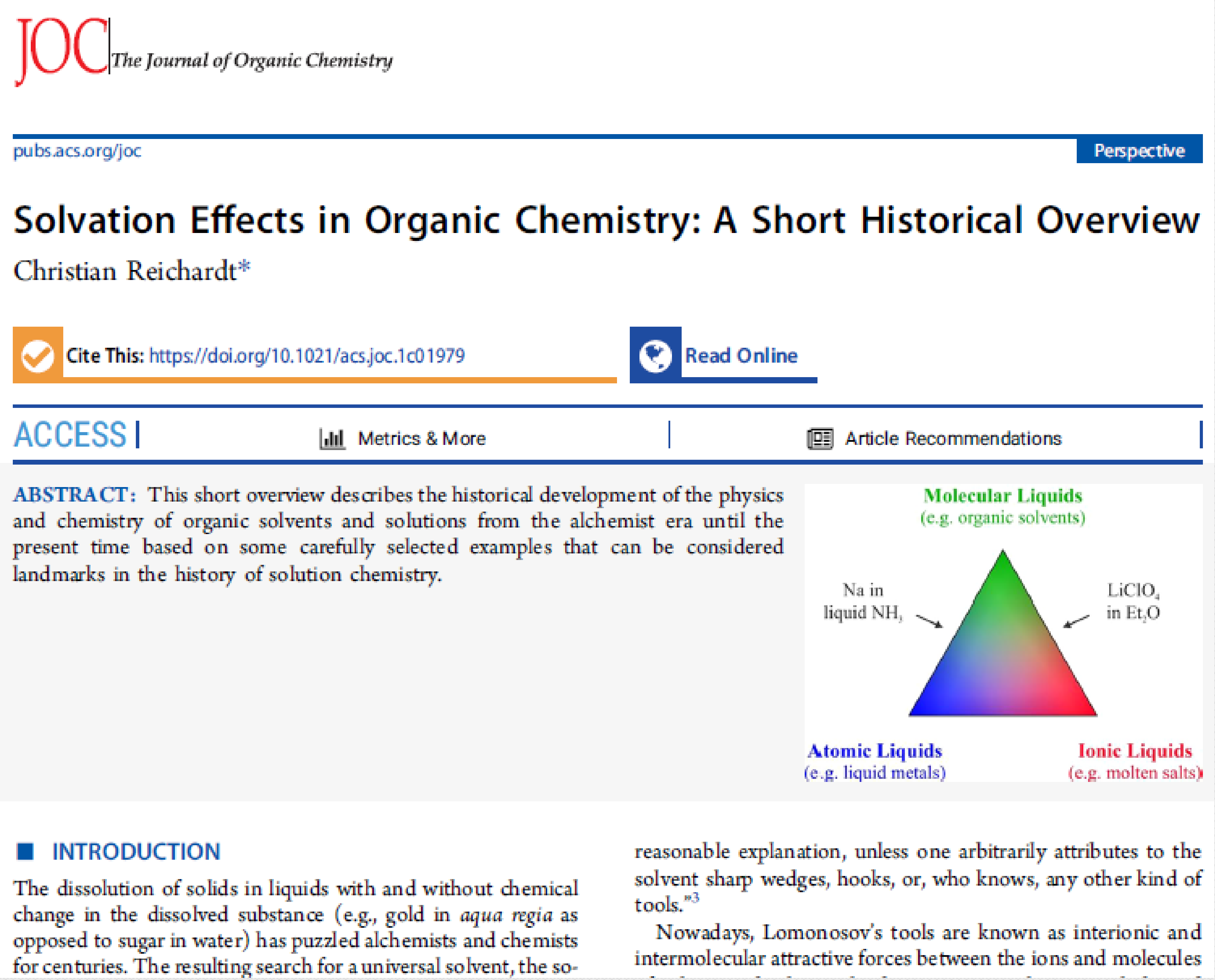

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Solvation Effects in Organic Chemistry: A Short Historical Overview

Christian Reichardt*

Cite This: https://doi.org/10.1021/acs.joc.1c01979 Read Online

ABSTRACT: This short overview describes the historical development of the physics and chemistry of organic solvents and solutions from the alchemist era until the present time based on some carefully selected examples that can be considered landmarks in the history of solution chemistry.

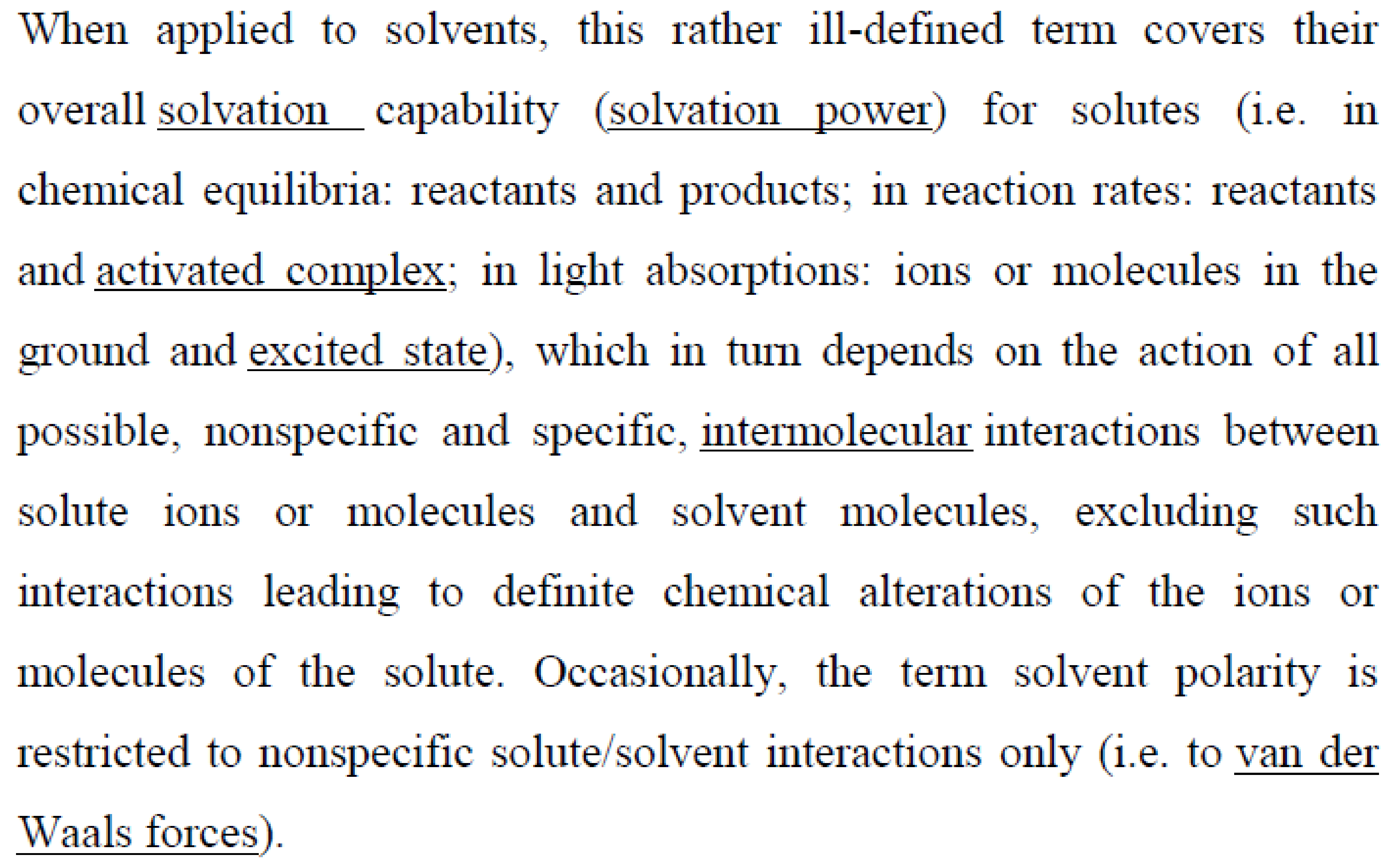
INTRODUCTION

The dissolution of solids in liquids with and without chemical change in the dissolved substance (e.g., gold in *aqua regia* as opposed to sugar in water) has puzzled alchemists and chemists for centuries. The resulting search for a universal solvent, the so-

reasonable explanation, unless one arbitrarily attributes to the solvent sharp wedges, hooks, or, who knows, any other kind of tools."[3]

Nowadays, Lomonosov's tools are known as interionic and intermolecular attractive forces between the ions and molecules

IUPAC:



When applied to solvents, this rather ill-defined term covers their overall solvation capability (solvation power) for solutes (i.e. in chemical equilibria: reactants and products; in reaction rates: reactants and activated complex; in light absorptions: ions or molecules in the ground and excited state), which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute. Occasionally, the term solvent polarity is restricted to nonspecific solute/solvent interactions only (i.e. to van der Waals forces).

PURIFICATION OF SOLVENTS

AND PRECAUTIONS WHEN WORKING WITH THEM

Water determination by Karl Fischer

First stage:

$$C_5H_5N \cdot I_2 + C_5H_5N \cdot SO_2 + C_5H_5N + H_2O \rightarrow 2\ C_5H_5NH^+\ I^- + C_5H_5N \cdot SO_3$$

In this reaction, water is a source of oxygen (in the absence of methanol, the compound $C_5H_5N \cdot SO_3$ is isolated as an individual compound).

Second stage:

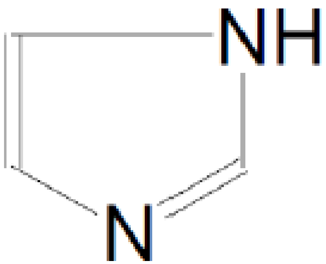
$$C_5H_5N \cdot SO_3 + CH_3OH \rightarrow C_5H_5NHOSO_2OCH_3$$

(in the absence of methanol, consumption of water (in the absence of methanol, the reaction would consume water to form the compound $C_5H_5NHOSO_2OH$).

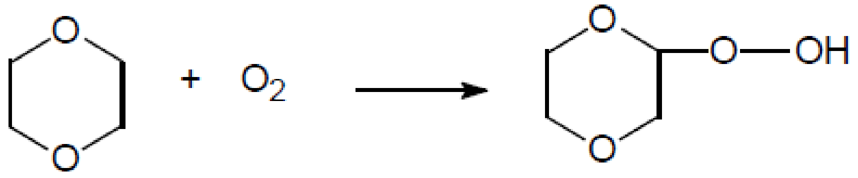
Oxidizing and reducing agents interfere with the reaction. Compounds with a carbonyl group also interfere. Aldehydes and ketones form acetals and ketals with alcohols, for example:

$$R–CHO + 2\ C_2H_5OH \rightarrow R–CH(OC_2H_5)_2$$

Presently, imidazole is used instead of the toxic pyridine



Undesirable processes



explosive!

(Analogously reacts tetrahydrofurane)

$CHCl_3$ over time forms HCl

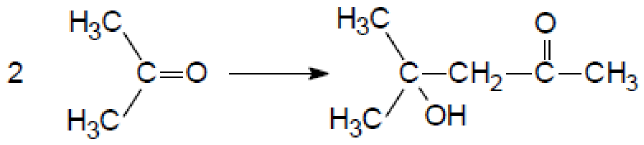
DMF → $(CH_3)_2NH$ and HCOOH

$CH_3CN \rightarrow NH_3$

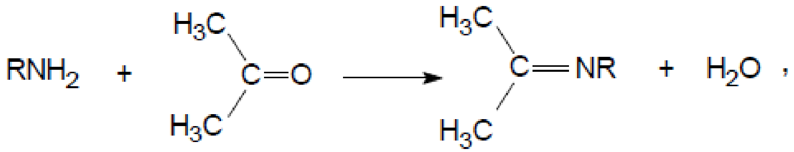
$CCl_4 + C_2H_5OH \rightarrow$ traces of $HCl + CO$

$CHCl_3 + H_2SO_4 \rightarrow COCl_2$ (phosgene)

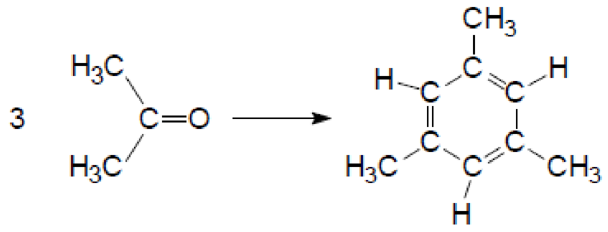
Acetone in the presence of alkali:



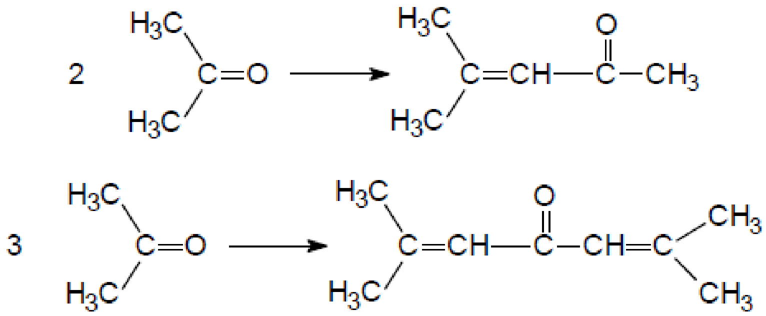
Acetone with primary amines:



Acetone with conc. sulfuric acid forms mesitylene:



Acetone with HCl (gas) forms mesityl oxide and phorone:



ELECTROLYTES IN SOLUTIONS

Electrolytes: chemical compounds whose solutions conduct the electrical current.

The theory of the electrolytic dissociation
(Arrhenius, 1883)

$$\alpha = \frac{\Lambda}{\Lambda_0}$$ (Kohlrausch)

$$K = \frac{\alpha^2 c}{1-\alpha} = \frac{\Lambda^2 c}{\Lambda_0 (\Lambda_0 - \Lambda)}$$ (Ostwald)

The division of electrolytes into "strong" and "weak" as a result of studies in aqueous solutions.

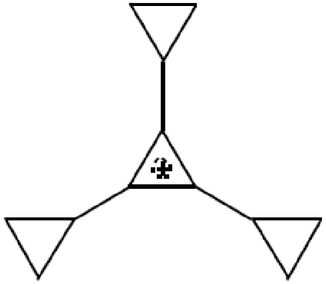
Investigation of electrolytes in non-aqueous solutions and limited understanding of "strong" electrolytes
(Walden, Kraus, Fuoss, Izmailov)

More correct classification of electrolytes:

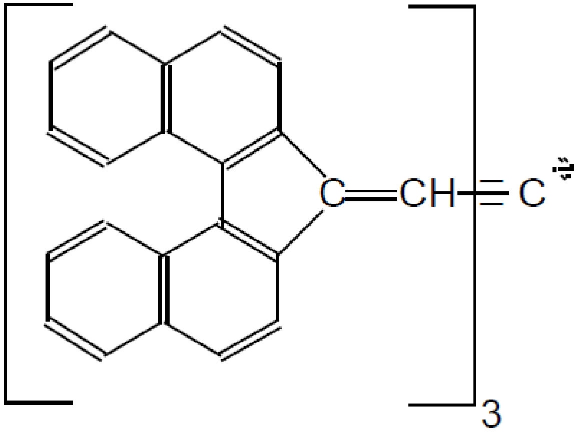
IONOPHORES, or **true electrolytes** – compounds consisting of ions and without contact with a solvent (first of all, these are salts, both inorganic and organic)
IONOGENES, or **pseudoelectrolytes** – compounds that form ions only in solutions (e.g., HCl, CH_3COOH).

Some exceptions:

A green salt with Agranate cation and Kuhn anion:



$C_{12}H_{15}^{+}$



$C_{67}H_{39}^{-}$

Okamoto et al. (J. Org. Chem. 1990):

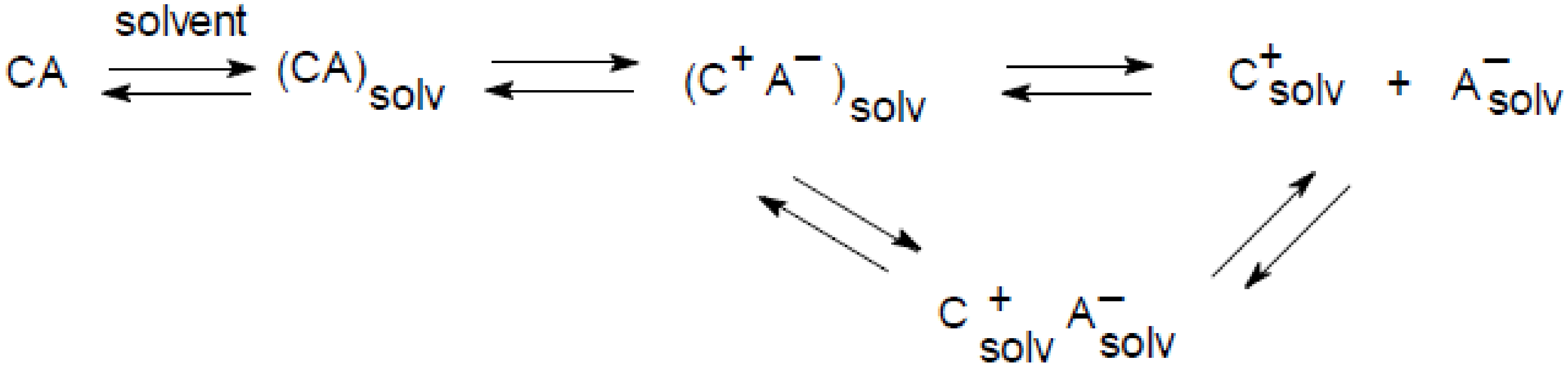
In DMSO the salt dissociates and forms ions;

In $CHCl_3$ a colorless hydrocarbon appears owing to formation of a C–C bond;

After evaporation the colored solid salt appears.

General dissociation scheme of electrolytes in solution

by Izmailov



$$K_{об}^{-1} = (K^{*}_{нест}+1)K_{дис}^{-1} + K_{асс} = K_{дис}^{-1}(K^{*}_{нест}+1+K_{пр})$$

$$K_{пр} = K_{дисс}K_{асс}$$

Ionization and dissociation.

Triphenylchloromethane in liquid SO_2, 0 °C (Walden, Lichtin):

$$\underset{\text{colorless}}{(C_6H_5)_3C{-}Cl} \overset{K_i}{\rightleftarrows} \underset{\text{yellow}}{(C_6H_5)_3C^+Cl^-} \overset{K_d}{\rightleftarrows} \underset{\text{yellow}}{(C_6H_5)_3C^+ + Cl^-}$$

$$\text{Spectroscopy:}\quad \frac{[(C_6H_5)_3C^+Cl^-]+[(C_6H_5)_3C^+]}{[(C_6H_5)_3C-Cl]}$$

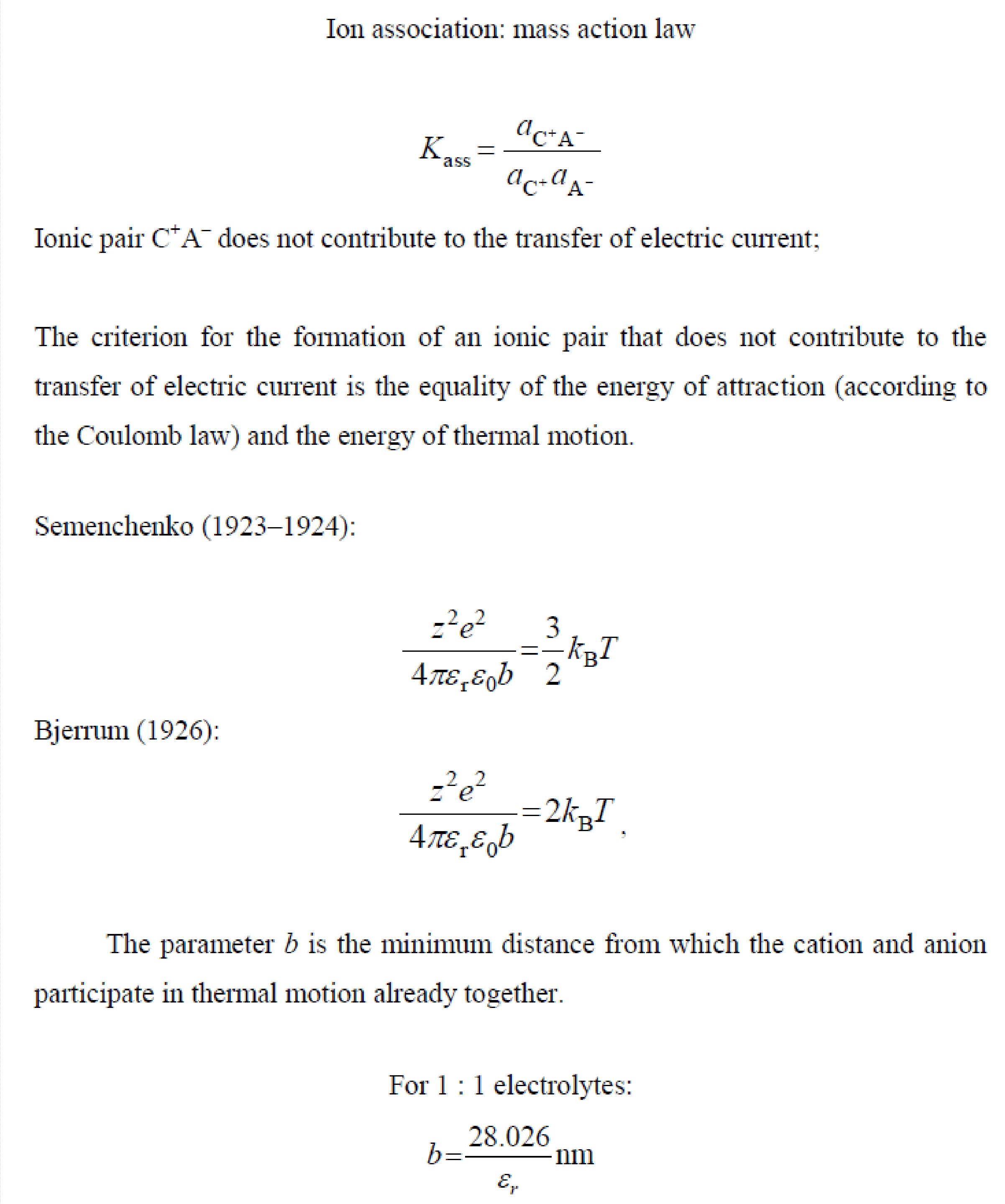
$$K_{\text{over–all}} = \frac{[(C_6H_5)_3C^+]\ \times\ [Cl^-]}{[(C_6H_5)_3C-Cl]\ +\ [(C_6H_5)_3C^+Cl^-]}\ .$$

$$K_{\text{over–all}} = \frac{K_i\,K_d}{1\ +\ K_i}$$

At 0 °C: $K_i = 1.46\times10^{-2}$, $K_d = 2.88\times10^{-3}\,\text{M}$, $K_{\text{over–all}} = 4.1\times10^{-5}\,\text{M}$.

SO_2 is a Lewis acid and solvates the Cl^- ion.

Addition of $LiClO_4$ results in decrease in the concentration of $(C_6H_5)_3C{-}Cl$ because of formation of Li^+Cl^-.



Ion association: mass action law

$$K_{\mathrm{ass}} = \frac{a_{\mathrm{C^+A^-}}}{a_{\mathrm{C^+}}a_{\mathrm{A^-}}}$$

Ionic pair C^+A^- does not contribute to the transfer of electric current;

The criterion for the formation of an ionic pair that does not contribute to the transfer of electric current is the equality of the energy of attraction (according to the Coulomb law) and the energy of thermal motion.

Semenchenko (1923–1924):

$$\frac{z^2e^2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 b} = \frac{3}{2}k_{\mathrm{B}}T$$

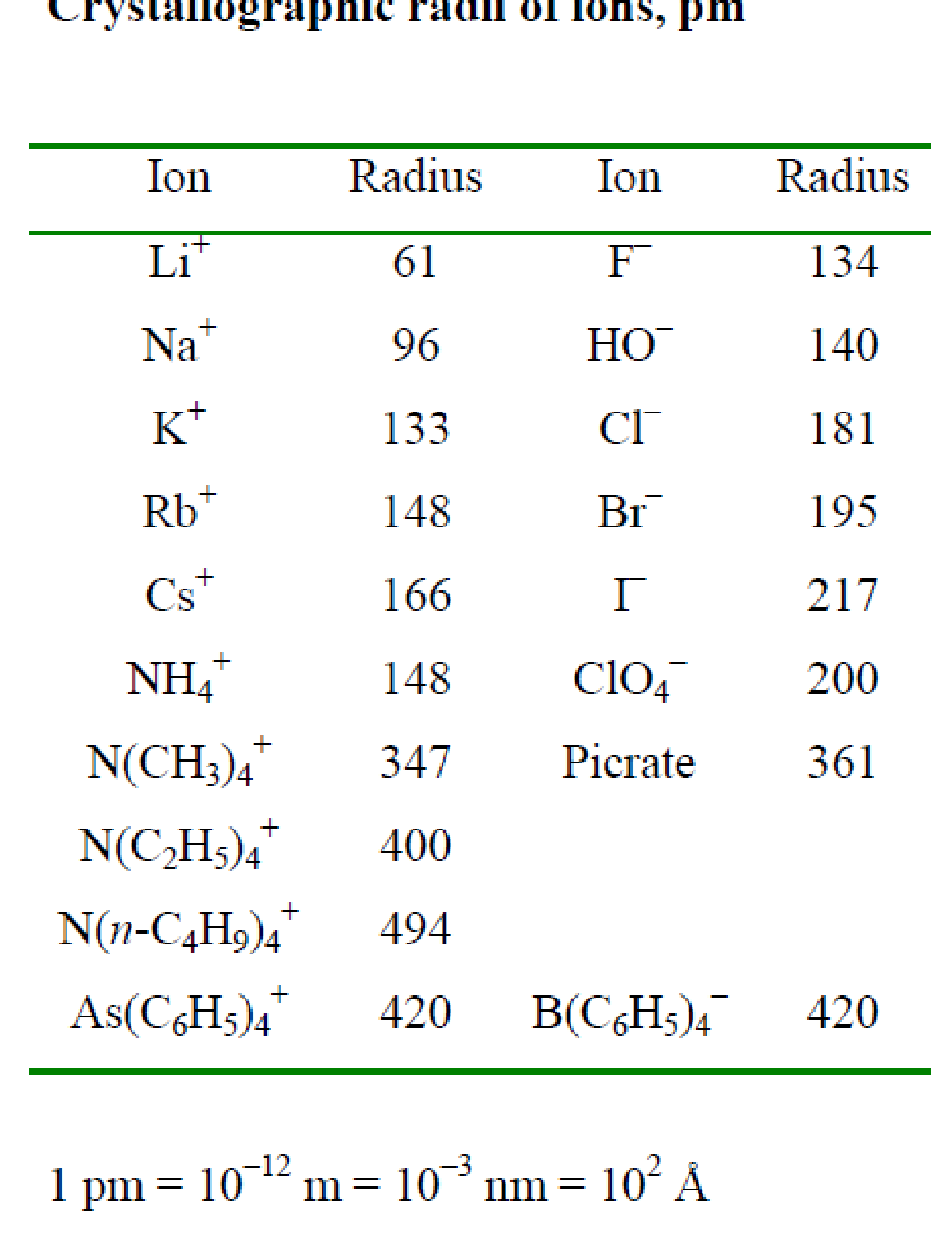
Bjerrum (1926):

$$\frac{z^2e^2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 b} = 2k_{\mathrm{B}}T\ ,$$

The parameter b is the minimum distance from which the cation and anion participate in thermal motion already together.

For 1 : 1 electrolytes:

$$b = \frac{28.026}{\varepsilon_r}\ \mathrm{nm}$$



Crystallographic radii of ions, pm

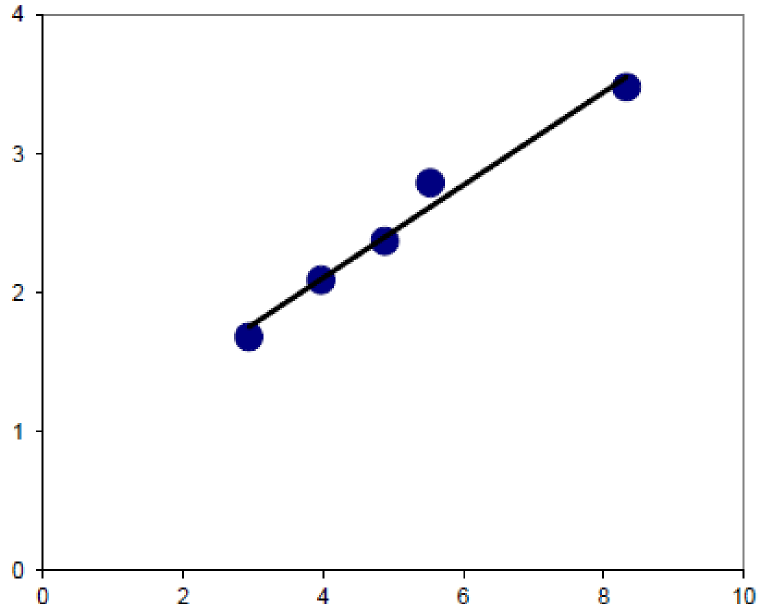
Ion	Radius	Ion	Radius
Li^+	61	F^-	134
Na^+	96	HO^-	140
K^+	133	Cl^-	181
Rb^+	148	Br^-	195
Cs^+	166	I^-	217
NH_4^+	148	ClO_4^-	200
$N(CH_3)_4^+$	347	Picrate	361
$N(C_2H_5)_4^+$	400		
$N(n\text{-}C_4H_9)_4^+$	494		
$As(C_6H_5)_4^+$	420	$B(C_6H_5)_4^-$	420

1 pm = 10^{-12} m = 10^{-3} nm = 10^{2} Å

Association constants $\{N(n\text{-}C_4H_9)_4^+ + C_6H_2(NO_2)_3O^- \rightleftharpoons \text{ion pair}\}$ in different solvents; 25 °C

Solvent	ε_r	K_{ass}, M^{-1}
Acetonitrile	35.94	13
Methanol	32.66	8
Acetone	20.56	45
Nitromethane	35.87	50
Methylisobutylketone	12.92	2.0×10^3
1,2-Dichloroethane	10.23	3.2×10^3
1,3-Dichlorobenzene	9.93	5.9×10^4
n-Butylacetate	5.10	1.2×10^7

An example of the linear dependence of $\log K_{\text{ass}}$ vs. ε_r^{-1}



Tetramethylammonium perchlorate in different solvents

From left to right: in nitrobenzene, benzonitrile, acetone, 2-butanone, pyridine

$$\log K_{\text{ass}} = 0.765 + 33.46\,\varepsilon_r^{-1},\ r = 0.99$$

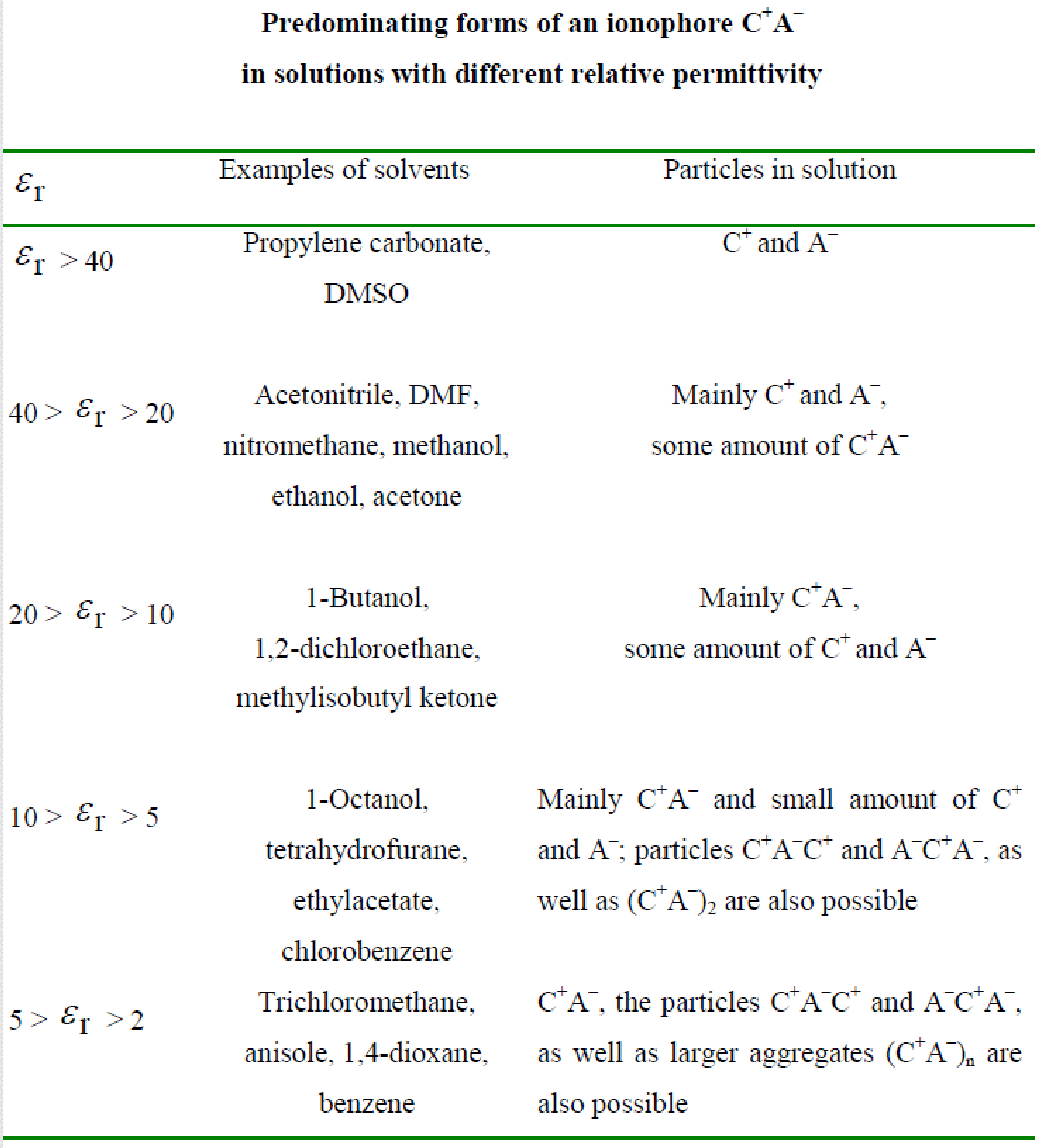
(P.C. Ho, J.B. Ramsey. J. Chem. Eng. Data 1986. Vol. 31. No. 4. P. 430-434.)

When should ion pairs be considered? A reasonable criterion is the value of the degree of electrolyte dissociation, , for average electrolyte concentrations, for example, 0.001–0.01 M.

$$K_{\text{ass}} = \frac{1-\alpha}{\alpha^2 c}$$

Simple estimates show that if the constant $K_{\text{ass}} < 10^3\ \text{M}^{-1}$, then, in the first approximation, the electrolyte can be considered dissociated into ions.

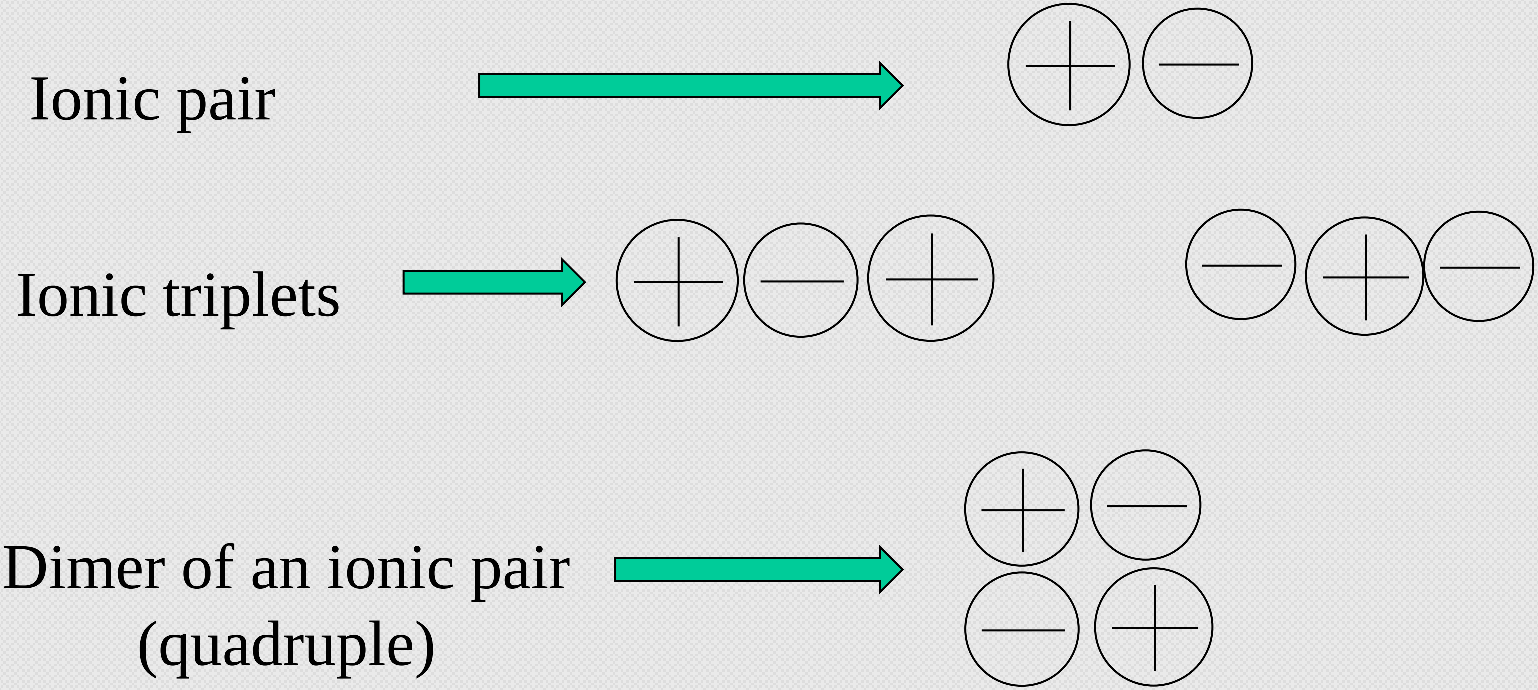
The below data are obtained mainly by conductance method.



Predominating forms of an ionophore C^+A^- in solutions with different relative permittivity

ε_r	Examples of solvents	Particles in solution
$\varepsilon_r > 40$	Propylene carbonate, DMSO	C^+ and A^-
$40 > \varepsilon_r > 20$	Acetonitrile, DMF, nitromethane, methanol, ethanol, acetone	Mainly C^+ and A^-, some amount of C^+A^-
$20 > \varepsilon_r > 10$	1-Butanol, 1,2-dichloroethane, methylisobutyl ketone	Mainly C^+A^-, some amount of C^+ and A^-
$10 > \varepsilon_r > 5$	1-Octanol, tetrahydrofurane, ethylacetate, chlorobenzene	Mainly C^+A^- and small amount of C^+ and A^-; particles $C^+A^-C^+$ and $A^-C^+A^-$, as well as $(C^+A^-)_2$ are also possible
$5 > \varepsilon_r > 2$	Trichloromethane, anisole, 1,4-dioxane, benzene	C^+A^-, the particles $C^+A^-C^+$ and $A^-C^+A^-$, as well as larger aggregates $(C^+A^-)_n$ are also possible

Fuoss and Kraus: ionic triplets formation



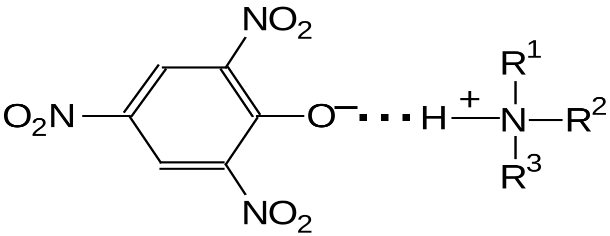
Ionic pair

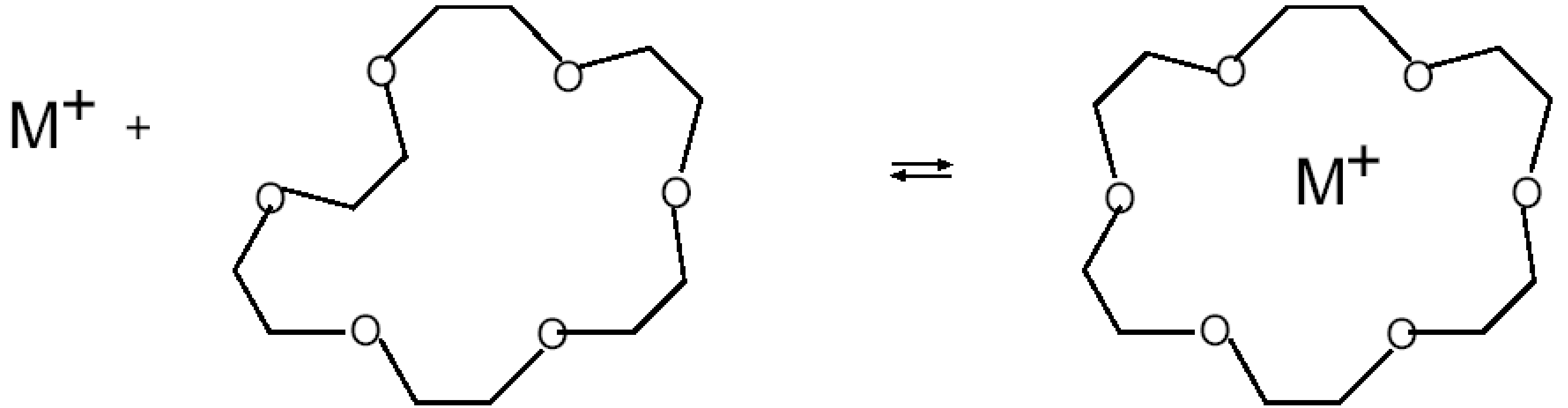
Ionic triplets

Dimer of an ionic pair
(quadruple)

Association constants of picrate anion $C_6H_2(NO_2)_3O^-$ with different cations C^+ in nitrobenzene; $\varepsilon_r = 35.7$

Cation C^+	$K_A \times 10^{-3}$, M^{-1}
Li^+	16000
Na^+	35
K^+	0.014
$(CH_3)_4N^+$	0.025
$(C_2H_5)_4N^+$	0.0071
$(\textit{н-}C_4H_9)_4N^+$	0.0075
$(\textit{н-}C_4H_9)_3NH^+$	5.3
$(\textit{н-}C_4H_9)_2NH_2^+$	6.4
$(\textit{н-}C_4H_9)NH_3^+$	6.6
NH_4^+	6.9




M+ +
O
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M+
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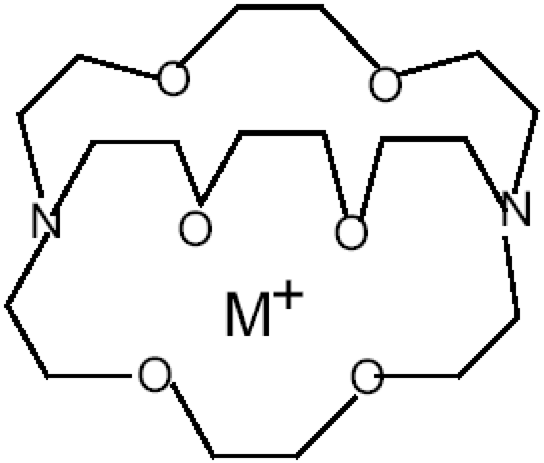

O
O
N
O
O
N
M+
O
O

The logarithms of the stability constants of alkali metal cations with 18-crown-6 in different solvents 25 °C

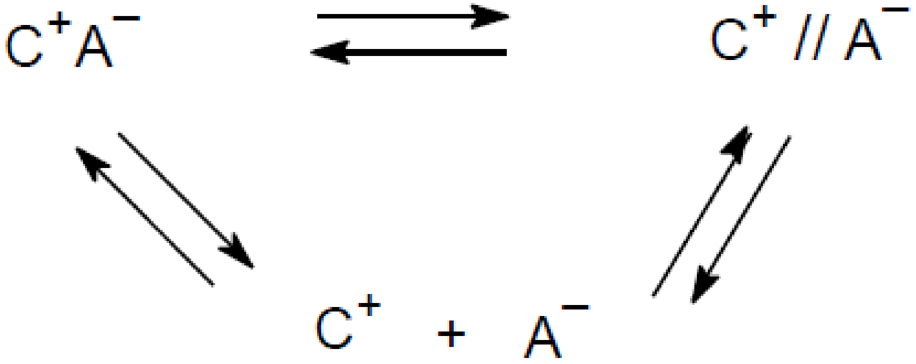
Solvent	log K^f	
	Na^+	K^+
Protophobic (cationophobic):		
Acetone	4.46	5.89
Acetonitrile	4.6	5.76
Protophilic (cationophilic):		
N,N-Dimethylformamide	2.5	4.2
Dimethylsulfoxide	1.43	3.25

Multiplicity of ionic pairs

Two types of ionic pairs $(C^+A^-)_{solv}$ and $(C^+_{solv}\ A^-_{solv})$

(see the general scheme by Izmailov)

Winstein, Grunwald, Fuoss, Izmailov



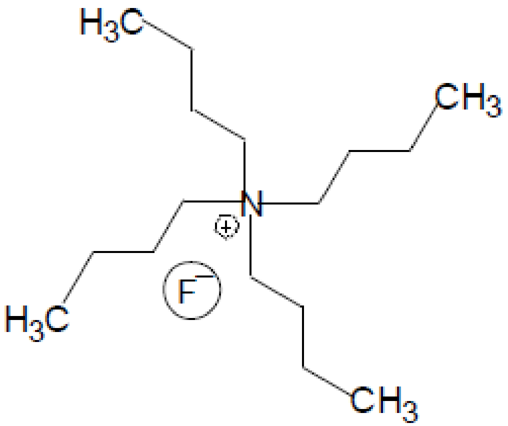
(all particles are solvated)

Ionic pairs:

Contact (**CIP**)	Solvent-separated (**SSIP**)
Short	Long
IUPAC recommendation:	
Tight	Loose

Solvent-separated and solvent-shared ionic pairs

Penetrated («проникнутые») ionic pairs:



TRANSPORT PROPERTIES OF IONS IN SOLUTION

$$\Lambda_0 = \Lambda_+ + \Lambda_-$$

The relation between the ion mobility and its velocity in liquid phase at infinite dilution, v':

$$\Lambda_{ion} = v'\, lF/E,$$

l is the distance between the electrode, E is the potential difference.

The ionic mobility must be dependent on the solvent viscosity.

Pisarzhevskiy – Walden (1905 – 1906):

$$\Lambda_0\eta = \text{const}$$

<u>Theoretical explanation:</u>

Einstein–Smoluchowsky:

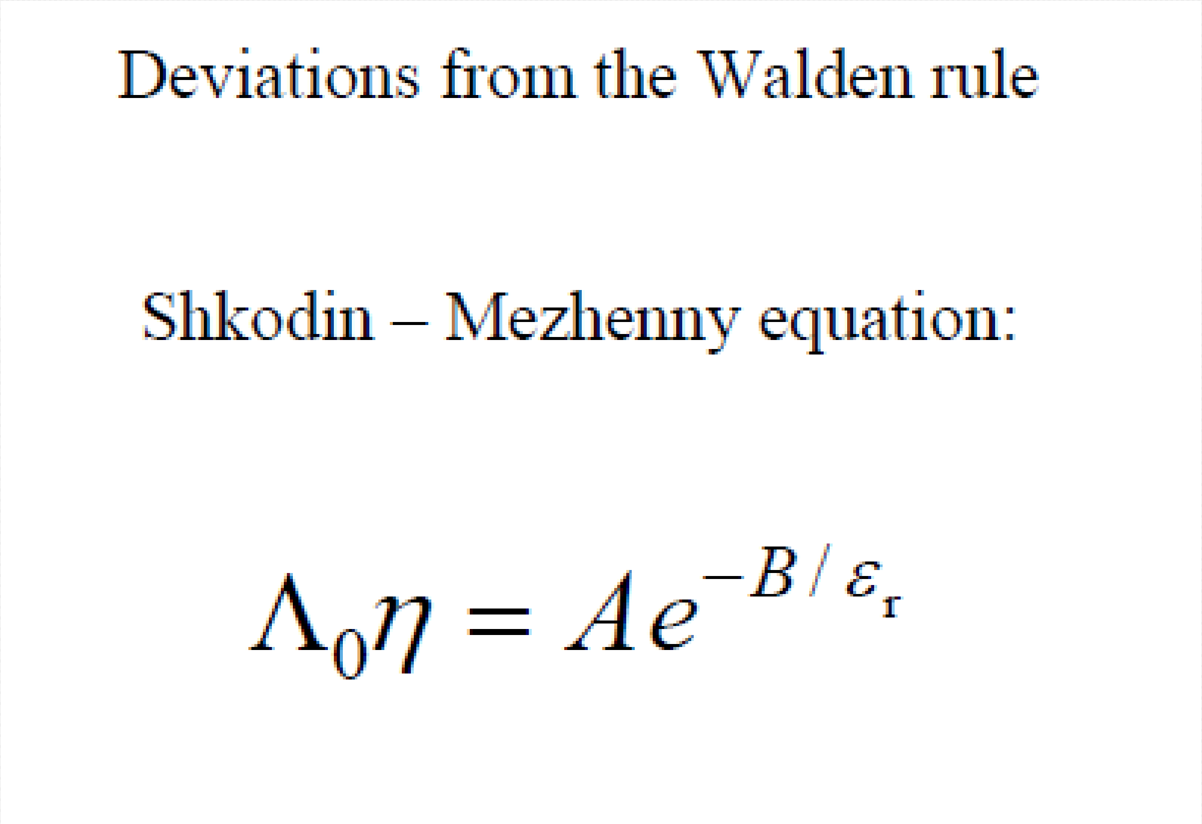
Nernst:

$$\begin{tikzcd}
 & D = \dfrac{k_B T}{6\pi\eta r_i} \arrow[d] \\
D = \dfrac{RT\Lambda_i}{|z_i|F^2}\,. \arrow[r] & \Lambda_i\eta = \dfrac{|z_i|F^2}{6\pi N_A r_i}
\end{tikzcd}$$

Verification of the Walden's rule:

tetra-*n*-butylammonium picrate, 25 °C

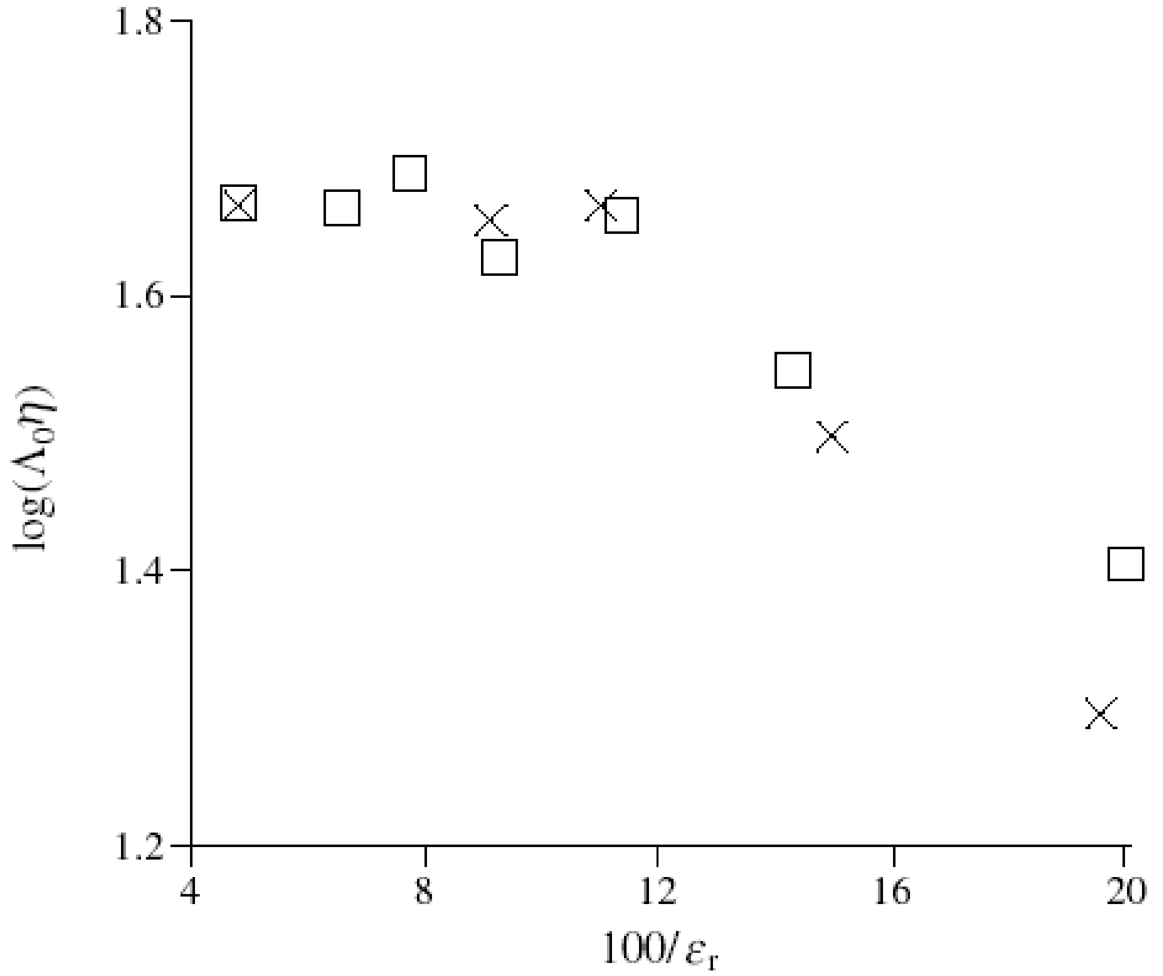
Solvent	$\Lambda_0\eta\ \times 10^7$, $C^2\ m^{-1}\ mole^{-1}$
Formamide	53.8
N,N-Dimethylformamide	50.7
Acetone	46.2
Acetonitrile	47.5
Methanol	46.7
Ethanol	48.6
Nitrobenzene	51.3
Propylenecarbonate	55.4



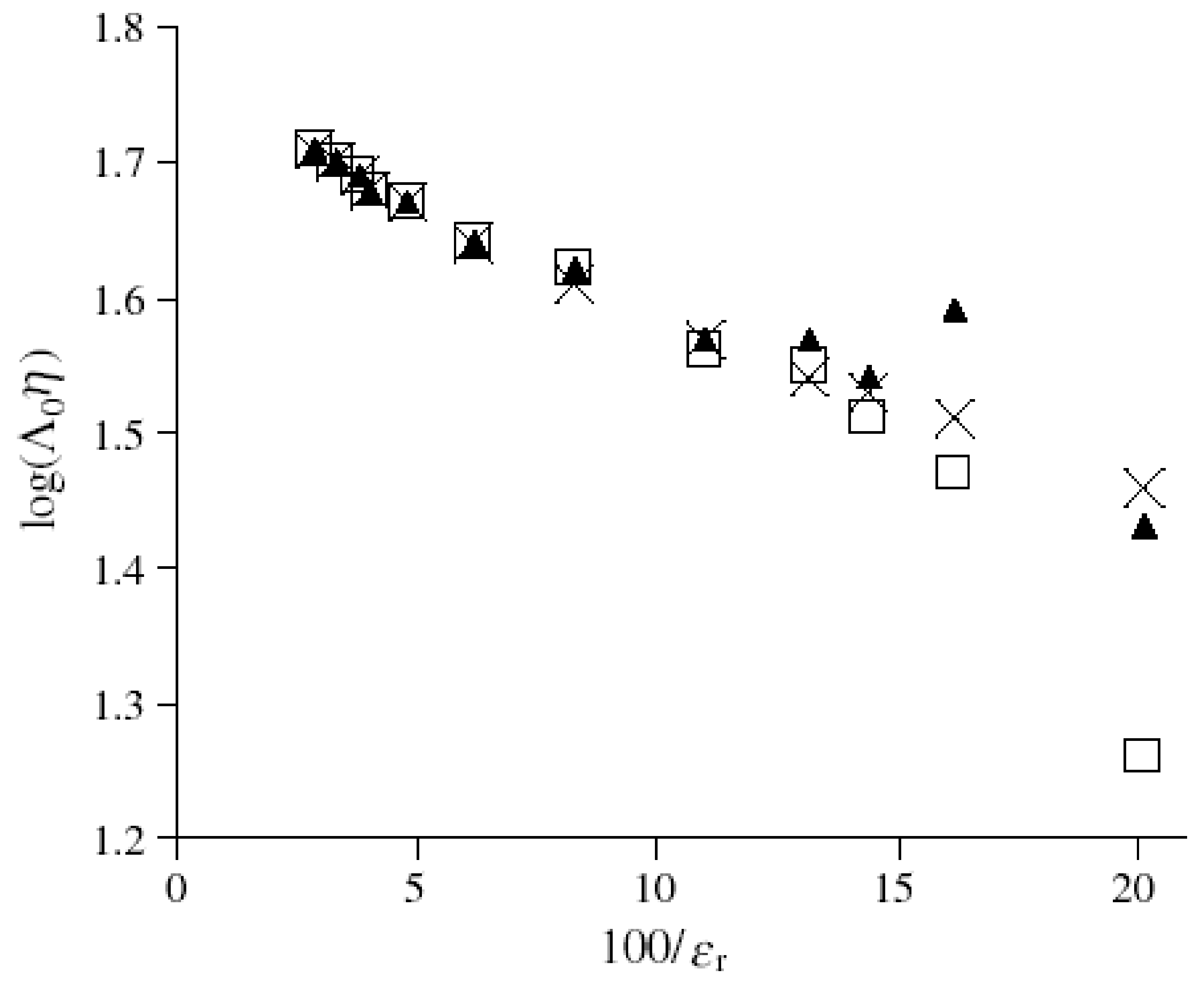
Deviations from the Walden rule

Shkodin – Mezhenny equation:

$$\Lambda_0 \eta = A e^{-B / \varepsilon_r}$$

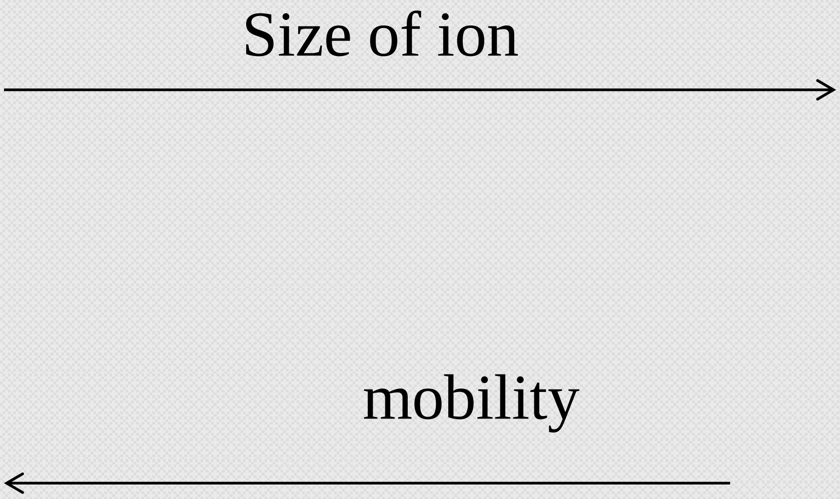


Tetra-*n*-butylammonium picrate in binary mixtures of acetone with *n*-butylacetate and *n*-hexane (I.N. Palval, A.V. Lebed, N.O. Mchedlov-Petrossyan. J. Mol. Liquids. 2011. V. 158. No. 1. P. 33-37).

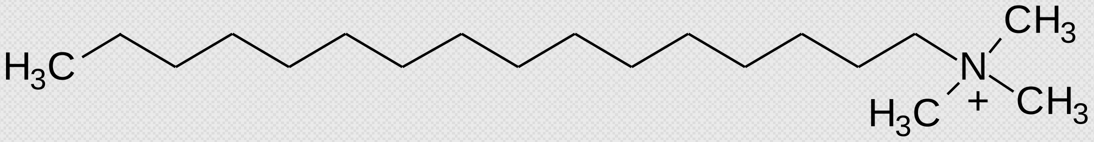


Tetra-*n*-butylammonium picrate in nitrobenzene-tetrachloromethane solvent (Fuoss and Hirsch, 1960.)

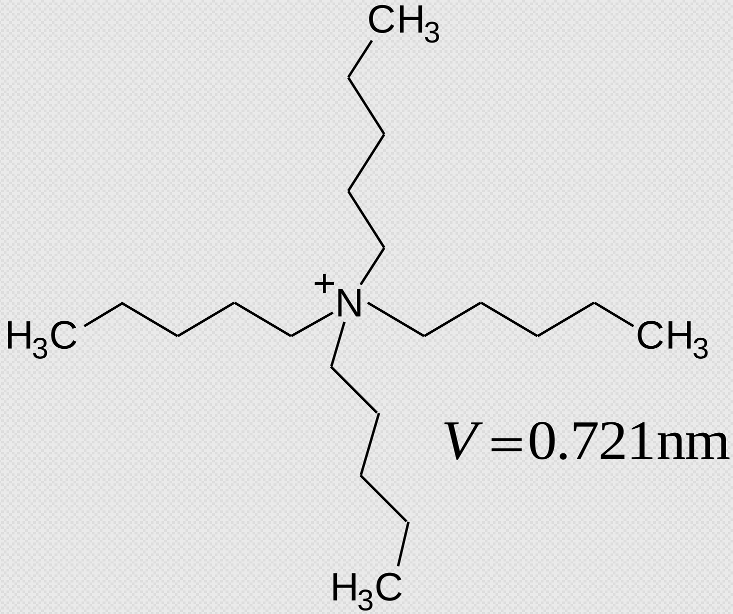
Relation between the ion mobility with size



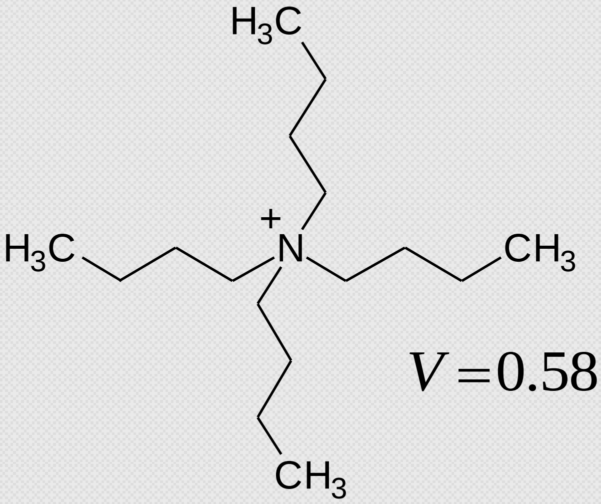
(in the absence of specific solvation)



$V = 0.687\,\mathrm{nm}^3$

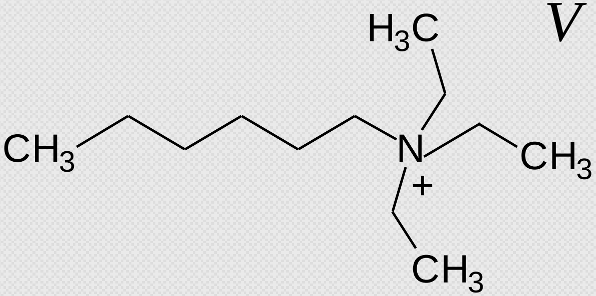


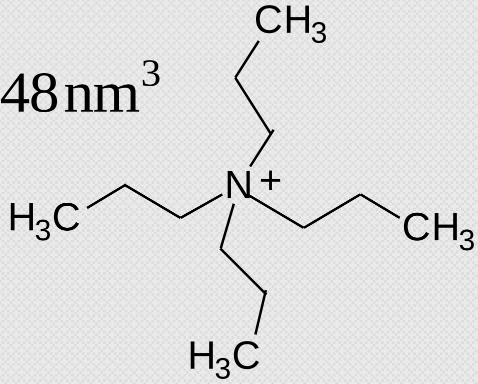
$V = 0.721\,\mathrm{nm}^3$



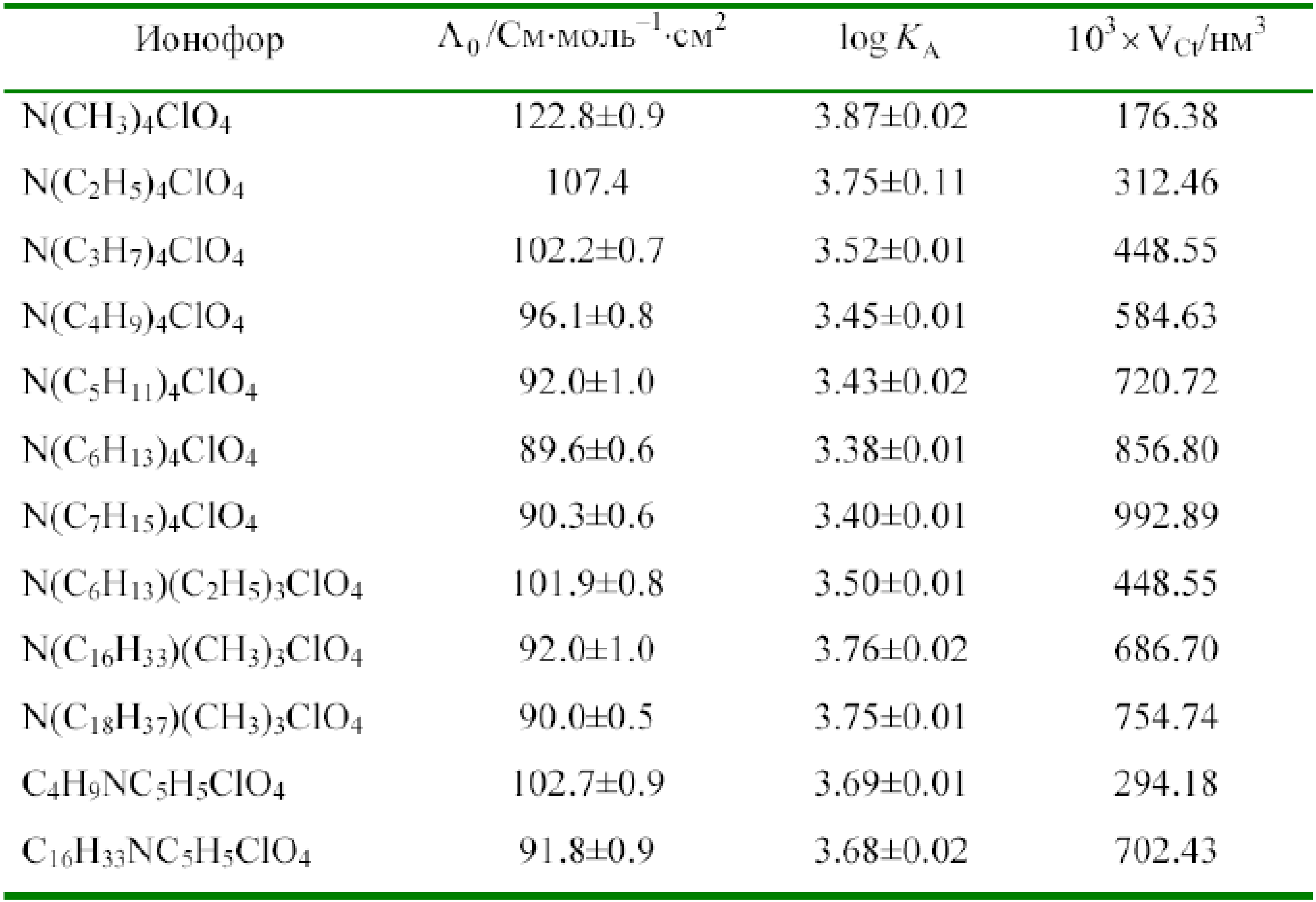
$V = 0.585\,\mathrm{nm}^3$

$V = 0.448\,\mathrm{nm}^3$





Tetraalkylammonium perchlorates in methyl *iso*-butylketone; 25 ^{0}C



Ионофор	Λ_0 /См·моль$^{-1}$·см^2	log K_A	$10^3 \times V_{Ct}$/нм^3
$N(CH_3)_4ClO_4$	122.8±0.9	3.87±0.02	176.38
$N(C_2H_5)_4ClO_4$	107.4	3.75±0.11	312.46
$N(C_3H_7)_4ClO_4$	102.2±0.7	3.52±0.01	448.55
$N(C_4H_9)_4ClO_4$	96.1±0.8	3.45±0.01	584.63
$N(C_5H_{11})_4ClO_4$	92.0±1.0	3.43±0.02	720.72
$N(C_6H_{13})_4ClO_4$	89.6±0.6	3.38±0.01	856.80
$N(C_7H_{15})_4ClO_4$	90.3±0.6	3.40±0.01	992.89
$N(C_6H_{13})(C_2H_5)_3ClO_4$	101.9±0.8	3.50±0.01	448.55
$N(C_{16}H_{33})(CH_3)_3ClO_4$	92.0±1.0	3.76±0.02	686.70
$N(C_{18}H_{37})(CH_3)_3ClO_4$	90.0±0.5	3.75±0.01	754.74
$C_4H_9NC_5H_5ClO_4$	102.7±0.9	3.69±0.01	294.18
$C_{16}H_{33}NC_5H_5ClO_4$	91.8±0.9	3.68±0.02	702.43

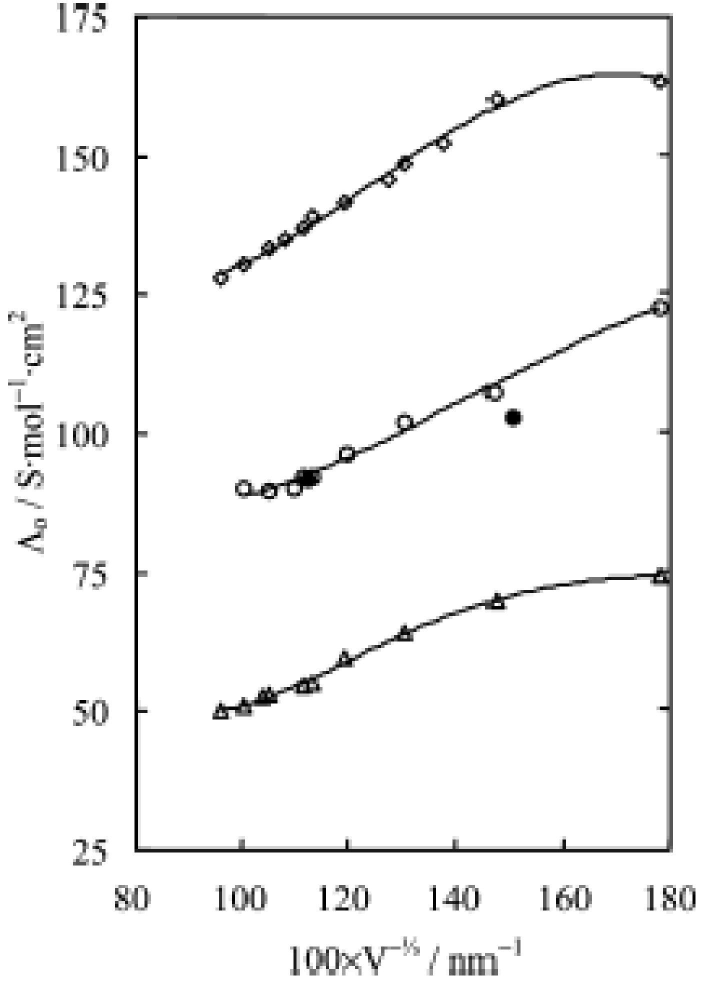
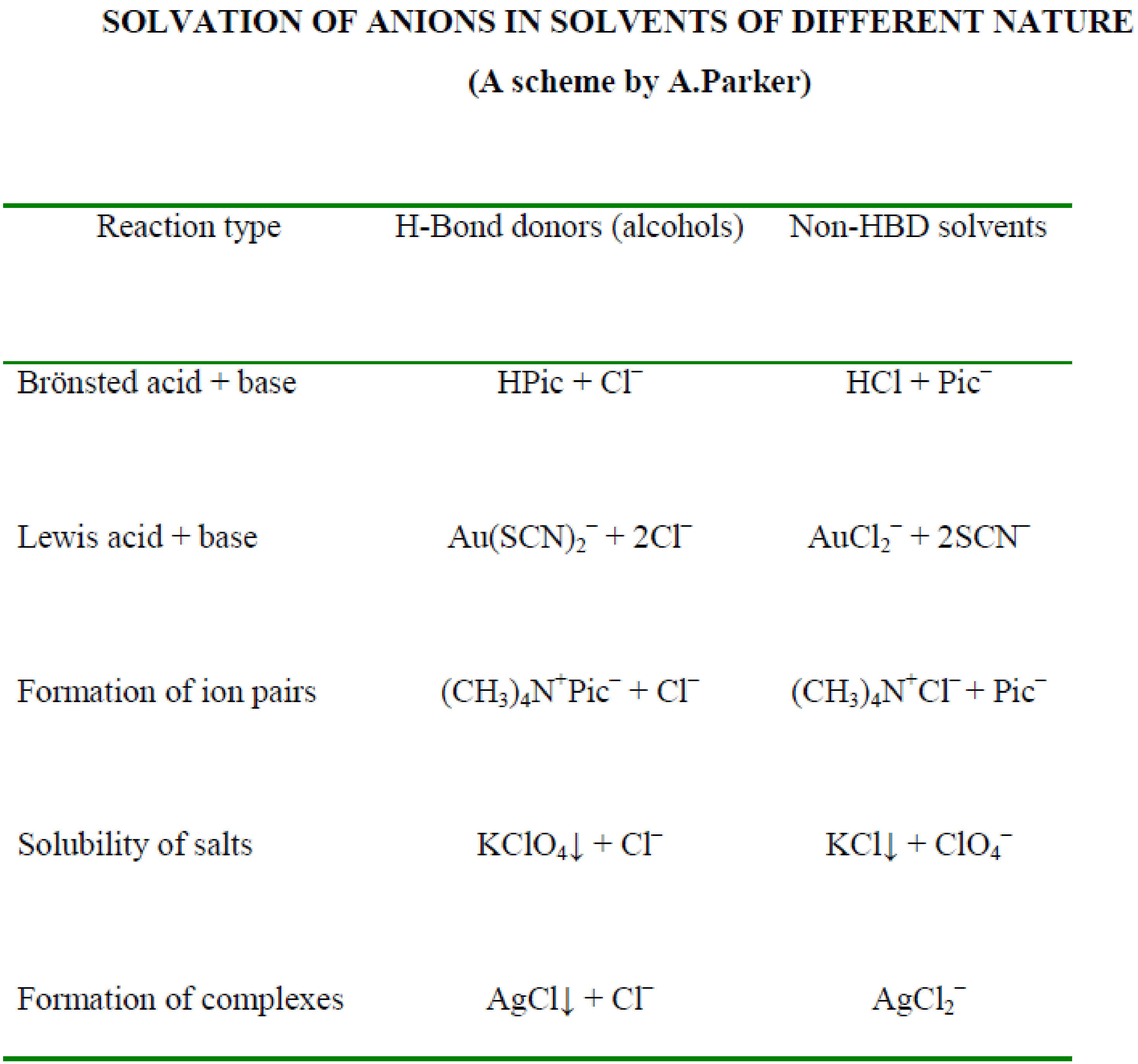


Figure 2. Dependence of the limiting molar conductivities of the quaternary ammonium salts on the reciprocal cube root of the total van der Waals volume of the cations: ◇, tetraalkylammonium iodides in methyl ethyl ketone,[24] ○, TAA$^+$ perchlorates in MIBK; ●, pyridinium perchlorates in MIBK; △, TAA$^+$ picrates in 1,2-dichloroethane (Λ_0 values from ref 29). These data[29] refer both to symmetrical TAA$^+$ ions (up to n = 8) and to trioctylmethylammonium and hexadecyltrimethylammonium ions.



SOLVATION OF ANIONS IN SOLVENTS OF DIFFERENT NATURE

(A scheme by A.Parker)

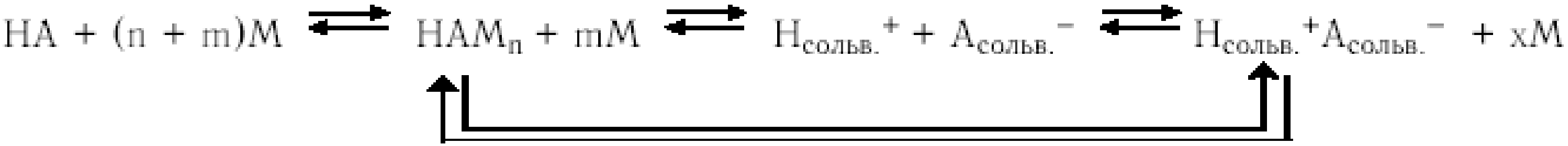
Reaction type	H-Bond donors (alcohols)	Non-HBD solvents
Brönsted acid + base	$HPic + Cl^-$	$HCl + Pic^-$
Lewis acid + base	$Au(SCN)_2^- + 2Cl^-$	$AuCl_2^- + 2SCN^-$
Formation of ion pairs	$(CH_3)_4N^+Pic^- + Cl^-$	$(CH_3)_4N^+Cl^- + Pic^-$
Solubility of salts	$KClO_4\downarrow + Cl^-$	$KCl\downarrow + ClO_4^-$
Formation of complexes	$AgCl\downarrow + Cl^-$	$AgCl_2^-$

PROTOLYTIC EQUILIBRIA

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

$$K_\mathrm{a} = \frac{a_{\mathrm{H}^+} a_{\mathrm{A}^-}}{a_{\mathrm{HA}}}; \quad \mathrm{p}K_\mathrm{a} \equiv -\log K_\mathrm{a}$$

General dissociation scheme of acids according to Izmailov



$$HA + (n + m)M \rightleftarrows HAM_n + mM \rightleftarrows H_{сольв.}^{+} + A_{сольв.}^{-} \rightleftarrows H_{сольв.}^{+}A_{сольв.}^{-} + xM$$

Autoionization

In the simplest case:

$2HL \rightleftharpoons H_2L^+ + L^-;$ $\qquad K_s = a_{H_2L^+} a_{L^-}$

Examples:

Alcohols: $2ROH \rightleftharpoons ROH_2^+ + RO^-$

Ammonia: $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

DMSO: $2(CH_3)_2SO \rightleftharpoons (CH_3)_2SOH^+ + CH_3SOCH_2^-$.

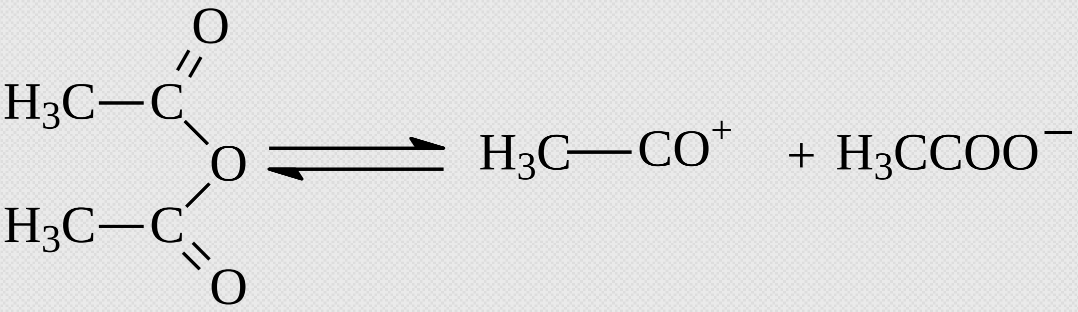
Acetic acid: $2CH_3COOH \rightleftharpoons CH_3COOH_2^+ + CH_3COO^-$

Sometimes the reactions are more complicated:

$$2HCOOH \rightleftharpoons HCOOH_2^+ + HCOO^-$$

$$HCOOH_2^+ \rightarrow CO + H_3O^+$$

Acetic anhydride: two possible mechanisms



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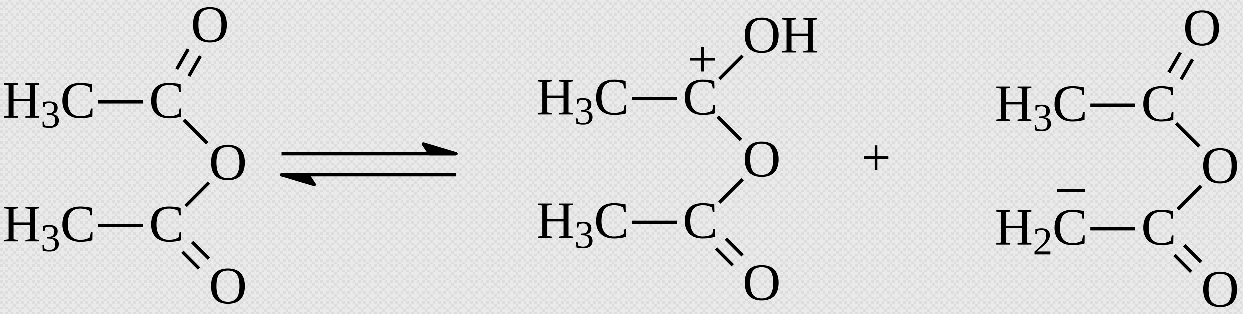
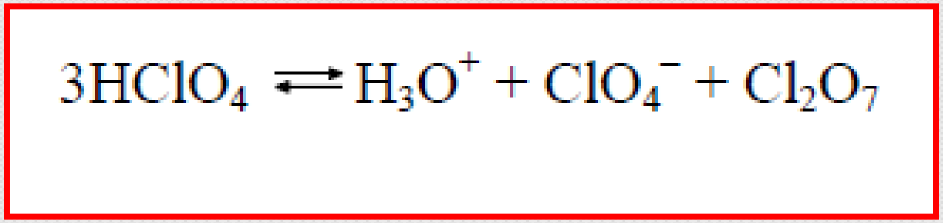
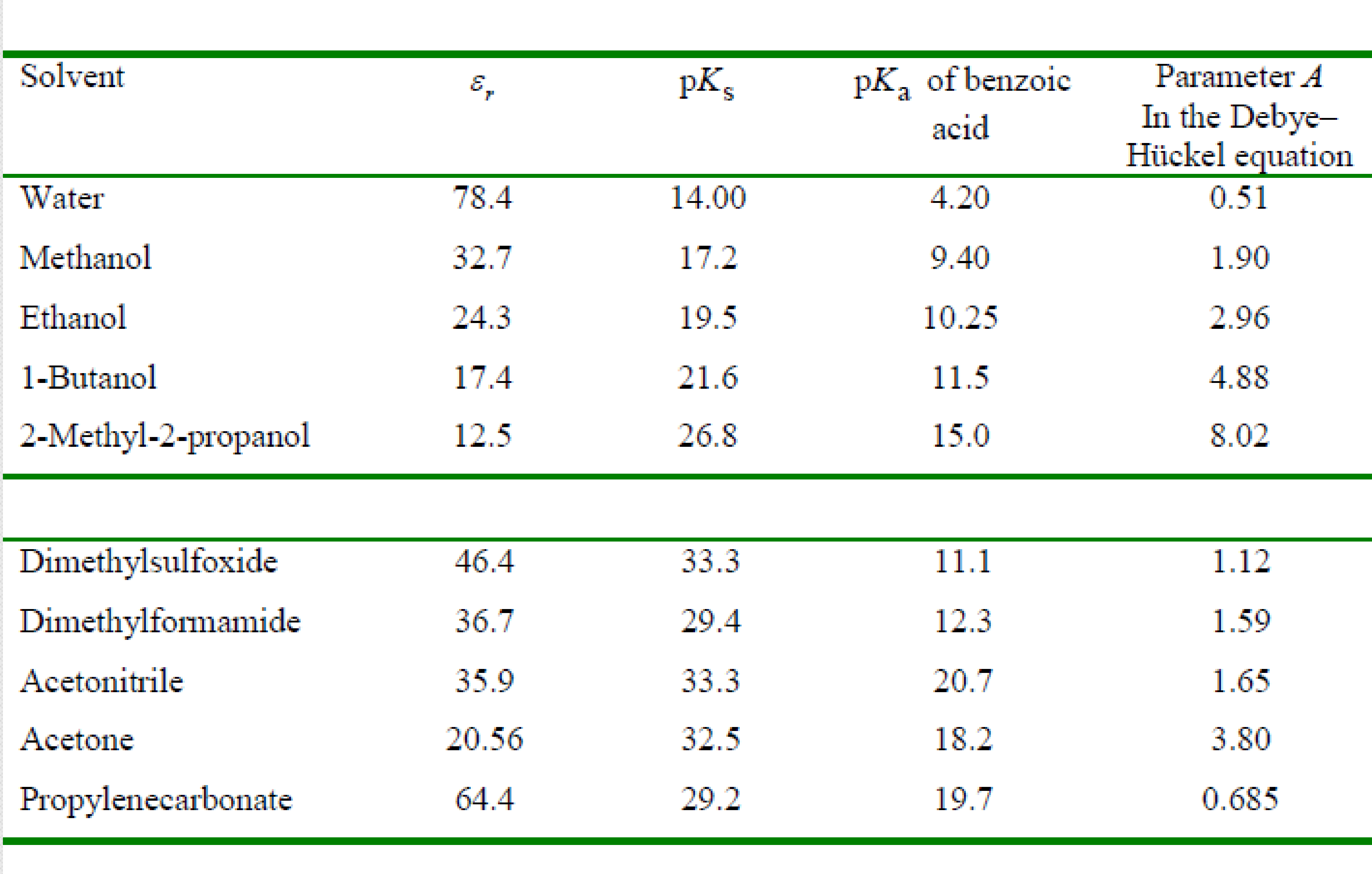


Perchloric acid:



$3HClO_4 \rightleftharpoons H_3O^+ + ClO_4^- + Cl_2O_7$

Important parameters of solvents



Solvent	ε_r	pK_s	pK_a of benzoic acid	Parameter A In the Debye–Hückel equation
Water	78.4	14.00	4.20	0.51
Methanol	32.7	17.2	9.40	1.90
Ethanol	24.3	19.5	10.25	2.96
1-Butanol	17.4	21.6	11.5	4.88
2-Methyl-2-propanol	12.5	26.8	15.0	8.02
Dimethylsulfoxide	46.4	33.3	11.1	1.12
Dimethylformamide	36.7	29.4	12.3	1.59
Acetonitrile	35.9	33.3	20.7	1.65
Acetone	20.56	32.5	18.2	3.80
Propylenecarbonate	64.4	29.2	19.7	0.685

Lyonium and lyate ions

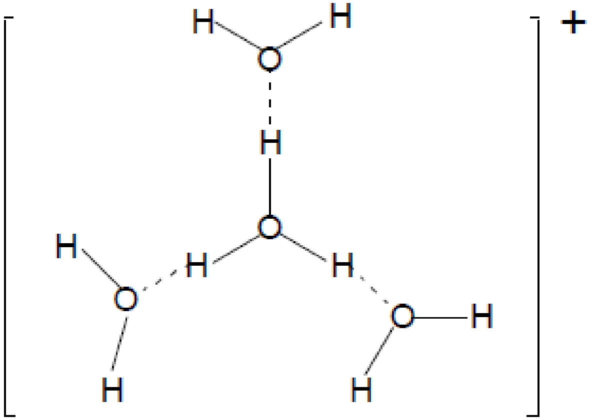
The proton is ca. 10 000 times smaller than other ions

In water first of all: H_3O^+

According to Zundel: $H_5O_2^+$ ($H_2O \cdots {}^+H_3O$, or $H_2O \cdots {}^+H \cdots OH_2$)

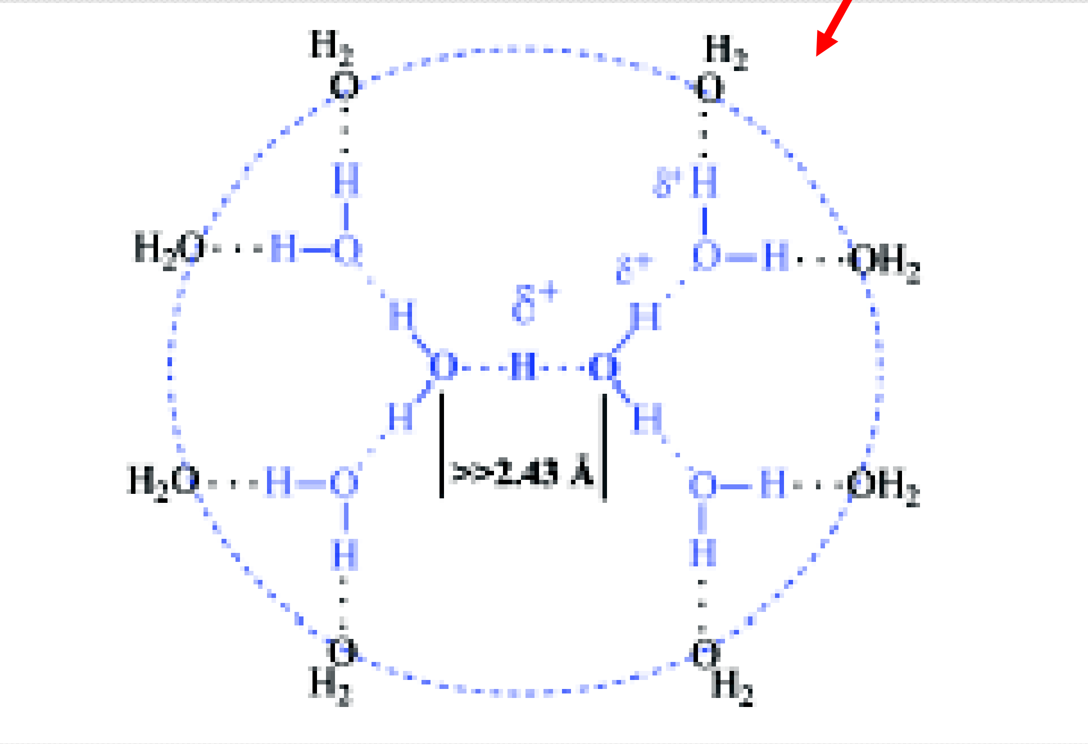
and instead of HO^- : $H_3O_2^-$

Eigen: $H_9O_4^+$



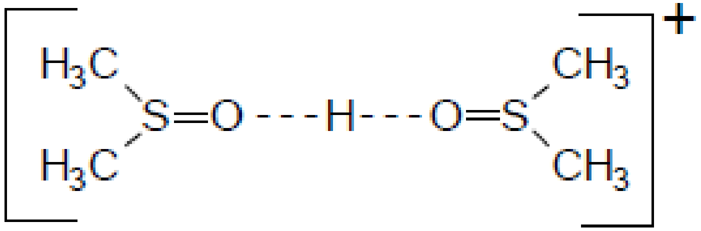
Wells: $H_{11}O_5^+$

Based on the analysis of the IR spectra of carborane acids and perchloric acid, at concentrations from 0.176 to 0.75 M, the structure $H(H_2O)_6^+$ was proposed as the most probable:

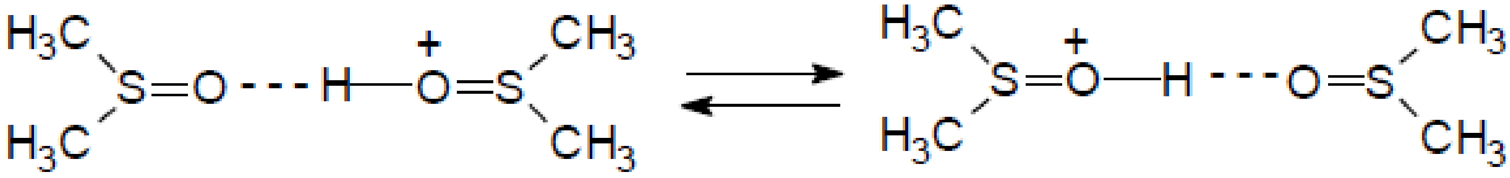


E.S. Stoyanov, I.V. Stoyanova, C.A. Reed JACS 2010. V. 132. P. 1484.

In organic solvents, the stoichiometry also can be complicated. For example, in DMSO the ion $H(DMSO)_2^+$ is considered as lyonium ion:



Or, more correct:



Autoionization in inorganic aprotic solvents:

$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$

(V. Gutmann)

$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$

(Boiling temp. 21.3 °C , $\varepsilon_r = 2.42$ at 18 °C, $\mathrm{p}K_s \approx 25$

Proton exchange between two solvents: in fact, a chemical reaction

$$H_3O^+ + CH_3OH \rightleftharpoons CH_3OH_2^+ + H_2O$$

$$H_3O^+ + (CH_3)_2SO \rightleftharpoons (CH_3)_2SOH^+ + H_2O$$

Such reactions determine the interfering water influence in organic solvents.

In methanol and ethanol, admixture of **water about 0.1 %** leads to the presence of a **substantial fraction of hydrated protons**.

In acetonitrile as solvent, **DMSO is 2 000 times more basic than water**.

In protophobic solvents, water traces are much less desirable.

In acetonitrile at water content of 1 M, the proton state is from H_3O^+ to $H(H_2O)_4^+$ (Kolthoff, 1968-1971)

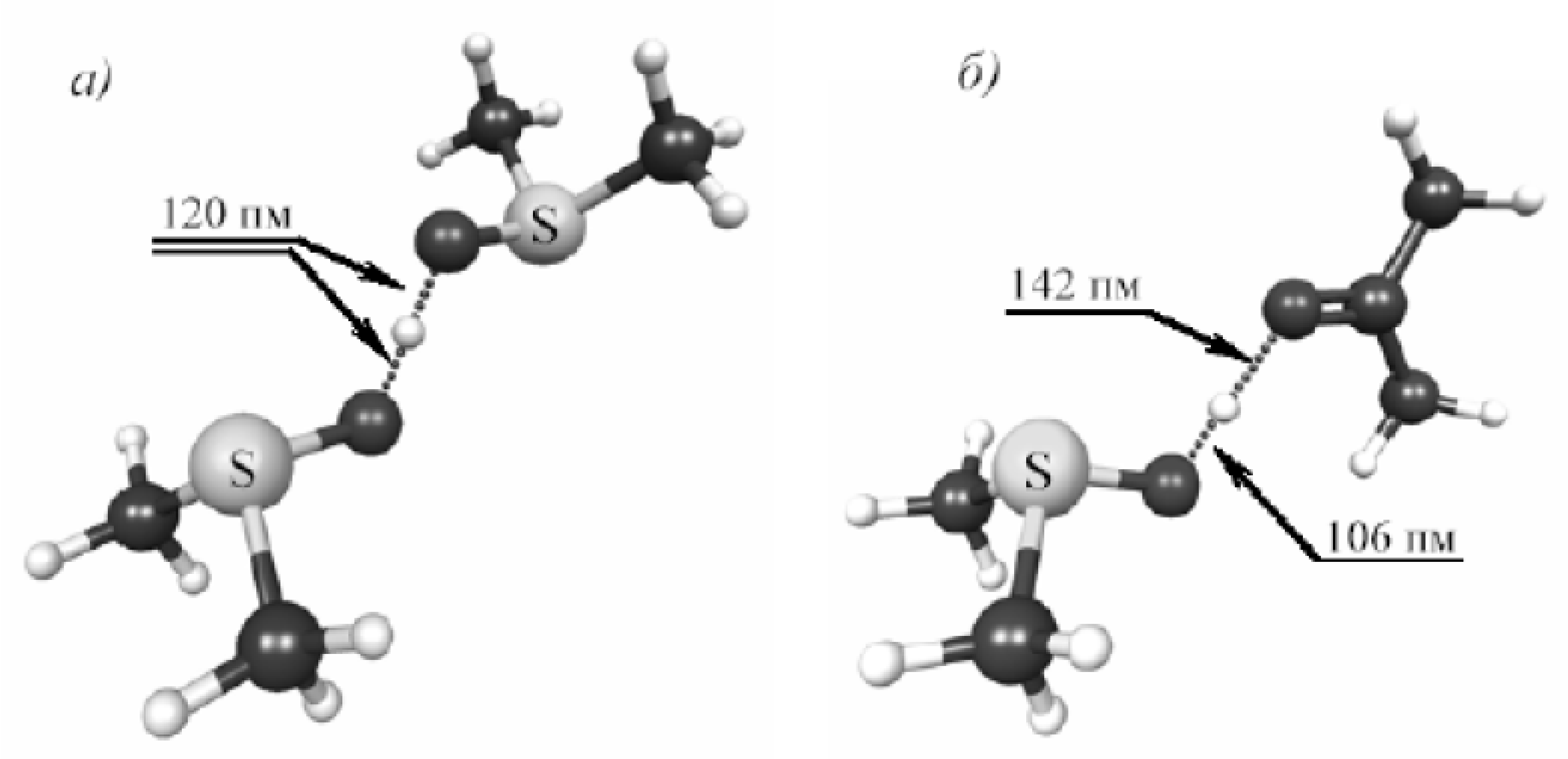
In 0.001 M solution of $HClO_4$ in acetonitrile at 0.0024 M H_2O the $H_3O^+ : H(CH_3CN)_n = 1:5$ (Coetzee, 1963).

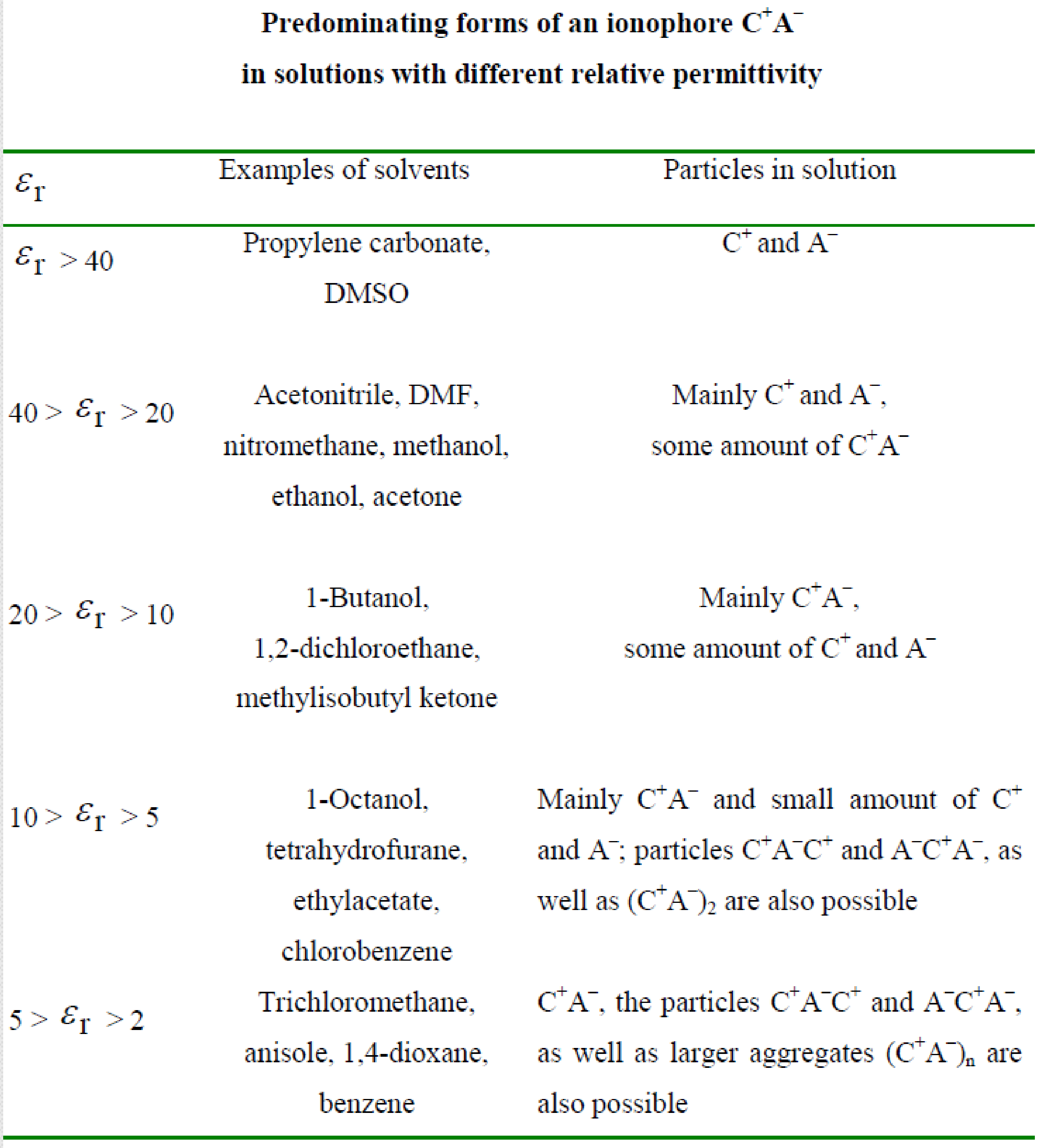
More surprising effects (e.g., in propylene carbonate):

$$FSO_3H + H_2O \rightleftharpoons HF + H_2SO_4$$

Titration shows three moles of acid instead of one!

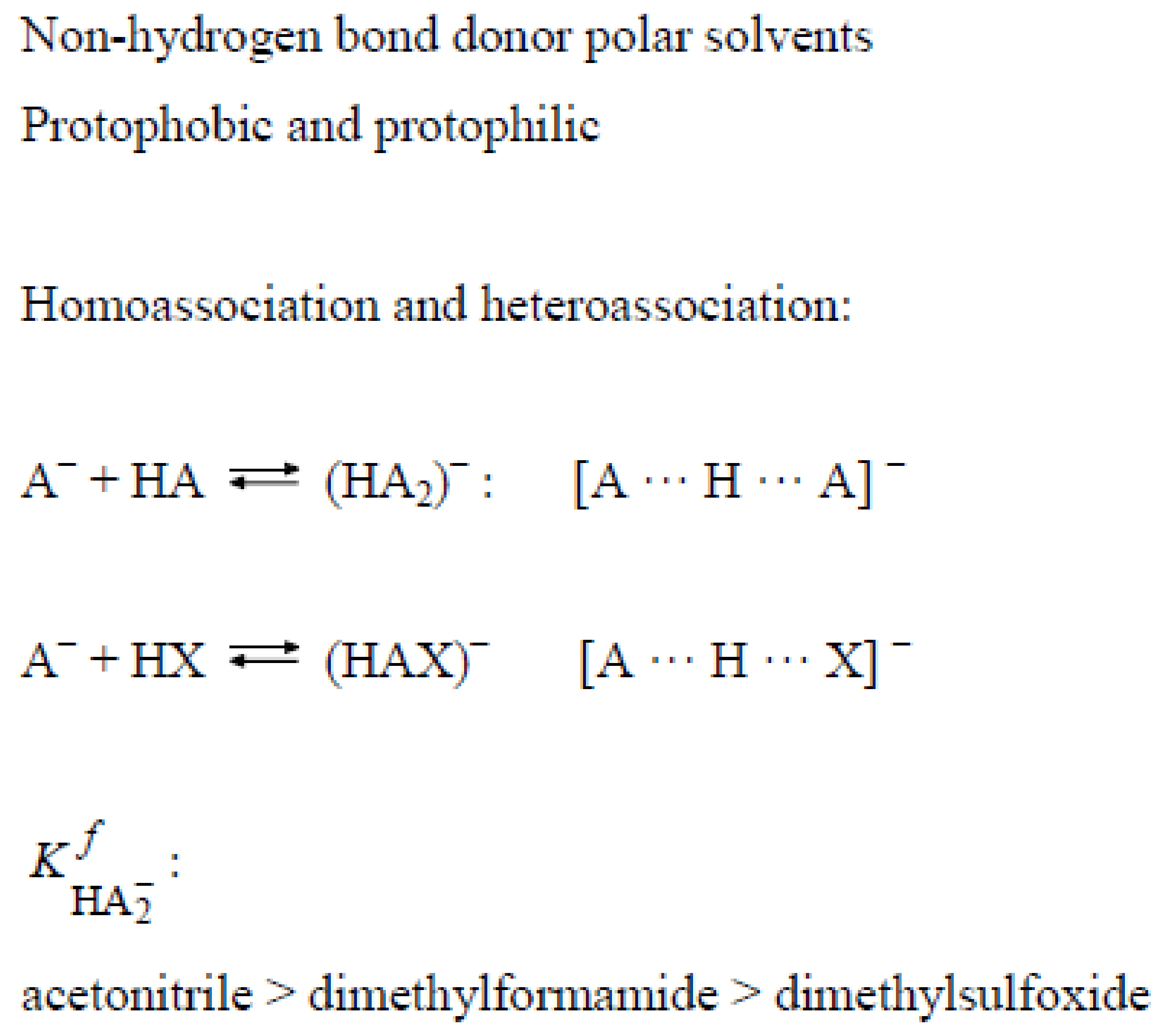
Relative basicity of organic solvents: DMSO vs. acetone





Predominating forms of an ionophore C^+A^- in solutions with different relative permittivity

ε_r	Examples of solvents	Particles in solution
$\varepsilon_r > 40$	Propylene carbonate, DMSO	C^+ and A^-
$40 > \varepsilon_r > 20$	Acetonitrile, DMF, nitromethane, methanol, ethanol, acetone	Mainly C^+ and A^-, some amount of C^+A^-
$20 > \varepsilon_r > 10$	1-Butanol, 1,2-dichloroethane, methylisobutyl ketone	Mainly C^+A^-, some amount of C^+ and A^-
$10 > \varepsilon_r > 5$	1-Octanol, tetrahydrofurane, ethylacetate, chlorobenzene	Mainly C^+A^- and small amount of C^+ and A^-; particles $C^+A^-C^+$ and $A^-C^+A^-$, as well as $(C^+A^-)_2$ are also possible
$5 > \varepsilon_r > 2$	Trichloromethane, anisole, 1,4-dioxane, benzene	C^+A^-, the particles $C^+A^-C^+$ and $A^-C^+A^-$, as well as larger aggregates $(C^+A^-)_n$ are also possible



Non-hydrogen bond donor polar solvents

Protophobic and protophilic

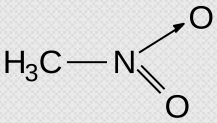
Homoassociation and heteroassociation:

$$A^- + HA \rightleftharpoons (HA_2)^- : \qquad [A \cdots H \cdots A]^-$$

$$A^- + HX \rightleftharpoons (HAX)^- \qquad [A \cdots H \cdots X]^-$$

$K^f_{HA_2^-}$:

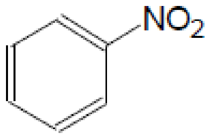
acetonitrile > dimethylformamide > dimethylsulfoxide



Nitromethane

H_3C-NO_2

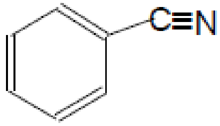
Nitrobenzene



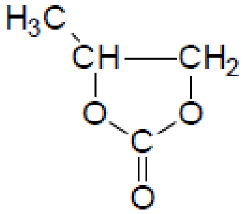
Acetonitrile

$H_3C-C\equiv N$

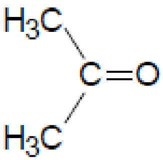
Benzonitrile



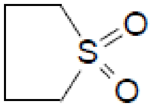
Propylenecarbonate (4-methyl-1,3-dioxolane-2-one)



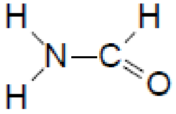
Acetone



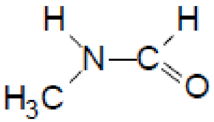
Sulfolane



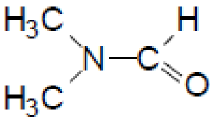
Formamide



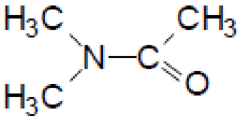
N-Methylformamide



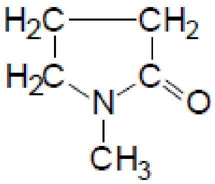
N,N-Dimethylformamide



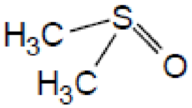
N,N-Dimethylacetamide



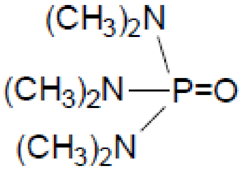
N-Methylpyrrolidone

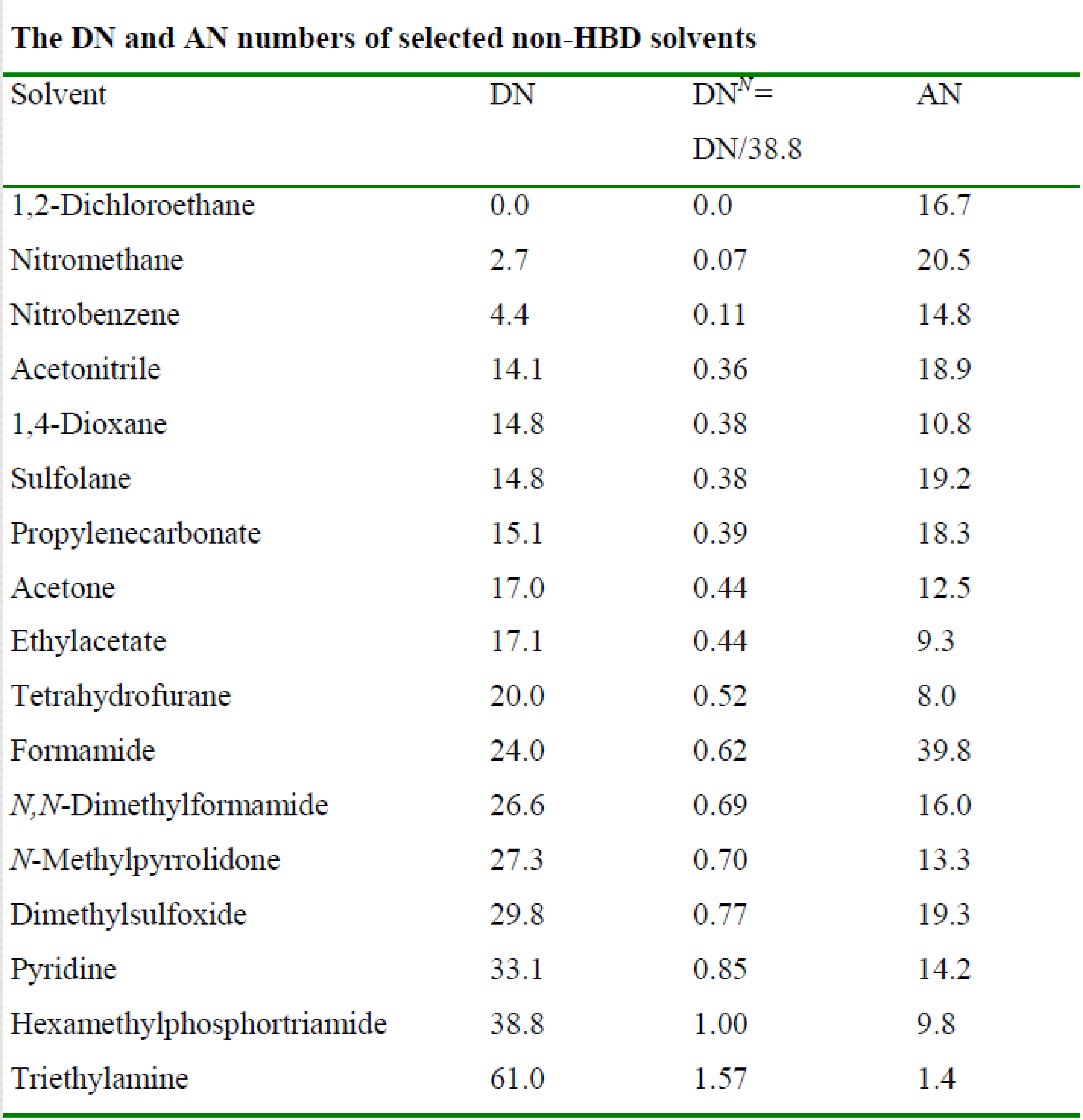


Dimethylsulfoxide



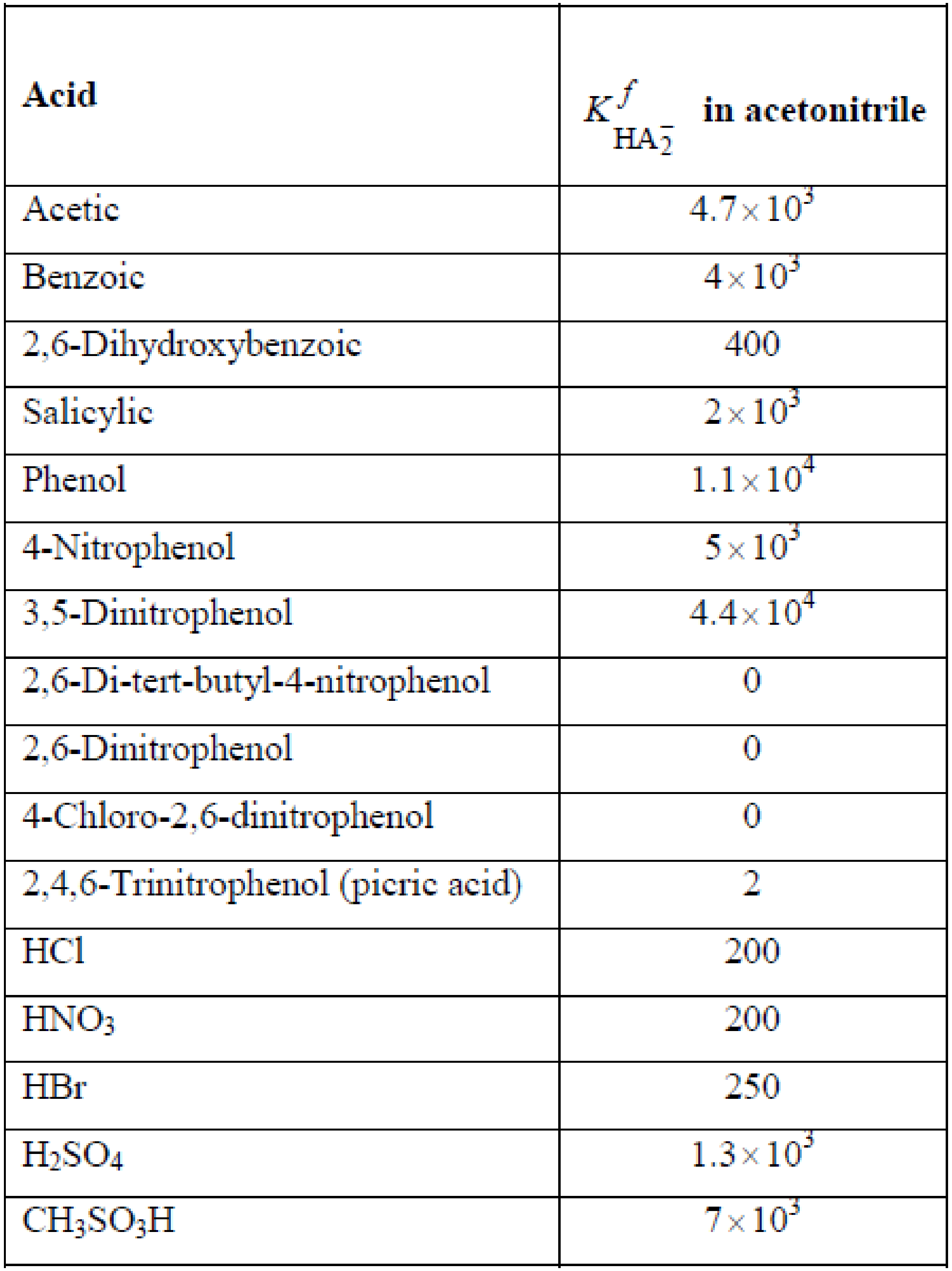
Hexamethylphosphortriamide



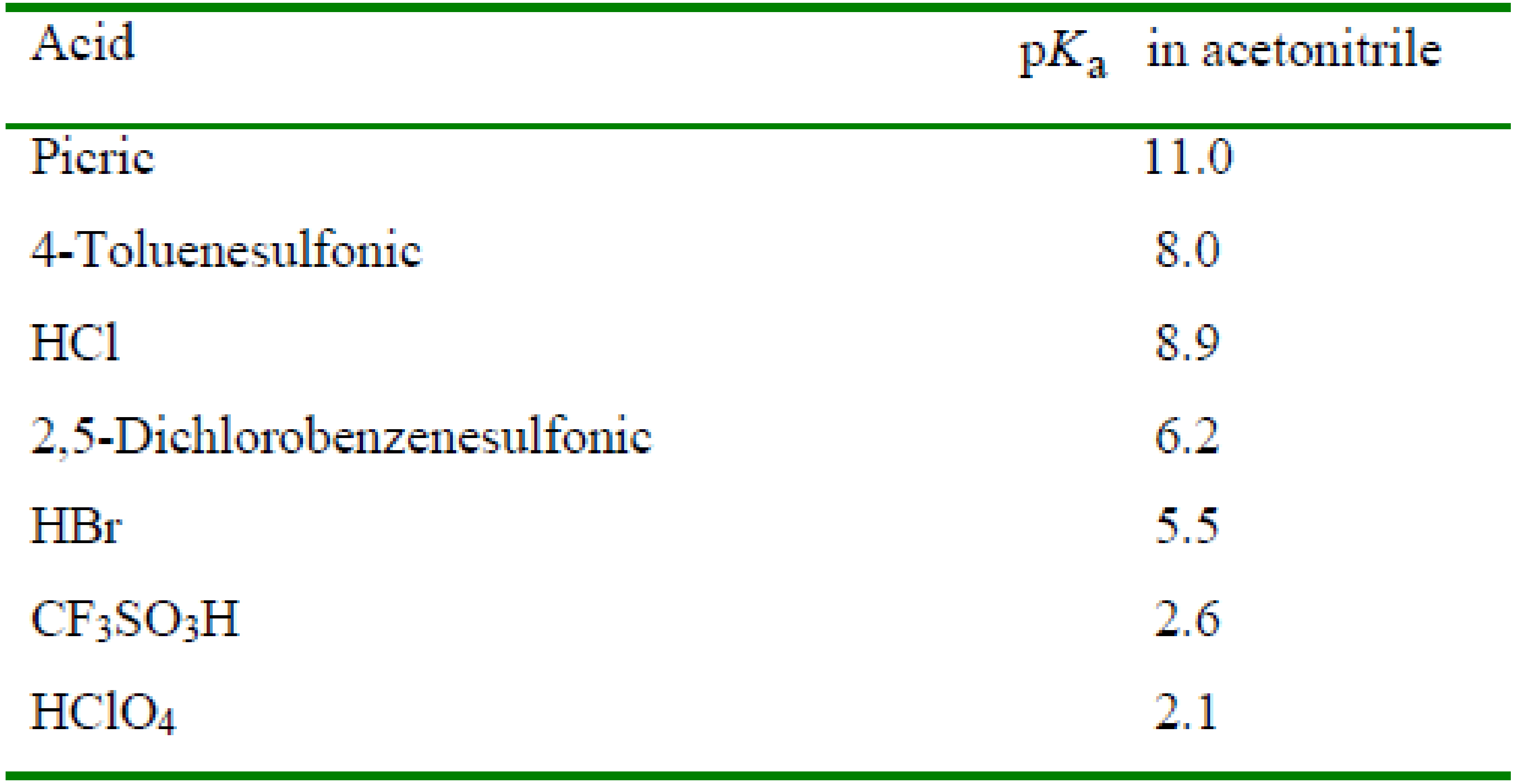


The DN and AN numbers of selected non-HBD solvents

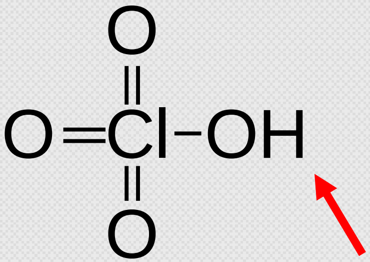
Solvent	DN	DN^{N}= DN/38.8	AN
1,2-Dichloroethane	0.0	0.0	16.7
Nitromethane	2.7	0.07	20.5
Nitrobenzene	4.4	0.11	14.8
Acetonitrile	14.1	0.36	18.9
1,4-Dioxane	14.8	0.38	10.8
Sulfolane	14.8	0.38	19.2
Propylenecarbonate	15.1	0.39	18.3
Acetone	17.0	0.44	12.5
Ethylacetate	17.1	0.44	9.3
Tetrahydrofurane	20.0	0.52	8.0
Formamide	24.0	0.62	39.8
N,*N*-Dimethylformamide	26.6	0.69	16.0
N-Methylpyrrolidone	27.3	0.70	13.3
Dimethylsulfoxide	29.8	0.77	19.3
Pyridine	33.1	0.85	14.2
Hexamethylphosphortriamide	38.8	1.00	9.8
Triethylamine	61.0	1.57	1.4



Acid	$K^{f}_{HA_2^-}$ **in acetonitrile**
Acetic	4.7×10^{3}
Benzoic	4×10^{3}
2,6-Dihydroxybenzoic	400
Salicylic	2×10^{3}
Phenol	1.1×10^{4}
4-Nitrophenol	5×10^{3}
3,5-Dinitrophenol	4.4×10^{4}
2,6-Di-tert-butyl-4-nitrophenol	0
2,6-Dinitrophenol	0
4-Chloro-2,6-dinitrophenol	0
2,4,6-Trinitrophenol (picric acid)	2
HCl	200
HNO_3	200
HBr	250
H_2SO_4	1.3×10^{3}
CH_3SO_3H	7×10^{3}

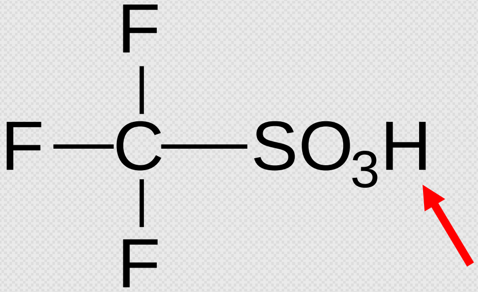


Acid	pK_a in acetonitrile
Picric	11.0
4-Toluenesulfonic	8.0
HCl	8.9
2,5-Dichlorobenzenesulfonic	6.2
HBr	5.5
CF_3SO_3H	2.6
$HClO_4$	2.1

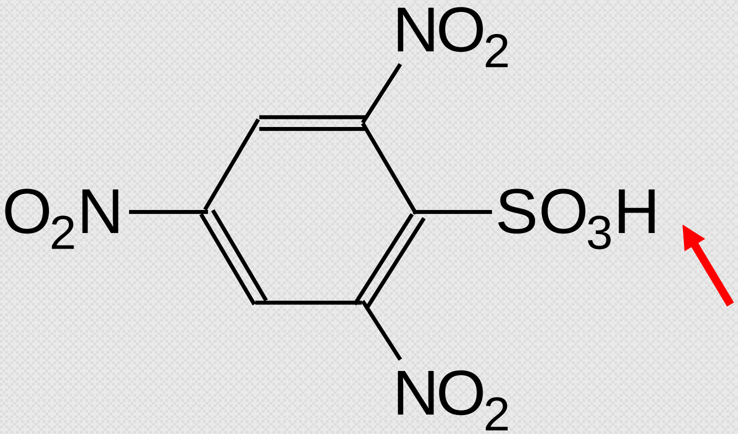


$HClO_4$

$F-SO_3H$

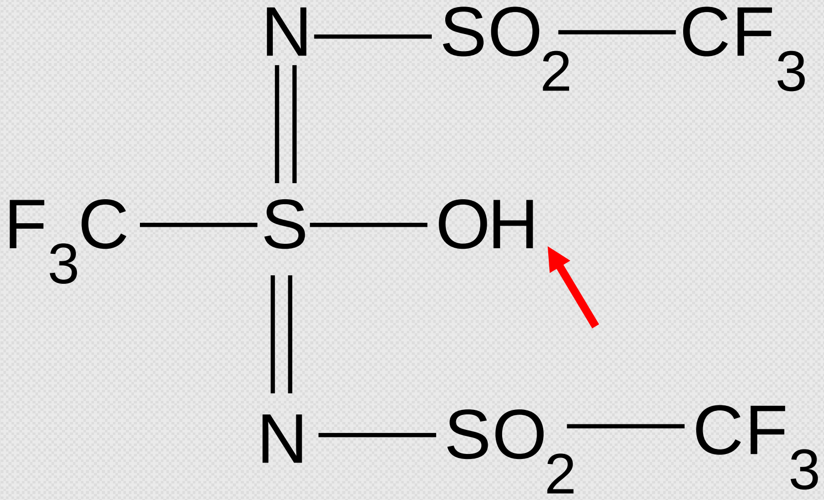


CF_3SO_3H



Strong acids;
«superacids»

«The strongest acid
(Л. М. Ягупольский и сотр.,
1986, 1988, 2001) →



Carborane acid

Also «the strongest ones»:

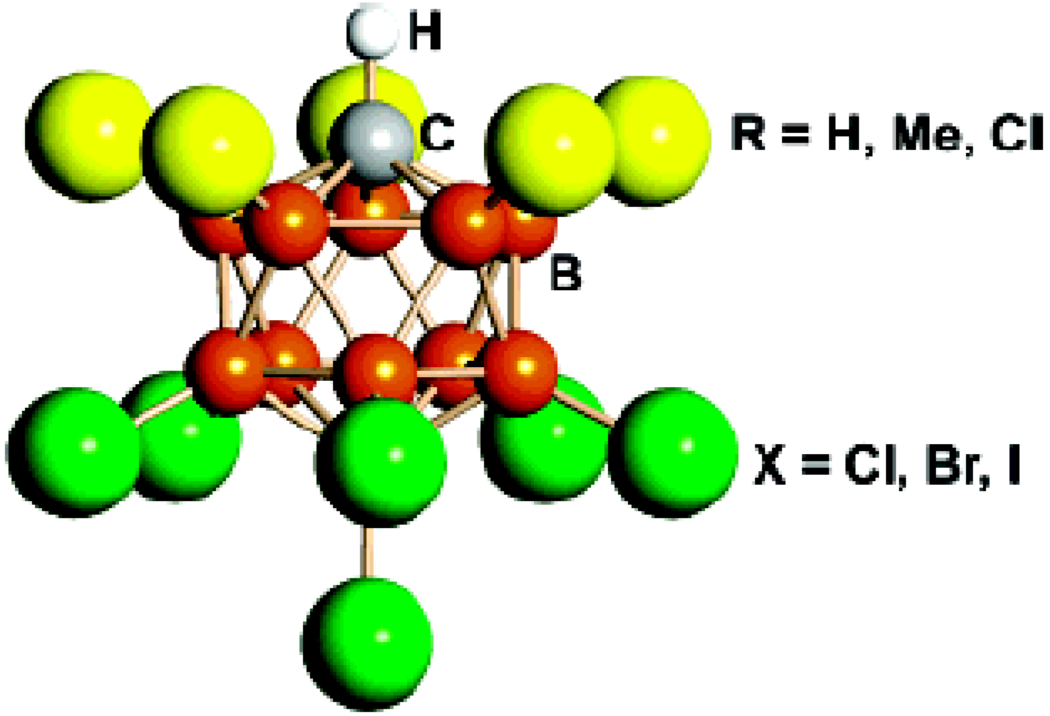
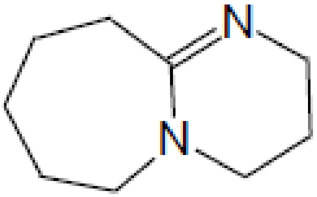


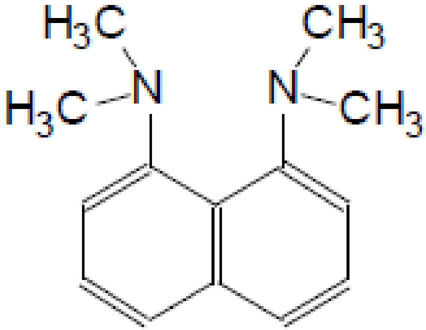
Figure 1. Icosahedral carborane anions of the type $CB_{11}R_5X_6^-$, used in this work (abbreviated $\{R_5X_6\}^-$).

C. A. Reed et al., Angew. Chem. 2004, 2009.

Bases used in non-HBD solvents

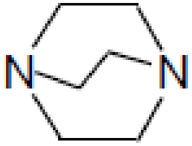


1,8-Diaza-bicyclo-[5.4.0]-7-undecene (**DBU**)



1,8-Bis-(dimethylamino)naphthalene

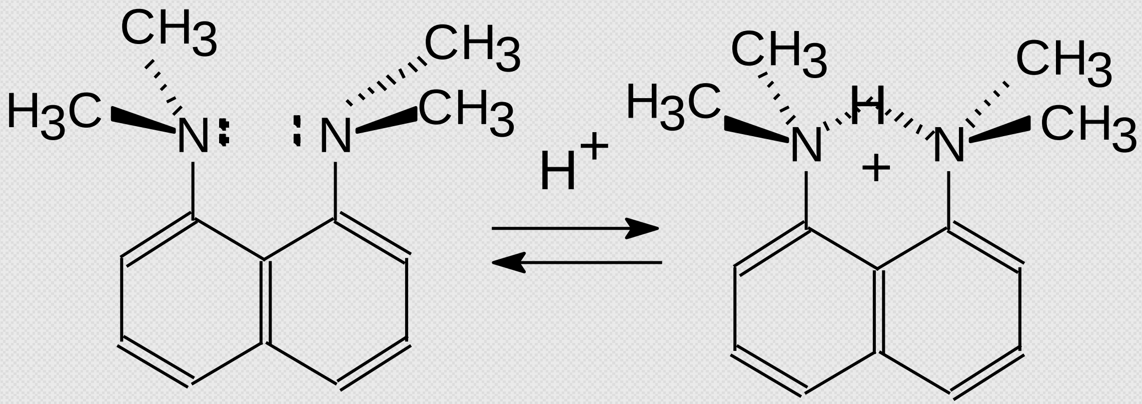
("proton sponge")



1,2-Diazabicyclo[2.2.2]octane

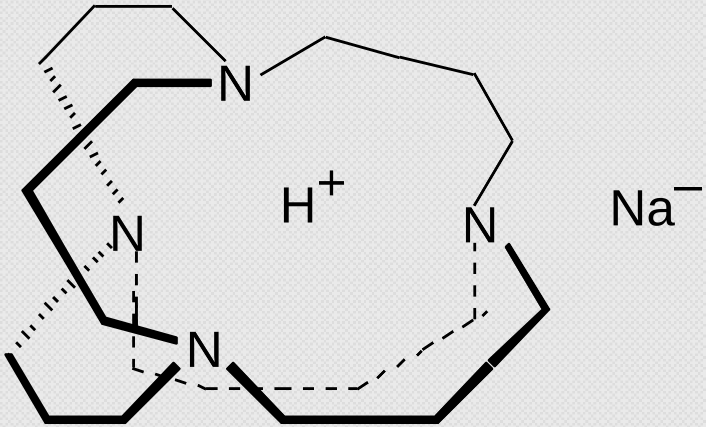
SUPERBASES

«Proton sponge», 1972



R. W. Alder et al., Chem. Comm. 1968. P. 723

А. Ф. Пожарский и др. ХГС. 2012. С. 208–228.
(Обзор по гетероциклическим суперооснованиям)



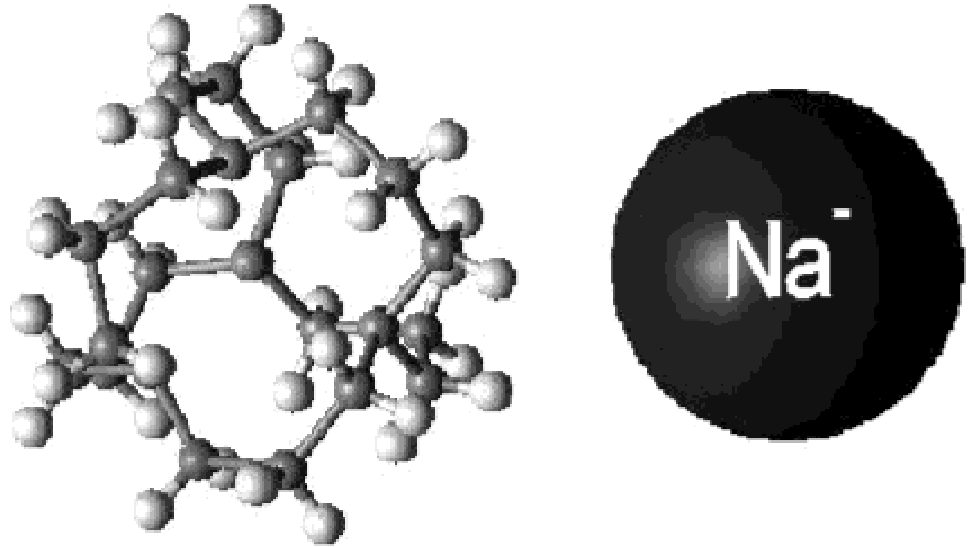


Figure 1. 3^6Adamanzane (from the glycolate structure) compared with the sodium anion.

«Reversed sodium hydride», or hydrogen natride

$$AdzH^+HOCH_2COO^- + 3Na \rightarrow \underline{AdzH^+Na^-} + NaOCH_2CO_2Na\downarrow + {}^1/_2H_2\uparrow$$

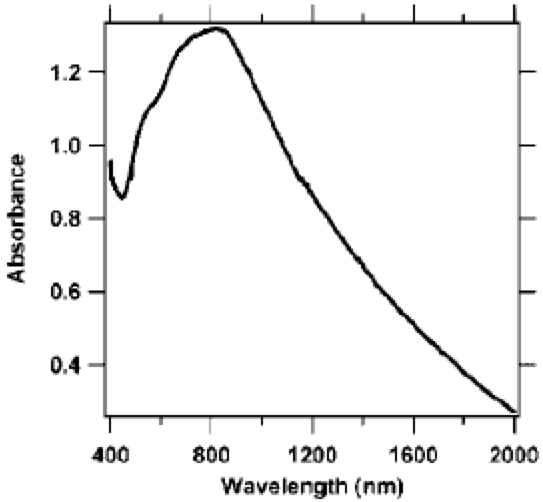


Figure 2. Optical absorption spectrum of a thin film of $AdzH^+Na^-$ produced by rapid evaporation of methylamine from solution.

M. Redko et al.,
JACS. 2002. P. 5928.

Complicated processes in nitromethane as solvent

$$(C_6H_5)_3C{-}Cl \rightleftharpoons (C_6H_5)_3C^+Cl^- \rightleftharpoons (C_6H_5)_3C^+ + Cl^-$$

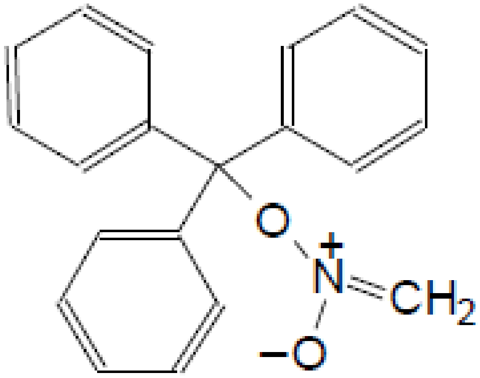
$$Cl^- + CH_3NO_2 \rightleftharpoons HCl + CH_2NO_2^-,$$

$$HCl + Cl^- \rightleftharpoons HCl_2^-$$

$$(C_6H_5)_3C^+ + HCl_2^- \rightleftharpoons (C_6H_5)_3C^+HCl_2^-, \text{ or:}$$

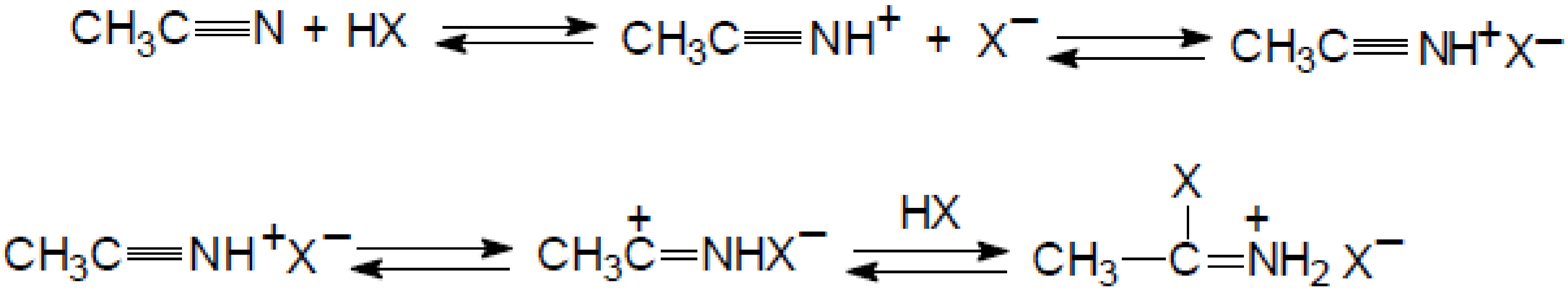
$$(C_6H_5)_3C^+Cl^- + HCl \rightleftharpoons (C_6H_5)_3C^+Cl^- \cdots HCl \rightleftharpoons (C_6H_5)_3C^+HCl_2^-,$$

Formation of an ester is also possible:



The solutions of HCl, HBr, and HI are not stable in acetonitrile;

their conductance increases over time:



$$\mathrm{CH_3C{\equiv}N + HX \rightleftharpoons CH_3C{\equiv}NH^+ + X^- \rightleftharpoons CH_3C{\equiv}NH^+X^-}$$

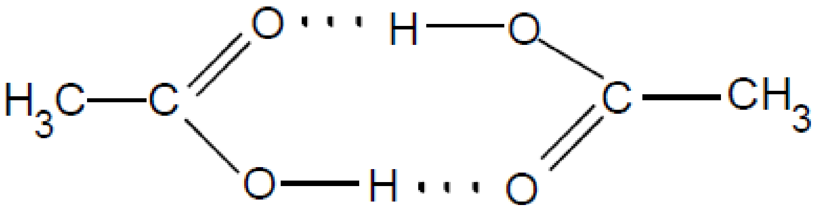
$$\mathrm{CH_3C{\equiv}NH^+X^- \rightleftharpoons CH_3\overset{+}{C}{=}NHX^- \overset{HX}{\rightleftharpoons} CH_3{-}\overset{X}{\overset{|}{C}}{=}\overset{+}{N}H_2\,X^-}$$

PROTOLYTIC EQUILIBRIA IN NON-POLAR SOLVENTS

Acid-base interaction occur as follows:

$$B + HA \rightleftharpoons B \cdots HA \rightleftharpoons BH^{+} \cdots {}^{-}A$$

Main methods of research: IR-, UV-visible spectroscopy, cryoscopy



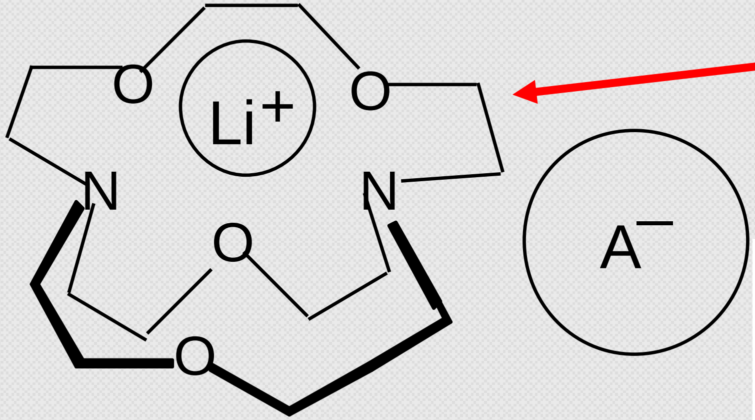
$2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$, in benzene: $K = (1.7–4.0)\times 10^{3}$;

For benzoic and nitric acids in benzene: 2.3×10^{3} and 1.2×10^{3}, respectively.

ACIDITY SCALE IN BENZENE AND OTHER INERT LOW-POLAR SOLVENTS

$$B + HA \rightleftarrows B \cdots HA \rightleftarrows BH^{+} \cdots {}^{-}A$$

$$M^{+}A_0^{-} + HA \rightleftarrows M^{+}A^{-} + HA_0$$

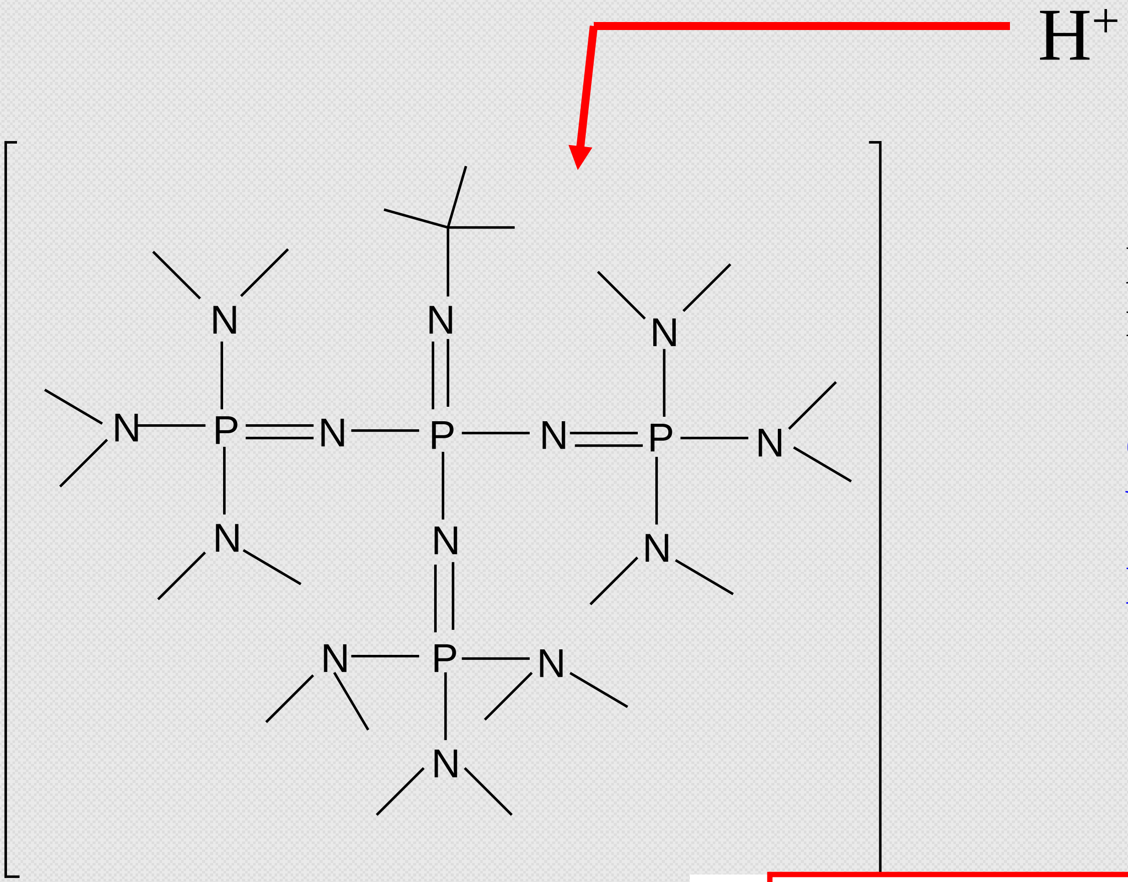


Cryptand [2.1.1]: masking of specific cation-anion interactions

$$[LiL]^{+}A_0^{-} + HA \rightleftarrows [LiL]^{+}A^{-} + HA_0$$

И. С. Антипин, Р. Ф. Гареев, А. Н. Ведерников, А. И. Коновалов, 1985-1994

DELOCALIZATION OF THE POSITIVE CHARGE



Superbases of the phosphazene series – most strong bases

Constraction of the basicity scales in non-polar solvents:

$$HB_1^+A^- + B_2 \rightleftarrows HB_2^+A^- + B_1$$

I. Leito et al. 1997-2006

IONIC EQUILIBRIUM IN GLACIAL ACETIC ACID

$$\varepsilon_r = 6.17$$

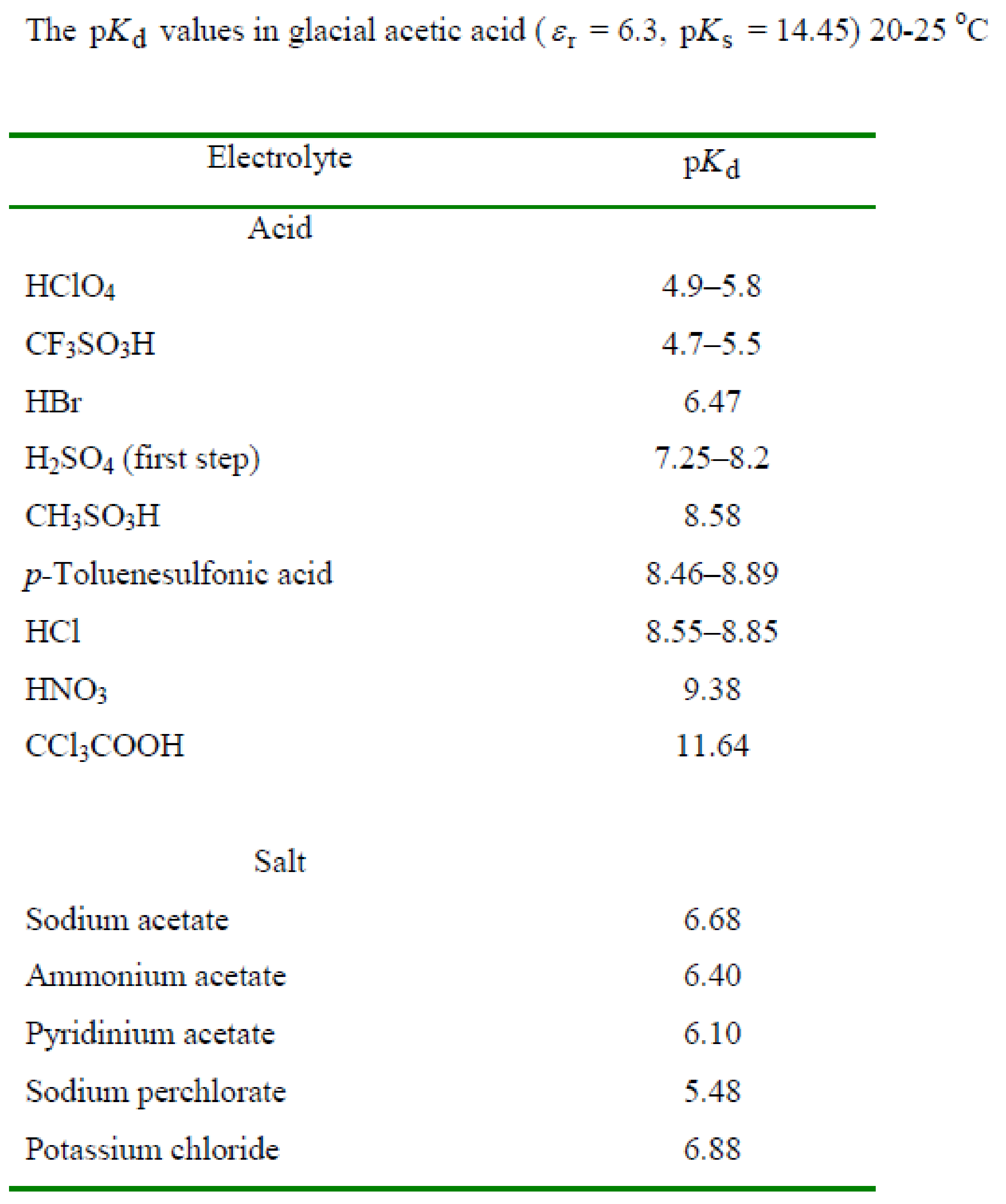
$$2CH_3COOH \Leftrightarrow CH_3COOH_2^+ + CH_3COO^-;\ pK_s = 14.45$$

The strength of the bases, except of some extremely weak ones, is leveled:

$$B + CH_3COOH \Leftrightarrow BH^+CH_3COO^- \Leftrightarrow BH^+ + CH_3COO^-$$

The strength of the acids is differenced

The dissociation of salts is incomplete

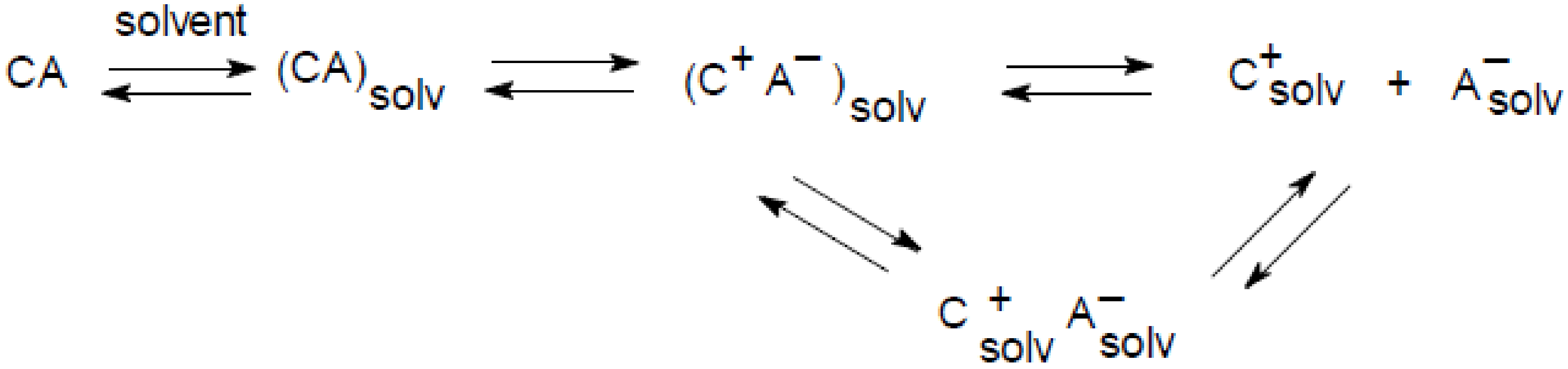


The pK_d values in glacial acetic acid ($\varepsilon_r = 6.3$, $pK_s = 14.45$) 20-25 °C

Electrolyte	pK_d
Acid	
$HClO_4$	4.9–5.8
CF_3SO_3H	4.7–5.5
HBr	6.47
H_2SO_4 (first step)	7.25–8.2
CH_3SO_3H	8.58
p-Toluenesulfonic acid	8.46–8.89
HCl	8.55–8.85
HNO_3	9.38
CCl_3COOH	11.64
Salt	
Sodium acetate	6.68
Ammonium acetate	6.40
Pyridinium acetate	6.10
Sodium perchlorate	5.48
Potassium chloride	6.88

General dissociation scheme of electrolytes in solution

by Izmailov



$$K_{\text{об}}^{-1} = (K^{*}_{\text{нест}} + 1)K_{\text{дис}}^{-1} + K_{\text{асс}} = K_{\text{дис}}^{-1}(K^{*}_{\text{нест}} + 1 + K_{\text{пр}})$$

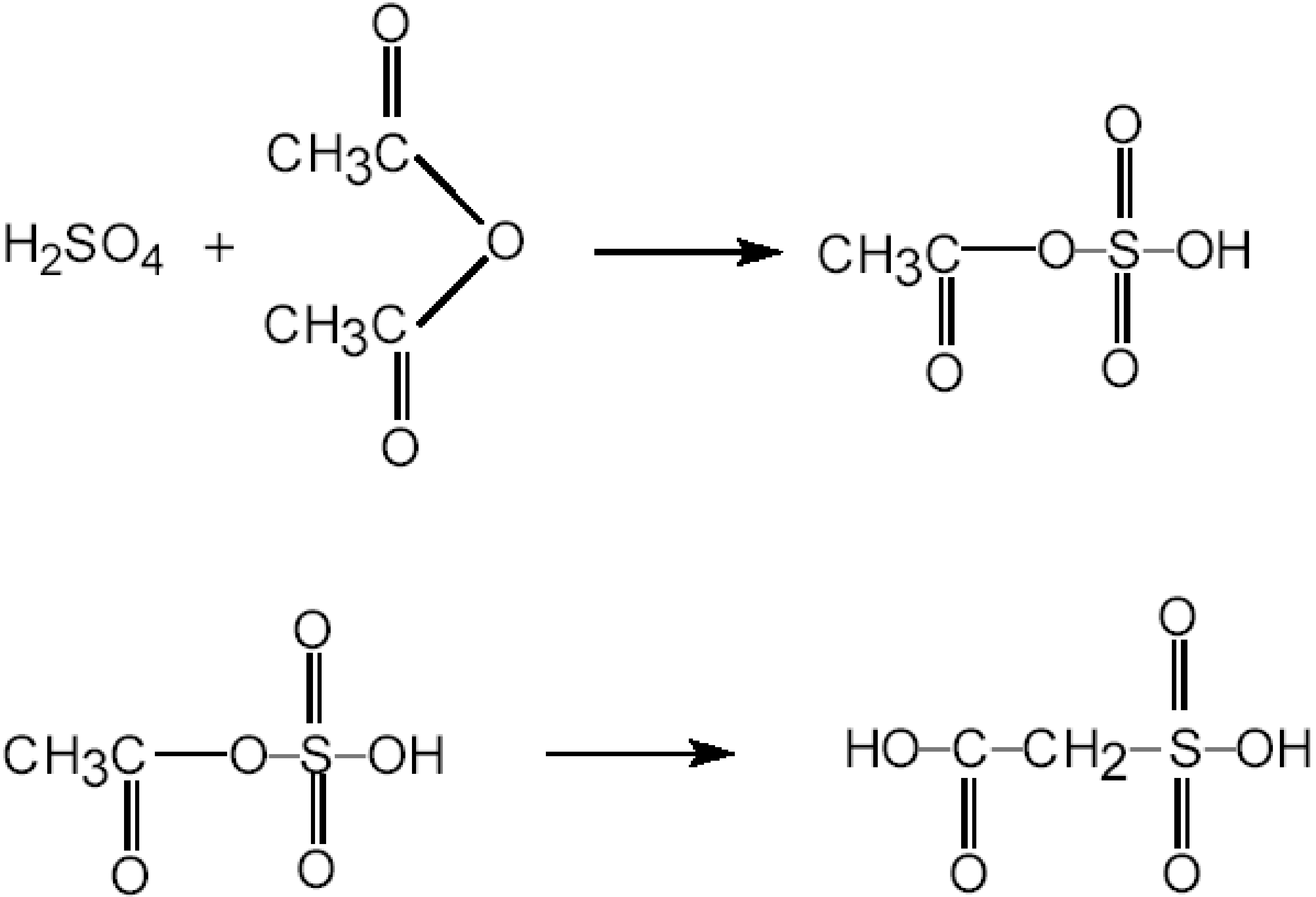
$$K_{\text{пр}} = K_{\text{дисс}} K_{\text{асс}}$$

$$\mathrm{CA} \rightleftharpoons \mathrm{C^{+}A^{-}}\ ,\ K_{\mathrm{i}}$$

$$\mathrm{C^{+}A^{-}} \rightleftharpoons \mathrm{C^{+}} + \mathrm{A^{-}}\ ,\ K_{\mathrm{d}}$$

$$K_{\mathrm{over-all}} = \frac{[\mathrm{C^{+}}][\mathrm{A^{-}}]}{[\mathrm{CA}] + [\mathrm{C^{+}A^{-}}]}$$

$$K_{\mathrm{over-all}} = \frac{K_{\mathrm{i}}\, K_{\mathrm{d}}}{1 + K_{\mathrm{i}}}$$


H2SO4
+
CH3C
O
CH3C
O
O
CH3C
O
O
S
OH
O
O
CH3C
O
O
S
OH
O
O
HO
C
CH2
S
OH
O
O
O

EQUILIBRIA IN LIQUID HF

$$\varepsilon_r = 83.6 \text{ at } 0\ ^{\circ}\text{C}$$

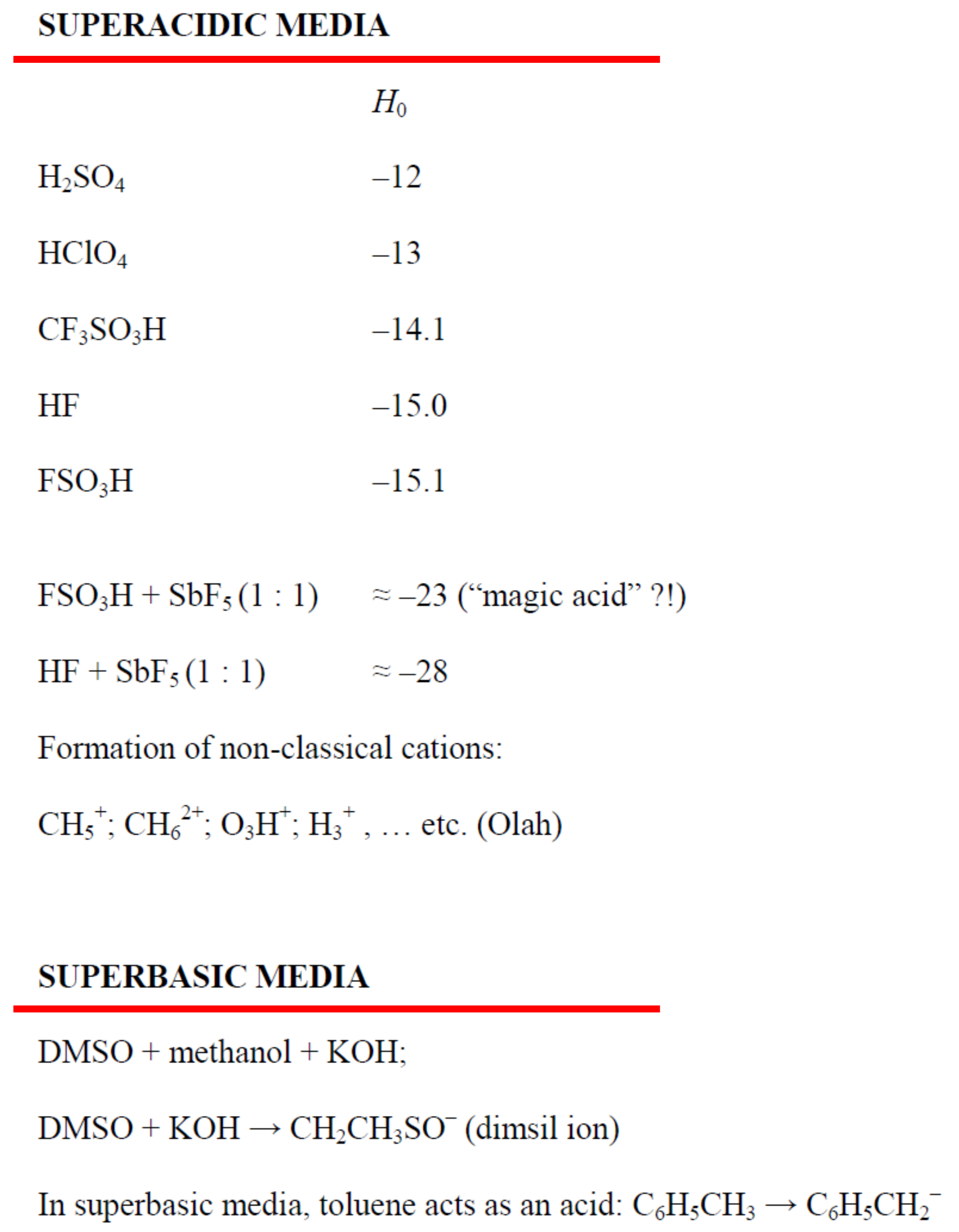
$$2\ \text{HF} \rightleftharpoons \text{H}_2\text{F}^+ + \text{F}^-$$

$$\text{p}K_s \approx 12$$

$$\text{Ar} + \text{HF} \rightleftharpoons \text{ArH}^+ + \text{F}^-$$

$$\text{Ar} + 2\ \text{HF} \rightleftharpoons \text{ArH}^+ + \text{HF}_2^-$$

$$\text{C}_6\text{H}_6 + \text{HF} + \text{BF}_3 \rightleftharpoons \text{C}_6\text{H}_7^+ + \text{BF}_4^-$$



SUPERACIDIC MEDIA

	H_0
H_2SO_4	–12
$HClO_4$	–13
CF_3SO_3H	–14.1
HF	–15.0
FSO_3H	–15.1
$FSO_3H + SbF_5$ (1 : 1)	≈ –23 (“magic acid” ?!)
$HF + SbF_5$ (1 : 1)	≈ –28

Formation of non-classical cations:

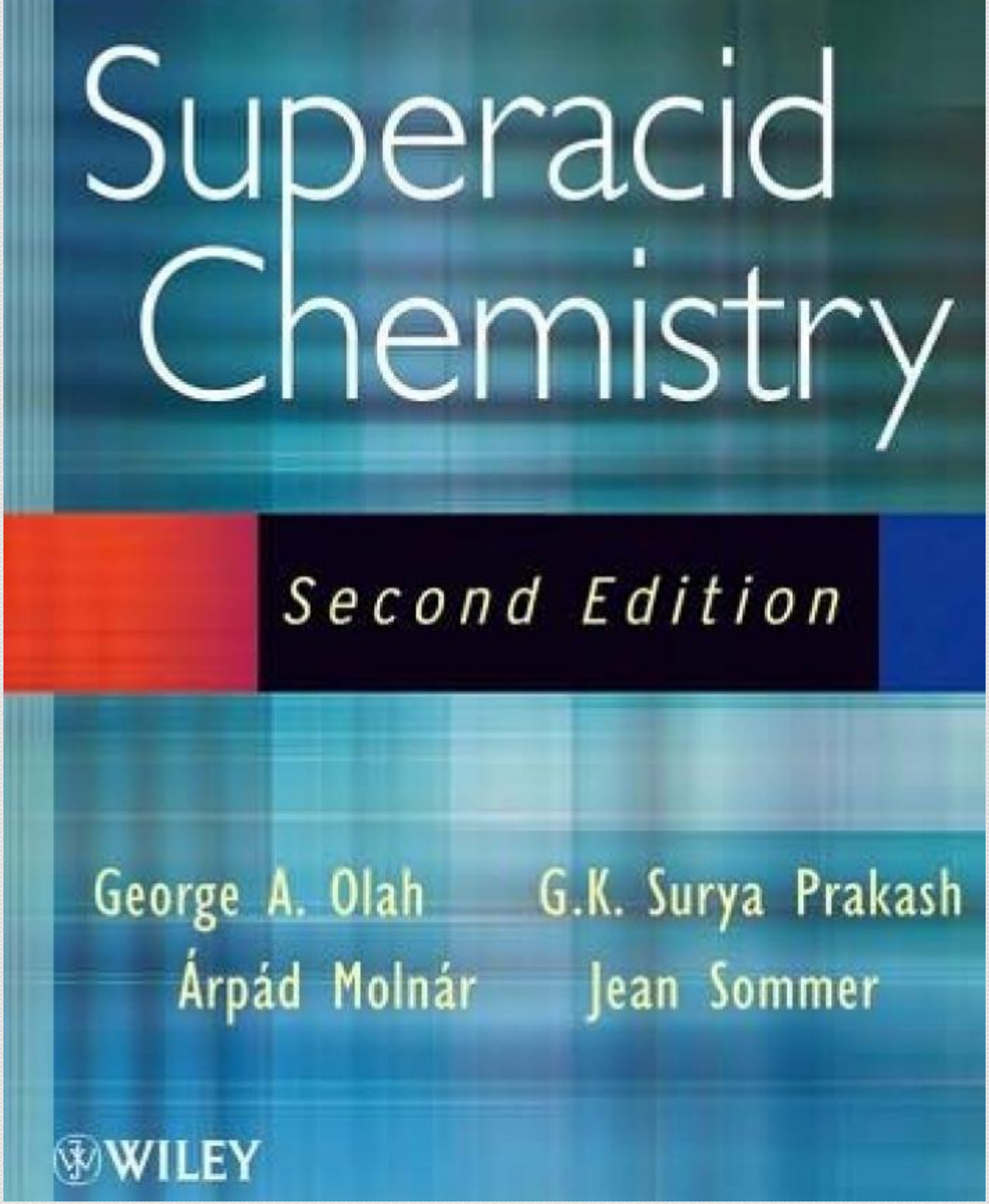
CH_5^+; CH_6^{2+}; O_3H^+; H_3^+ , … etc. (Olah)

SUPERBASIC MEDIA

DMSO + methanol + KOH;

DMSO + KOH → $CH_2CH_3SO^-$ (dimsil ion)

In superbasic media, toluene acts as an acid: $C_6H_5CH_3 \rightarrow C_6H_5CH_2^-$



Superacid Chemistry

Second Edition

George A. Olah
G.K. Surya Prakash
Árpád Molnár
Jean Sommer

WILEY

EQUILIBRIA IN LIQUID AMMONIA

$$\varepsilon_r = 16.9$$

$$2\ NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$\mathrm{p}K_s = 32.5 \text{ at } -33\ ^0C$$

$$M \rightarrow M^+ + e^-$$

The solvated electrons interact with the electrophilic fullerene (a Lewis acid):

$$C_{60} \rightarrow C_{60}{}^{\bullet\,5-} \rightarrow \text{association with } K^{+}$$

<u>The strength of acids is leveled</u>; normally, $pK = pK_{\text{over-all}} = 2.5\text{–}4.4$

$$\boxed{K_{\text{over-all}} = \frac{K_{\mathrm{i}}\,K_{\mathrm{d}}}{1 + K_{\mathrm{i}}}}$$

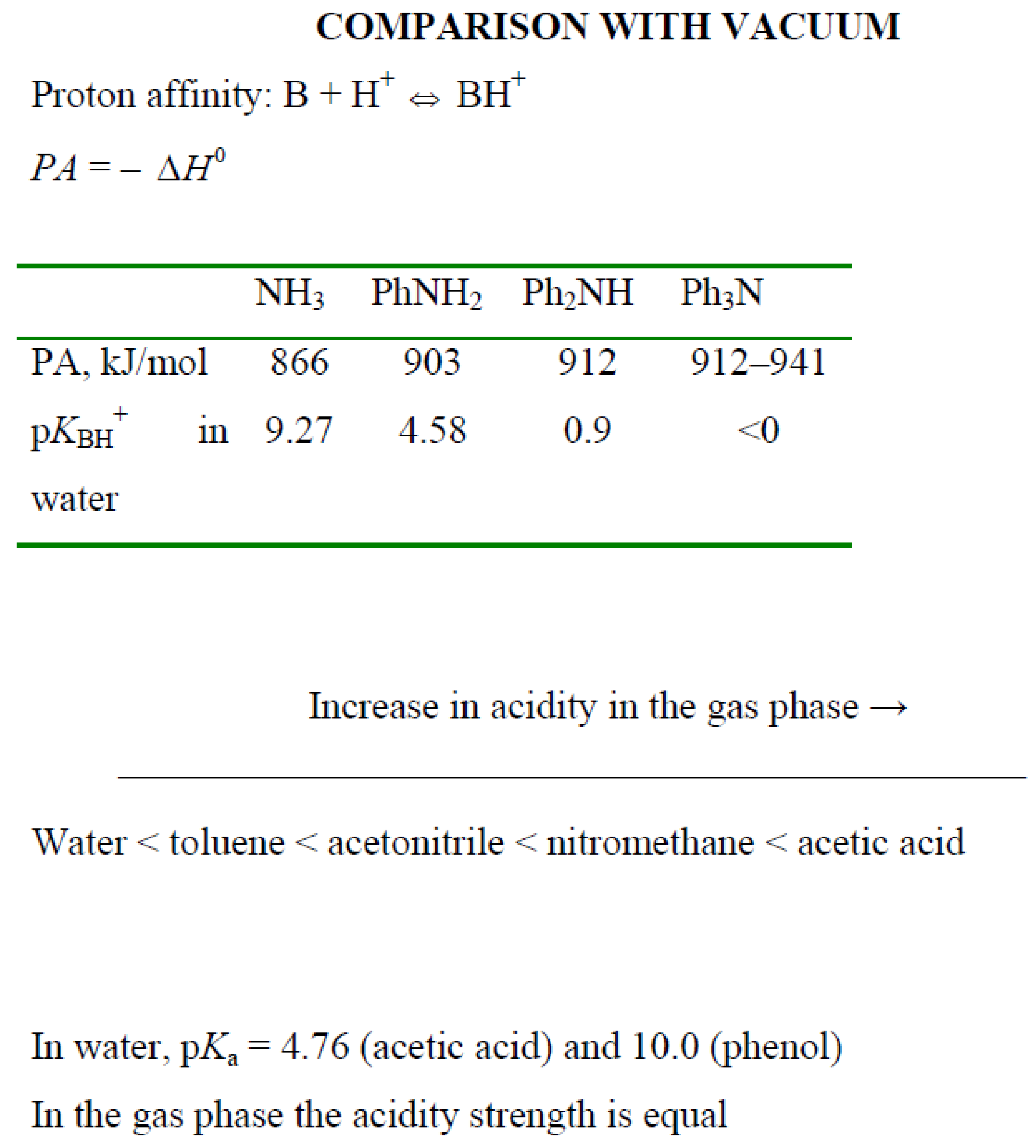
<u>For some weak acids:</u>

Di-(*p*-tolyl)methane	$pK = 27.1$
Aniline	21.2
Water	18.9
Phenol	3.5 (in water $pK = 10.0$)

Typical ionophores dissociate incomplete

For inorganic salts $pK = 2.3\text{–}2.5$

For the salt $NH_4(CH_2NO_2)$, $pK = 4.3$.



COMPARISON WITH VACUUM

Proton affinity: $B + H^+ \Leftrightarrow BH^+$

$$PA = -\ \Delta H^0$$

	NH_3	$PhNH_2$	Ph_2NH	Ph_3N
PA, kJ/mol	866	903	912	912–941
pK_{BH^+} in water	9.27	4.58	0.9	<0

Increase in acidity in the gas phase →

Water < toluene < acetonitrile < nitromethane < acetic acid

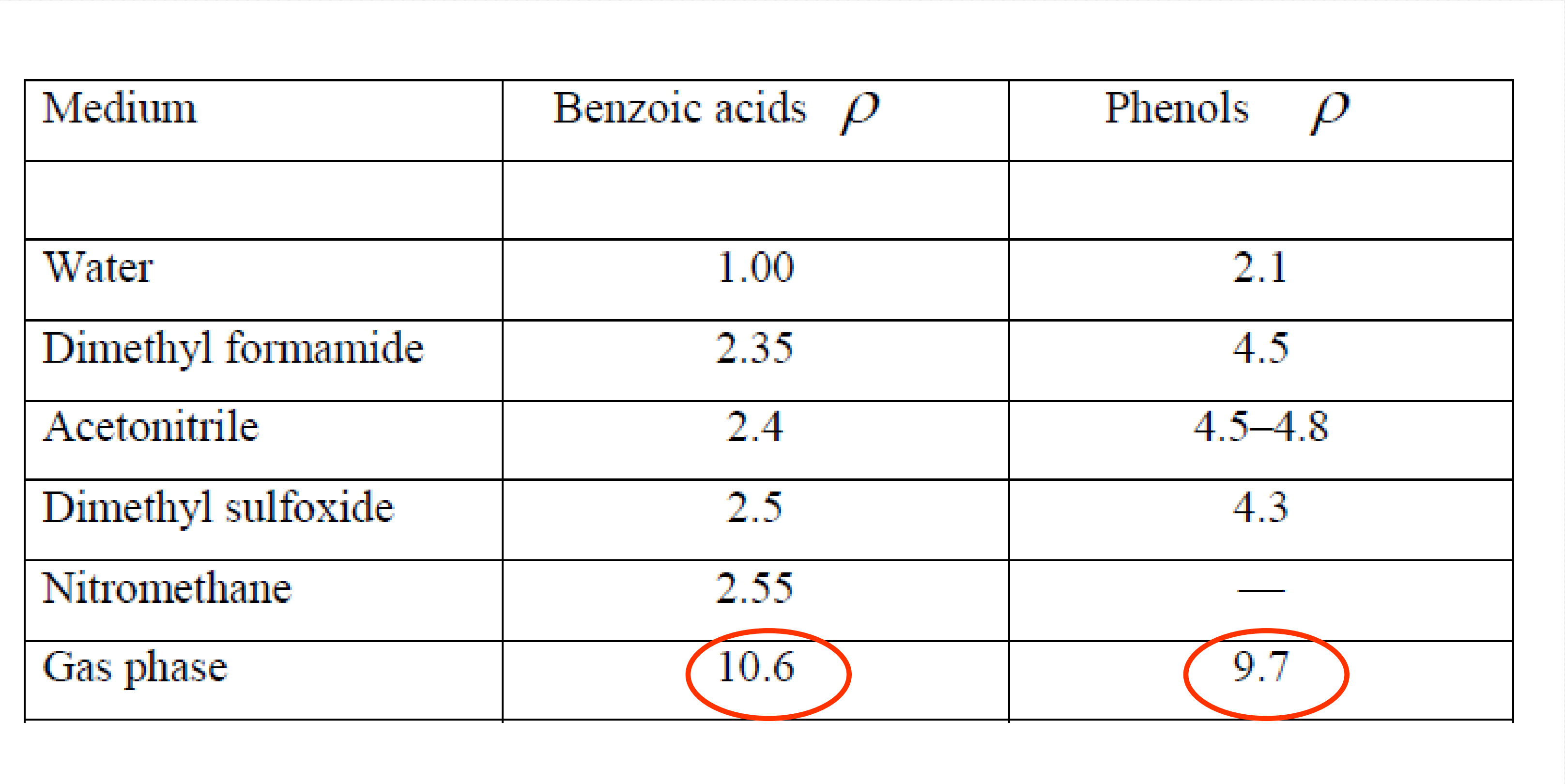
In water, $pK_a = 4.76$ (acetic acid) and 10.0 (phenol)

In the gas phase the acidity strength is equal

Two effects: conjugation (“mesomeric”) and inductive effects

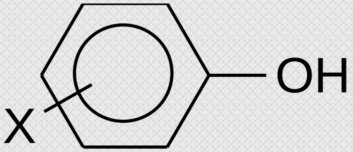
$$\rho = \frac{K_a^{\mathrm{H}} - \mathrm{p}K_a^{\mathrm{X}}}{\sigma}$$

Estimation of the “ro” constant in non-aqueous solvents

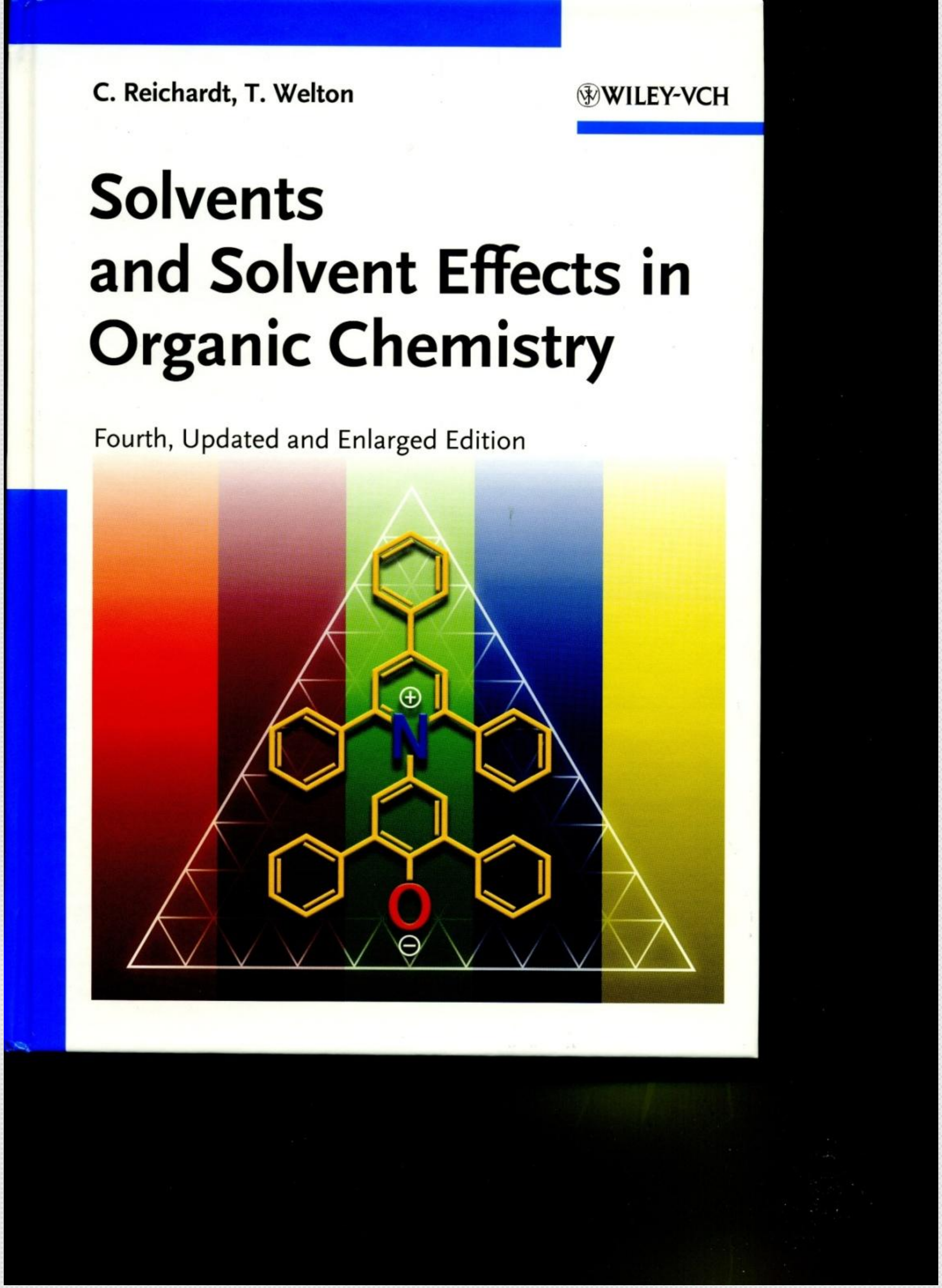


Medium	Benzoic acids ρ	Phenols ρ
Water	1.00	2.1
Dimethyl formamide	2.35	4.5
Acetonitrile	2.4	4.5–4.8
Dimethyl sulfoxide	2.5	4.3
Nitromethane	2.55	—
Gas phase	10.6	9.7

For



In water: $\rho = 2.1$



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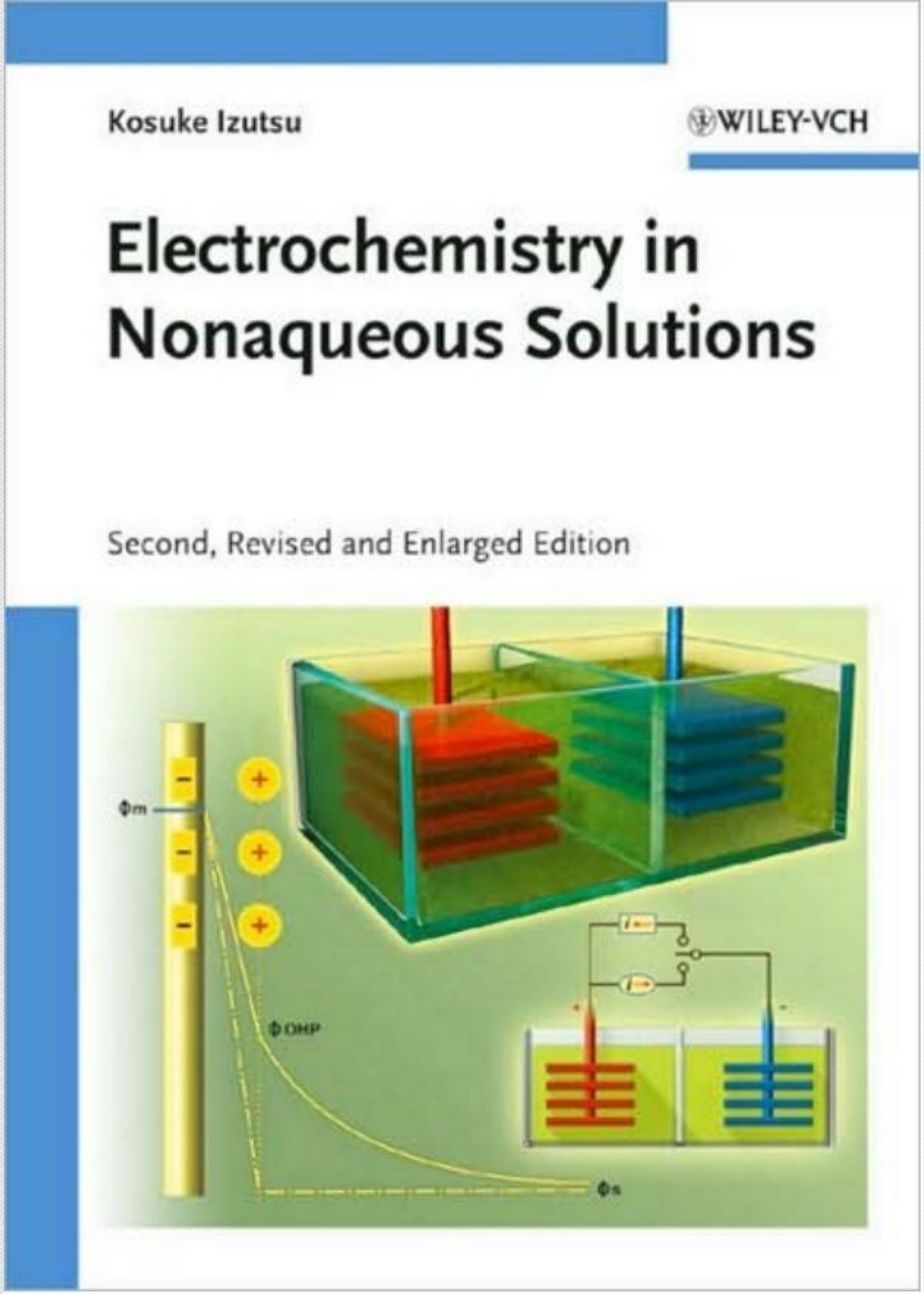

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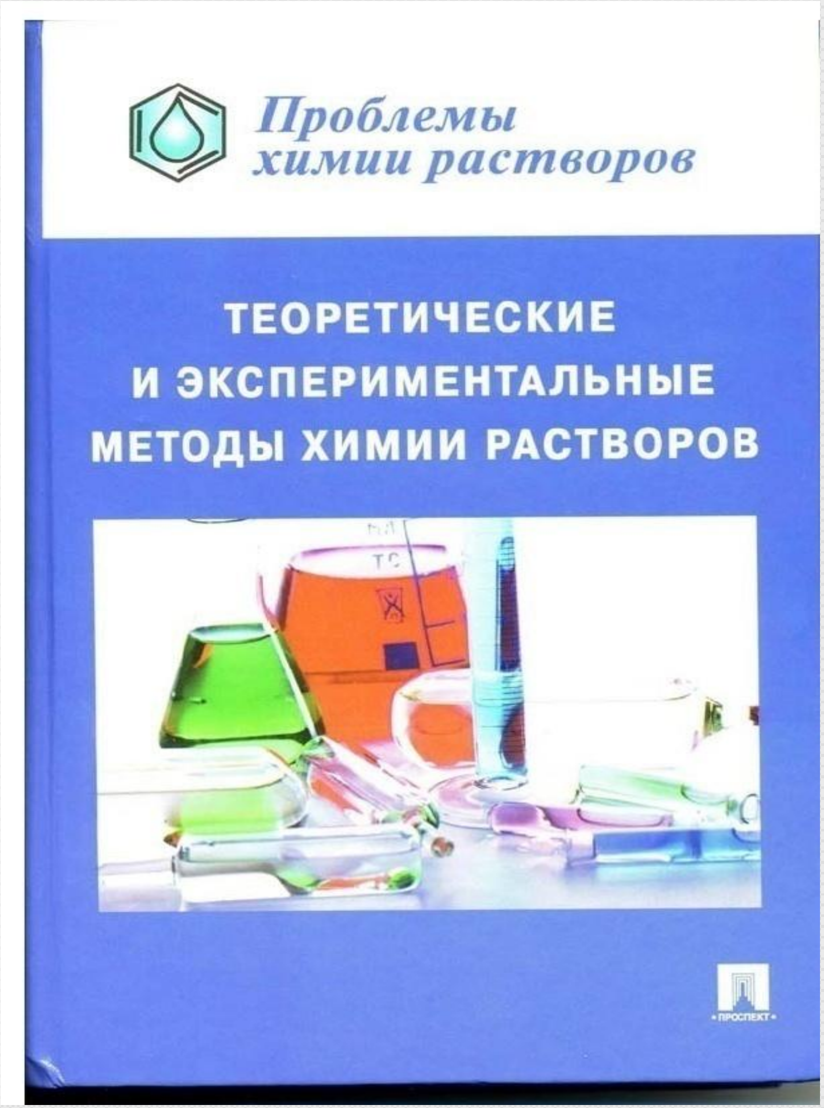
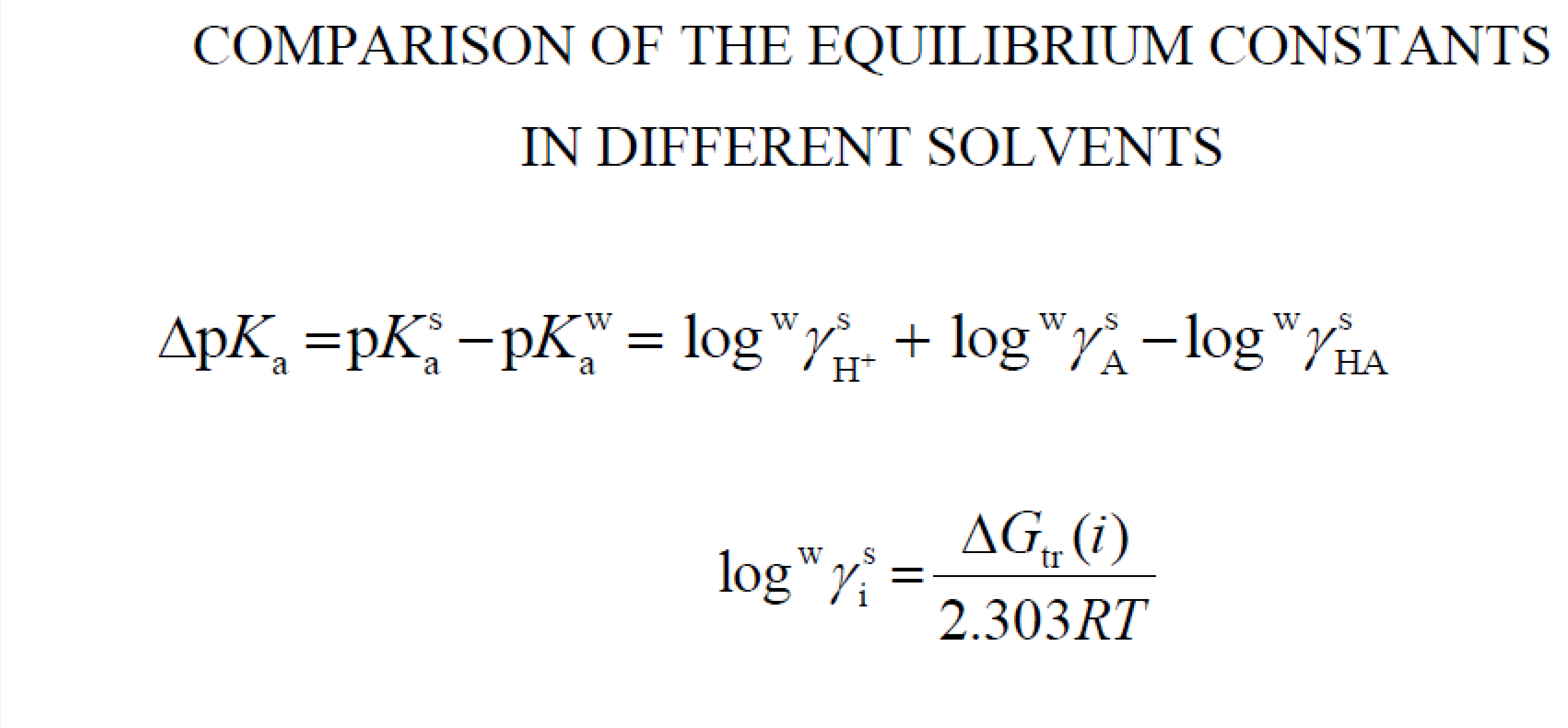


Проблемы
химии растворов

ТЕОРЕТИЧЕСКИЕ
И ЭКСПЕРИМЕНТАЛЬНЫЕ
МЕТОДЫ ХИМИИ РАСТВОРОВ

ПРОСПЕКТ

М.: Проспект, 2011.

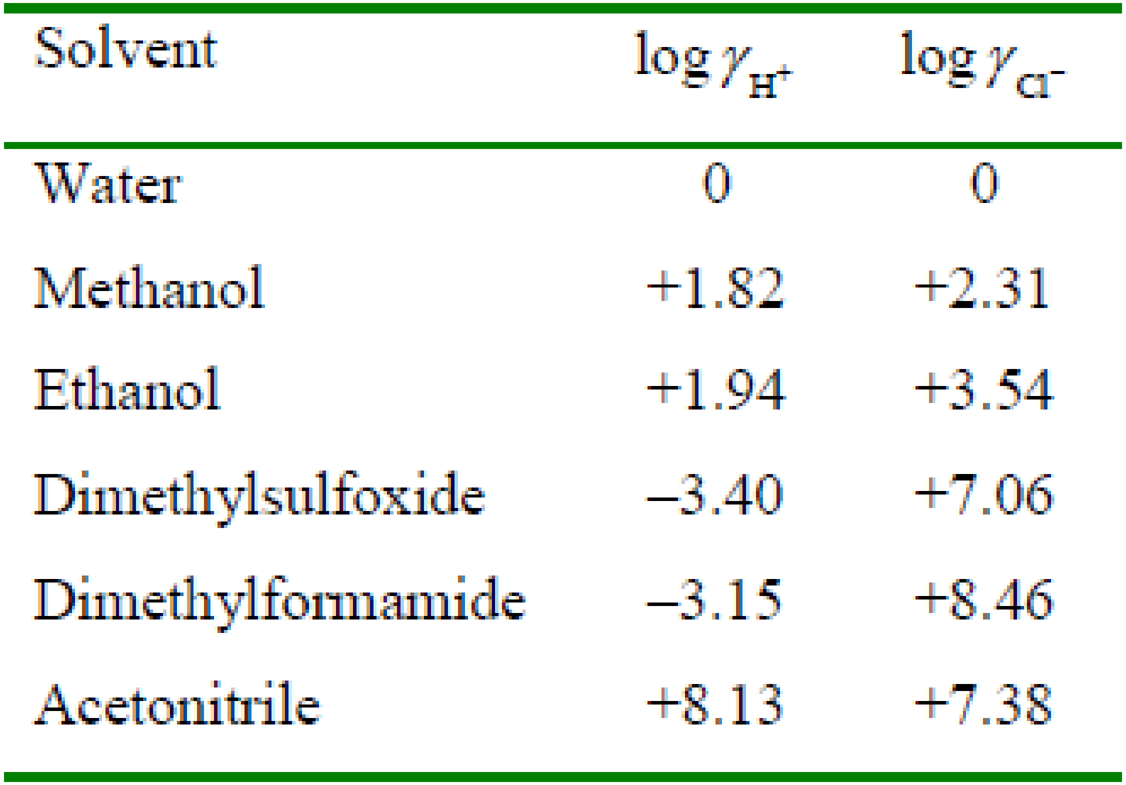


COMPARISON OF THE EQUILIBRIUM CONSTANTS IN DIFFERENT SOLVENTS

$$\Delta \mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}} = \log {}^{\mathrm{w}}\gamma_{\mathrm{H^+}}^{\mathrm{s}} + \log {}^{\mathrm{w}}\gamma_{\mathrm{A}}^{\mathrm{s}} - \log {}^{\mathrm{w}}\gamma_{\mathrm{HA}}^{\mathrm{s}}$$

$$\log {}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{\Delta G_{\mathrm{tr}}(i)}{2.303RT}$$

Some examples from a much larger body of data:

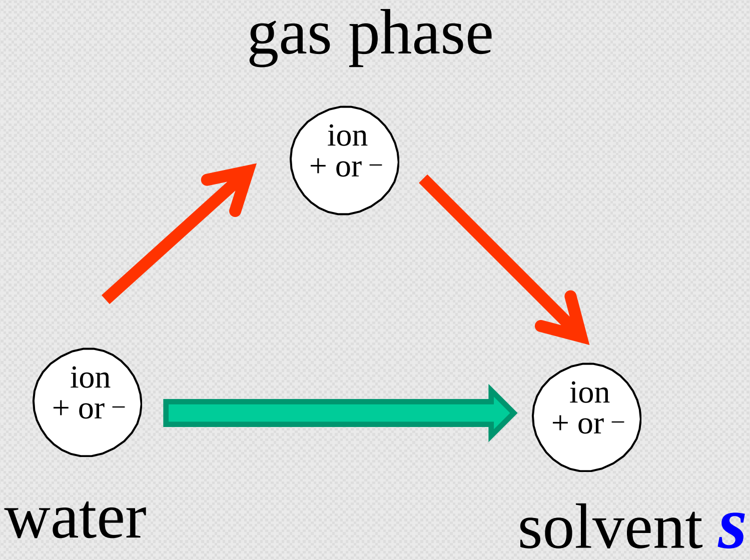


Solvent	$\log \gamma_{H^+}$	$\log \gamma_{Cl^-}$
Water	0	0
Methanol	+1.82	+2.31
Ethanol	+1.94	+3.54
Dimethylsulfoxide	–3.40	+7.06
Dimethylformamide	–3.15	+8.46
Acetonitrile	+8.13	+7.38

$\log \gamma_i < 0:$ profitable transfer

$\log \gamma_i > 0:$ unprofitable transfer

Attempts to estimate the transfer activity coefficients theoretically



gas phase

ion
+ or −

ion
+ or −

water

ion
+ or −

solvent ***s***

Born's equation for a charged sphere:

$$\log {}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{\Delta G_{\mathrm{tr}}(i)}{2.303RT} = \frac{e^2 z_{\mathrm{i}}^2 N_{\mathrm{A}}}{4.60\ RTr_{\mathrm{i}} \times 4\pi \times \varepsilon_0} \times \left[\frac{1}{\varepsilon_{\mathrm{r,s}}} - \frac{1}{\varepsilon_{\mathrm{r,w}}}\right]$$

Gibbs energy of transfer of an ion from vacuum to a solvent:

$$\Delta G_{solv} = -\frac{N_{\mathrm{A}}}{8\pi\varepsilon_0} \times \frac{z^2 e^2}{r} \times \left(1 - \frac{1}{\varepsilon_{\mathrm{r}}}\right)$$

Enthalpy of transfer of an ion from vacuum to a solvent:

$$\Delta H_{solv} = -\frac{N_{\mathrm{A}}}{8\pi\varepsilon_0} \times \frac{z^2 e^2}{r} \times \left(1 - \frac{1}{\varepsilon_{\mathrm{r}}} - \frac{T}{\varepsilon^2}\frac{d\varepsilon}{dT}\right)$$

Gibbs energy of transfer of an ion from one solvent to another:

$$\Delta G_{solv} = -\frac{N_{\mathrm{A}}}{8\pi\varepsilon_0} \times \frac{z^2 e^2}{r} \times \left(1 - \frac{1}{\varepsilon_{\mathrm{r}}}\right) \times \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)$$

$$\mathrm{p}K_\mathrm{a}^\mathrm{s} - \mathrm{p}K_\mathrm{a}^\mathrm{w} = \log\gamma_{\mathrm{H}^+} + \log\gamma_\mathrm{A} - \log\gamma_\mathrm{HA}$$

$$\log {}^\mathrm{w}\gamma_\mathrm{i}^\mathrm{s} = \frac{\Delta G_\mathrm{tr}(i)}{2.303RT} = \frac{e^2 \mathrm{z}_\mathrm{i}^2 N_\mathrm{A}}{4.60\ RTr_\mathrm{i}\ \times 4\pi\times\varepsilon_0}\times\left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_\mathrm{r,w}}\right]$$

$$\Downarrow$$

$$\mathrm{p}K_\mathrm{a}^\mathrm{s} - \mathrm{p}K_\mathrm{a}^\mathrm{w} = \frac{e^2 N_\mathrm{A}}{4.60\ RT\ \times 4\pi\times\varepsilon_0}\times\left[\frac{1}{r_{\mathrm{H}^+}} + \frac{(z_\mathrm{HA}-1)^2}{r_\mathrm{A}} - \frac{z_\mathrm{HA}^2}{r_\mathrm{HA}}\right]\times\left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_\mathrm{r,w}}\right]$$

(the so-called Bronsted equation)

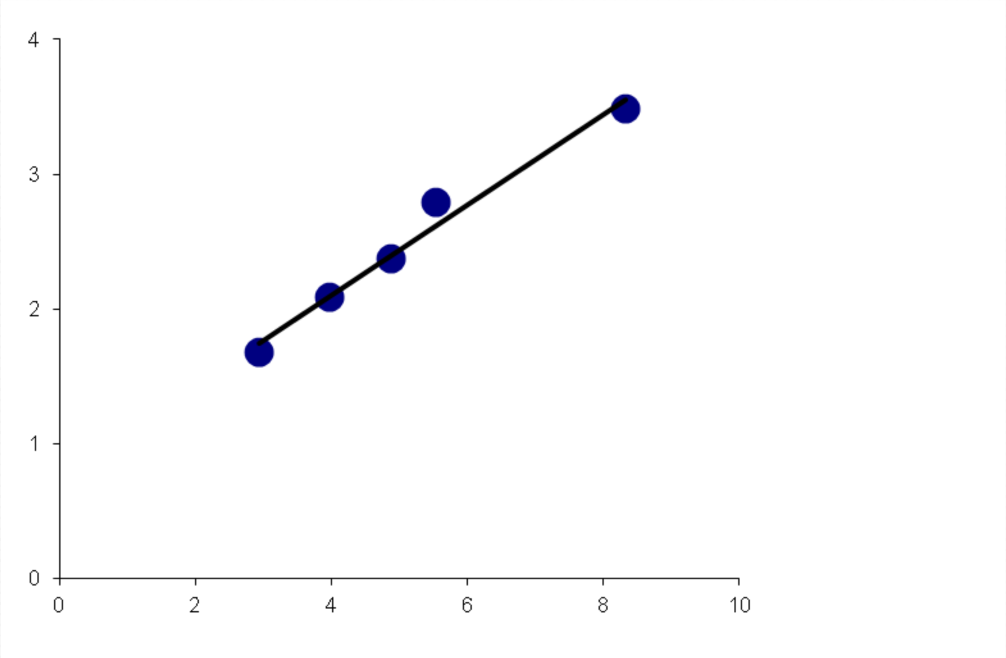
$$\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{el}} = \frac{N_{\mathrm{A}} e^2}{8\pi\varepsilon_0 \times 2.303RT} \times \left(\frac{1}{r_{\mathrm{H^+}}} + \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{HA}}} \right) \times \left(\frac{1}{\varepsilon_{\mathrm{s}}} - \frac{1}{\varepsilon_{\mathrm{w}}} \right)$$

If all the radii are equal:

CHARGE TYPE	If all the radii are equal:
$HA \Leftrightarrow H^+ + A^-$	$\left(\frac{1}{r_{\mathrm{H^+}}} + \frac{1}{r_{\mathrm{A^-}}} \right) = \frac{2}{r}$
$HA^+ \Leftrightarrow H^+ + A$	$\left(\frac{1}{r_{\mathrm{H^+}}} - \frac{1}{r_{\mathrm{HA^+}}} \right) = 0$
$HA^- \Leftrightarrow H^+ + A^{2-}$	$\left(\frac{1}{r_{\mathrm{H^+}}} + \frac{4}{r_{\mathrm{A^{2-}}}} - \frac{1}{r_{\mathrm{HA^-}}} \right) = \frac{4}{r}$

Tetramethylammonium perchlorate in:

nitrobenzene, benzonitrile, acetone, 2-butanone, pyridine

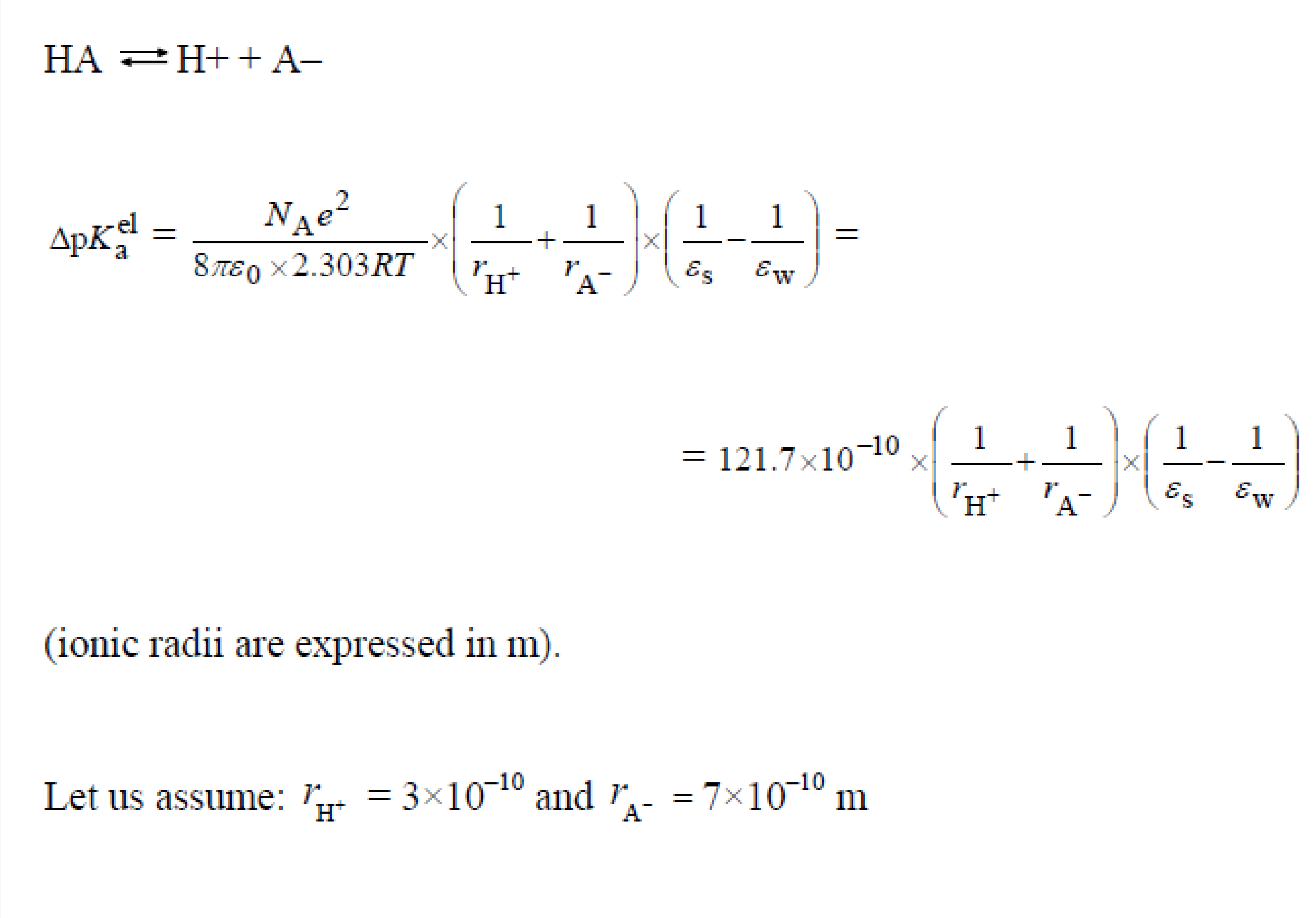


$$\log K_{\mathrm{ass}} = 0.765 + 33.46\varepsilon_{\mathrm{r}}^{-1}, \ r = 0.99$$

P.C. Ho, J.B. Ramsey. J. Chem. Eng. Data 1986. Vol. 31. No. 4. P. 430-434.

SOLVENT EFFECT UPON THE DISSOCIATION OF ACIDS

Verification of the simple electrostatic model



$HA \rightleftharpoons H^+ + A^-$

$$\Delta pK_a^{el} = \frac{N_A e^2}{8\pi\varepsilon_0 \times 2.303RT} \times \left(\frac{1}{r_{H^+}} + \frac{1}{r_{A^-}}\right) \times \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right) =$$

$$= 121.7 \times 10^{-10} \times \left(\frac{1}{r_{H^+}} + \frac{1}{r_{A^-}}\right) \times \left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)$$

(ionic radii are expressed in m).

Let us assume: $r_{H^+} = 3 \times 10^{-10}$ and $r_{A^-} = 7 \times 10^{-10}$ m

Solvent (ε_r at 25 °C)	ΔpK_a^{el}	Experimental ΔpK_a values for the benzoic acid (in water pK_a = 4.20)
Methanol (32.6)	1.03	5.20
Ethanol (24.4)	1.63	6.05
1-Butanol (17.5)	2.57	7.28
tert-Butanol (12.5)	3.90	10.8
Formamide (109.5)	–0.21	2.07
DMSO (46.5)	0.51	6.9
DMF (36.7)	0.84	8.1
Propylenecarbonate (65.0)	0.15	15.5
Acetonitrile (36.0)	0.87	16.5

Picric acid in two solvents of identical chemical nature

Solvent	ε_r	pK_a
Acetone	20.56	9.2
Methylisobutylketone	12.92	11.0

The difference between the pK_a is **1.8**

The calculated ΔpK_a^{el} is **1.67**

The electrostatic approach: Born-Bronsted equation:

$$\Delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{el}} = \frac{N_{\mathrm{A}} e^{2}}{8\pi\varepsilon_{0} \times 2.303RT} \times \left(\frac{1}{r_{\mathrm{H^{+}}}} + \frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{HA}}} \right) \times \left(\frac{1}{\varepsilon_{\mathrm{s}}} - \frac{1}{\varepsilon_{\mathrm{w}}} \right)$$

The Bronsted-Izmailov equation:

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}} = \frac{e^{2} N_{\mathrm{A}}}{4.60\,RT \ \times 4\pi \times \varepsilon_{0}} \times \left[\frac{1}{r_{\mathrm{H^{+}}}} + \frac{(\mathrm{z}-1)^{2}}{r_{\mathrm{B}}} - \frac{\mathrm{z}^{2}}{r_{\mathrm{HB}}} \right] \times \left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right] + \underline{\frac{\Delta G_{\mathrm{H^{+}}}^{\mathrm{solv}} + \Delta G_{\mathrm{B}}^{\mathrm{solv}} - \Delta G_{\mathrm{HB}}^{\mathrm{solv}}}{2.30RT}}$$

Differentiation influence of the organic solvents

1. Charge type of the acid-base couple
2. The chemical nature of the ionizing group

$$\Delta pK_a - \log {}^{w}\gamma^{s}_{H^+} = \log {}^{w}\gamma^{s}_{A} - \log {}^{w}\gamma^{s}_{HA}$$

Acid	Charge type	pK_a in water	pK_a in CH_3CN	ΔpK_a
3-Nitroanilinium	+/0	2.50	7.6	5.1
Methyl yellow	+/0	3.25	10.05	6.8
Picric acid	0/–	0.38	11.0	10.6
2,4-Dinitrophenol	0/–	4.11	16.0	11.9
4-Nitrophenol	0/–	7.15	20.7	13.5
Phenol	0/–	10.0	27.2	17.2
Salicylic acid	0/–	2.97	16.7	13.7
Benzoic acid	0/–	4.20	20.7	16.5
Acetic acid	0/–	4.76	22.3	17.5

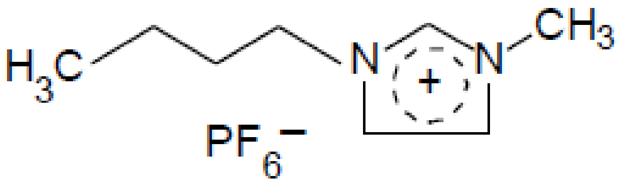
ACID	pK_a			
	CH_3CN	DMSO	Difference	Average
Picric	11.0	–(0.5–1.0)	11.5–12.0	
3,5-Dinitrophenol	20.5	10.6	9.9	
4-Nitrophenol	20.7	11.0	9.7	10.6
2-Nitrophenol	22.0	11.0	11.0	
Phenol	27.2	16.4	10.8	
Acetic acid	22.3	12.6	9.7	
Benzoic acid	20.7	11.1	9.6	9.7
Salicylic acid	16.7	6.8	9.9	

Kolthoff:

$$\mathrm{p}K_\mathrm{a}\ (\text{in } \mathrm{CH_3CN}) - \mathrm{p}K_\mathrm{a}\ (\text{in DMSO}) = \log {}^{\mathrm{D}}\gamma^{\mathrm{AN}}_{\mathrm{H^+}} + \log \frac{{}^{\mathrm{D}}\gamma^{\mathrm{AN}}_{\mathrm{A^-}}}{{}^{\mathrm{D}}\gamma^{\mathrm{AN}}_{\mathrm{HA}}}$$

$$\log {}^{\mathrm{D}}\gamma^{\mathrm{AN}}_{\mathrm{H^+}} = \log {}^{\mathrm{W}}\gamma^{\mathrm{AN}}_{\mathrm{H^+}} - \log {}^{\mathrm{W}}\gamma^{\mathrm{D}}_{\mathrm{H^+}} = 7.8 - (-3.4) = 11.2$$

“Green solvents” – Room Temperature Ionic Liquids



$[\text{bmim}]^+[\text{PF}_6]^-$, $t_{\text{melt}} = 12\ ^{\circ}\text{C}$.

Negligible vapor pressure, incombustibility, high thermostability, wide electrochemical window

$C_2H_5NH_3^+NO_3^-$: $t_{\text{melt}} = 13\text{–}14\ ^{\circ}\text{C}$.

(P. Walden, 1914).

Indices of the dissociation constants in water, organic molecular solvents and ionic liquids

Solvent	pK_a		Difference between the pK_a
	2,4-Dinitrophenol	Benzoic acid	
Water	4.11	4.20	0.1
Methanol	7.9	9.4	1.5
DMSO	5.1	11.1	6.0
DMF	6.3	12.3	6.0
Acetone	15.7	18.2	2.5
Acetonitrile	16.0	20.7	4.7
$bmim^+ CF_3SO_3^-$	9.5	13.3	3.8
$DBUH^+ CF_3SO_3^-$	9.0	11.0	2.0

Specificity of acid dissociation in ionic liquids

$HA_{solv} \Leftrightarrow H^{+}_{solv} + A^{-}_{solv}$

$HA + X^{-} \Leftrightarrow HX + A^{-};$

$(HA + b\underline{mim^{+}CF_3SO_3^{-}} \Leftrightarrow \underline{CF_3SO_3H} + bmim^{+}A^{-})$

Analogy with the acids behavior in acetic acid as solvent:

$HA + CH_3COOH \Leftrightarrow CH_3COOH_2^{+}A^{-}$

Increase in the basic strength:

$$\longrightarrow$$

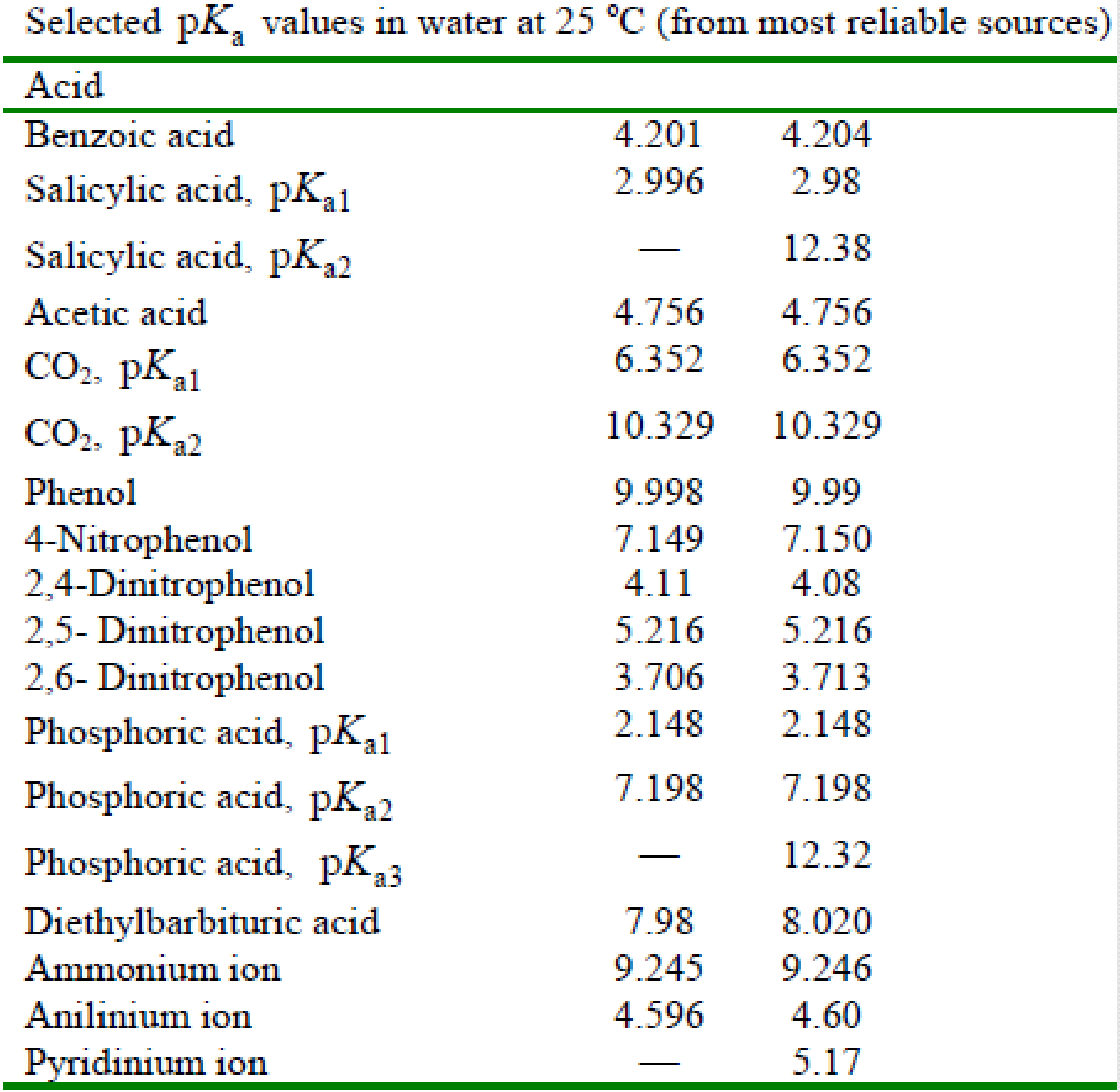
$PF_6^{-} < BF_4^{-} < (CF_3SO_2)_2N^{-} < CF_3SO_3^{-}$

p*K*a OF STRONG ACIDS IN WATER

	Water	Acetonitrile	Acetic acid
p-Toluenesulfonic	–(1.06–1.34)	8.01; 8.73	8.46–8.89
HNO_3	–1.38	8.9	9.38; 10.1
CH_3SO_3H	–(1.2–1.86)	10.0	8.58; 8.89
HCl	–(6–7)	8.1; 8.9	8.4; 8.85
HBr	–8	5.5	5.6; 6.47
HI	–9	—	—

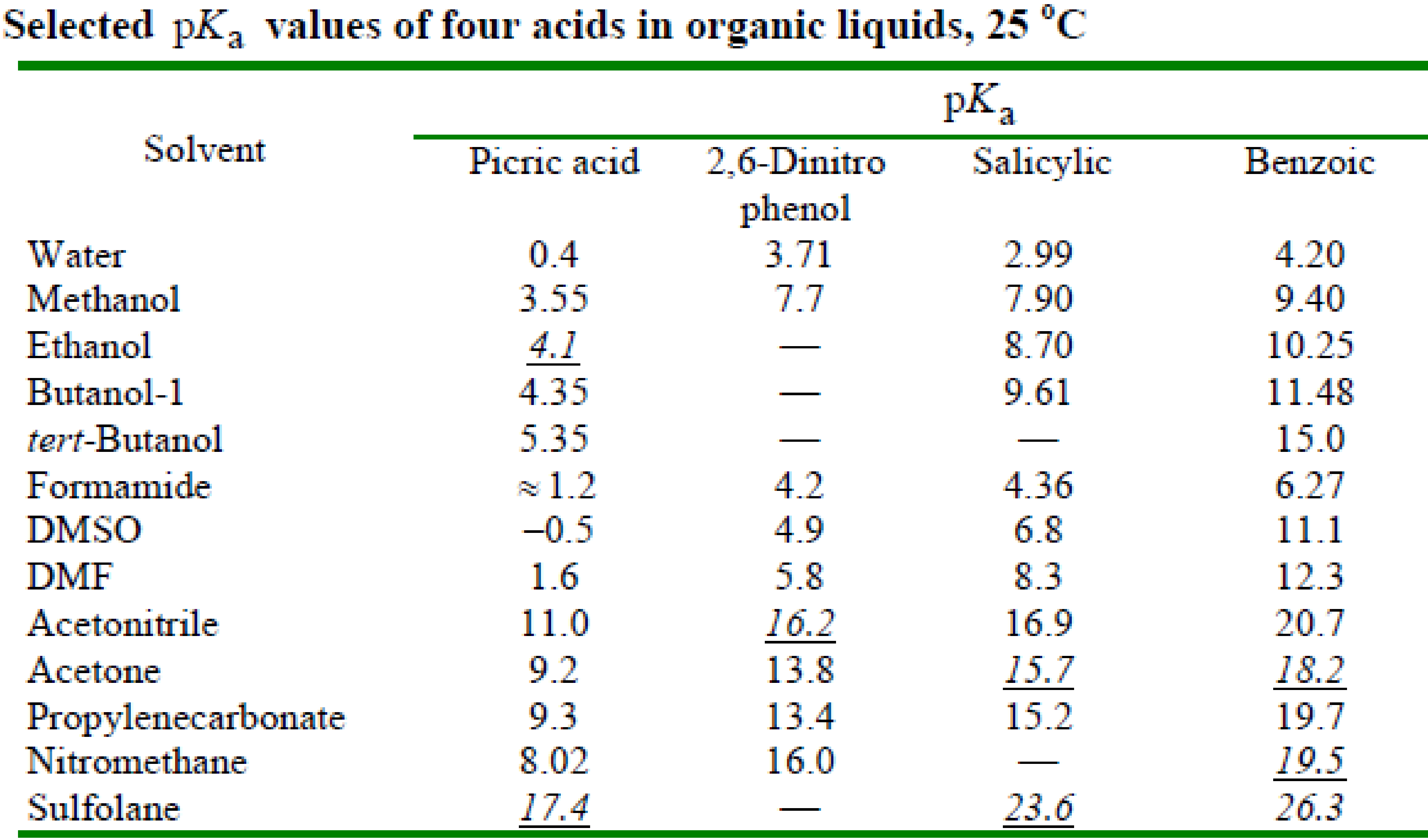
In water: HCl, HBr, HI – by vapor pressure; other acids – by NMR and Raman spectra.

In 75 % aq. H_2SO_4, *p*-toluenesulfonic acid forms $CH_3–C_6H_4–SO_3H_2^+$



Selected pK_a values in water at 25 °C (from most reliable sources)

Acid		
Benzoic acid	4.201	4.204
Salicylic acid, pK_{a1}	2.996	2.98
Salicylic acid, pK_{a2}	—	12.38
Acetic acid	4.756	4.756
CO_2, pK_{a1}	6.352	6.352
CO_2, pK_{a2}	10.329	10.329
Phenol	9.998	9.99
4-Nitrophenol	7.149	7.150
2,4-Dinitrophenol	4.11	4.08
2,5- Dinitrophenol	5.216	5.216
2,6- Dinitrophenol	3.706	3.713
Phosphoric acid, pK_{a1}	2.148	2.148
Phosphoric acid, pK_{a2}	7.198	7.198
Phosphoric acid, pK_{a3}	—	12.32
Diethylbarbituric acid	7.98	8.020
Ammonium ion	9.245	9.246
Anilinium ion	4.596	4.60
Pyridinium ion	—	5.17



Selected pK_a values of four acids in organic liquids, 25 °C

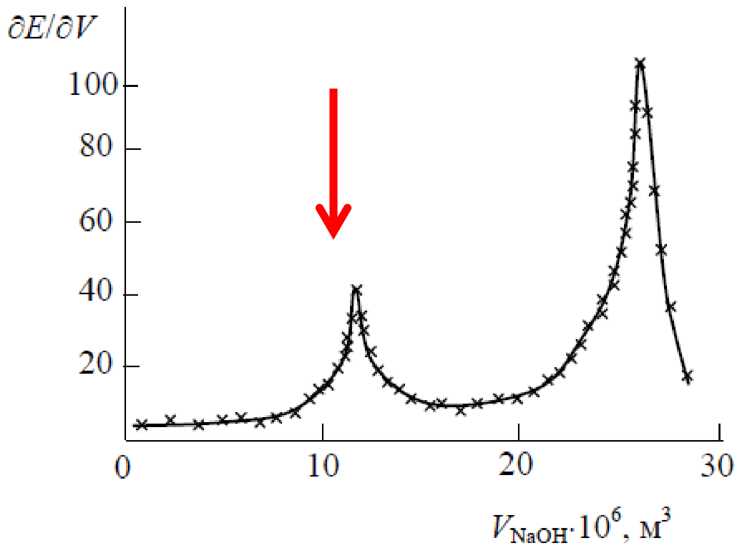
Solvent	pK_a			
	Picric acid	2,6-Dinitro phenol	Salicylic	Benzoic
Water	0.4	3.71	2.99	4.20
Methanol	3.55	7.7	7.90	9.40
Ethanol	*4.1*	—	8.70	10.25
Butanol-1	4.35	—	9.61	11.48
tert-Butanol	5.35	—	—	15.0
Formamide	≈ 1.2	4.2	4.36	6.27
DMSO	–0.5	4.9	6.8	11.1
DMF	1.6	5.8	8.3	12.3
Acetonitrile	11.0	*16.2*	16.9	20.7
Acetone	9.2	13.8	*15.7*	*18.2*
Propylenecarbonate	9.3	13.4	15.2	19.7
Nitromethane	8.02	16.0	—	*19.5*
Sulfolane	*17.4*	—	*23.6*	*26.3*

Solubility of gases at 20 °C, 1.013×10^5 Pa, molar fraction $\times 10^4$

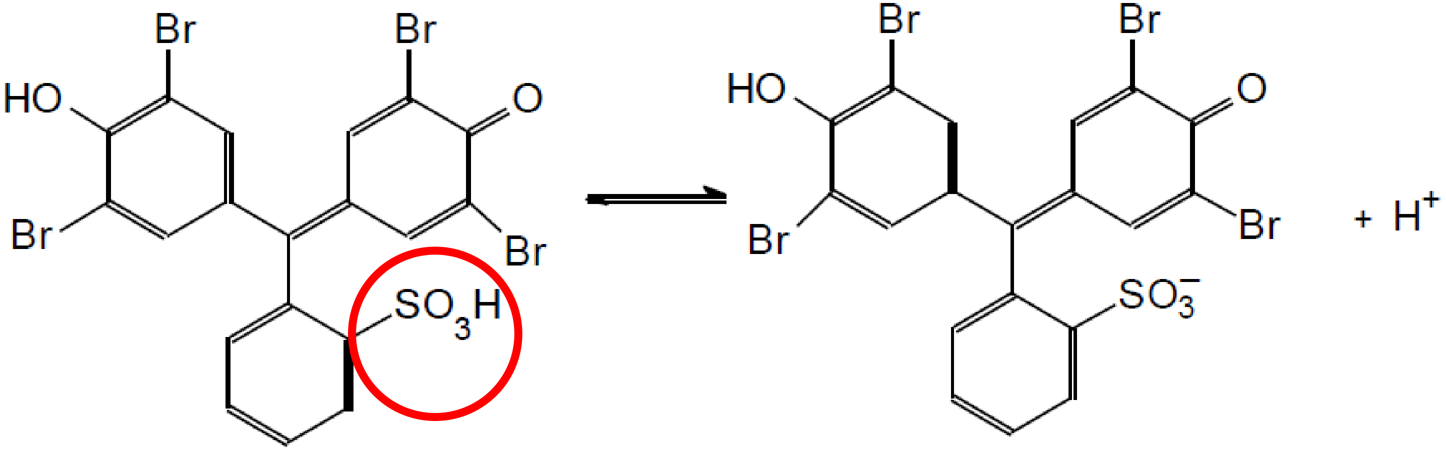
Solvent Gas	Water	Methanol	Acetone	Benzene
H_2	0.15	1.57	2.31	2.61
N_2	0.12	2.35	5.92	4.40
CO	0.13	3.25	8.54	6.24
O_2	0.23	3.18	9.25	8.16
CH_4	0.24	7.1	22.3	20.7
CO_2	6.1	70 (0 °C)	211 (0 °C)	91 (0 °C)

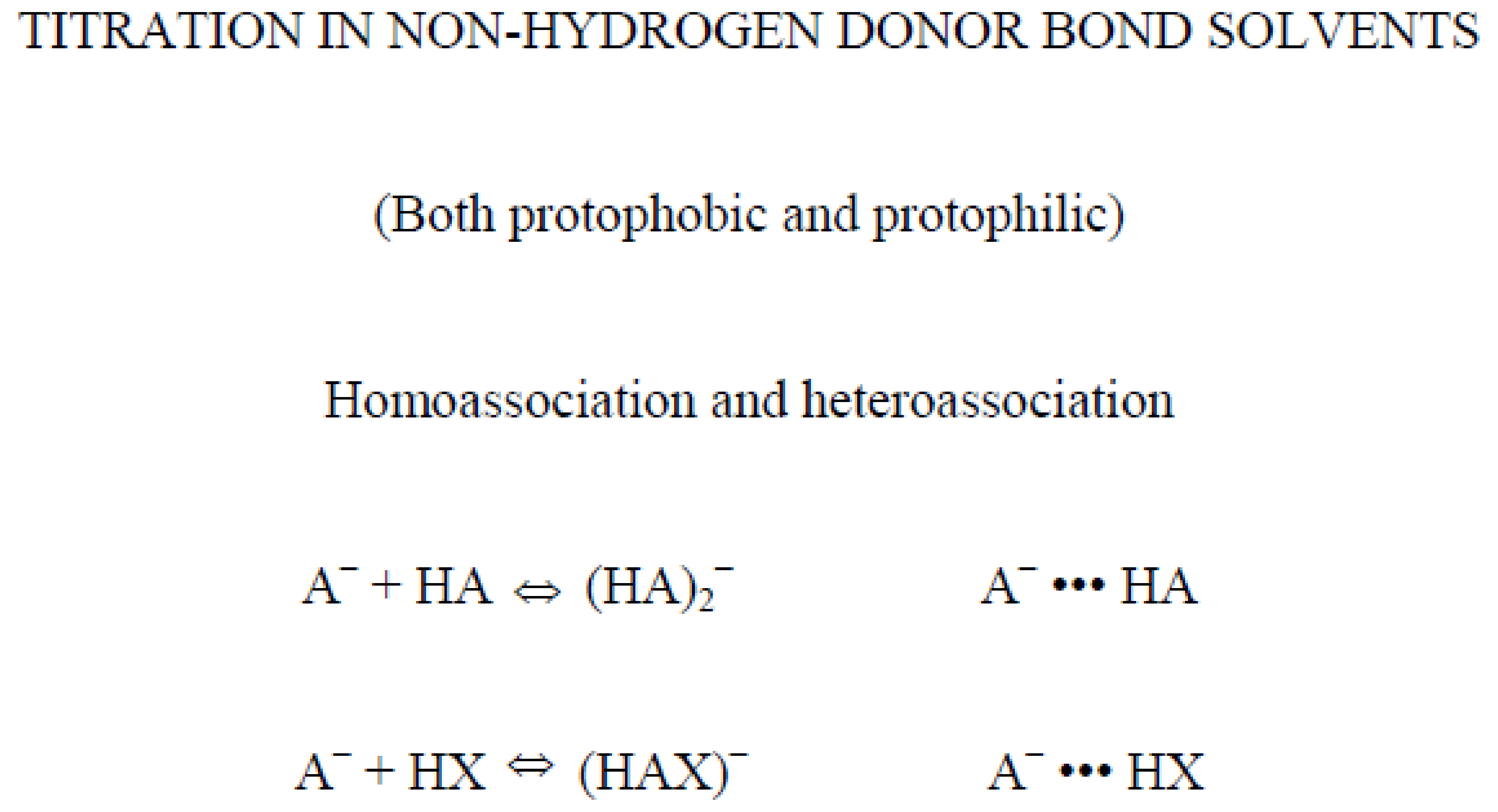
Henry law: $f_2 = k_2 x_2 \approx p_2$

Titration in 90 % Butanol-1



Differential curve of potentiometric titration of the dye bromophenol blue (0.00299 M) with a NaOH solution (0.0057 M); 0.05 M LiCl.





TITRATION IN NON-HYDROGEN DONOR BOND SOLVENTS

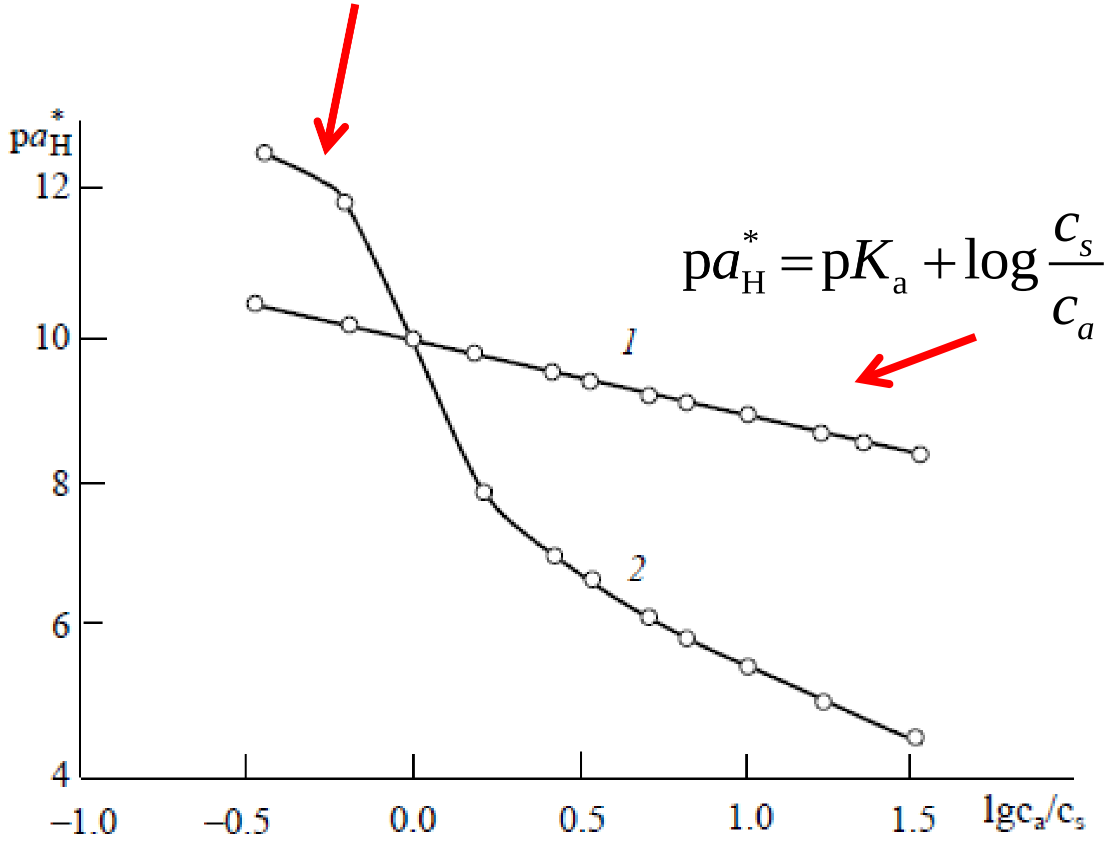
(Both protophobic and protophilic)

Homoassociation and heteroassociation

$A^- + HA \Leftrightarrow (HA)_2^-$ $\quad$ $A^- \bullet\bullet\bullet HA$

$A^- + HX \Leftrightarrow (HAX)^-$ $\quad$ $A^- \bullet\bullet\bullet HX$

$$a_{\mathrm{H}}^{*\,2} f_1^2 c_s - a_{\mathrm{H}}^{*} f_1 K_a [c_a + c_s + K^{\mathrm{f}}_{\mathrm{HA}_2^-}(c_a - c_s)^2] + K_a^2 c_a = 0$$



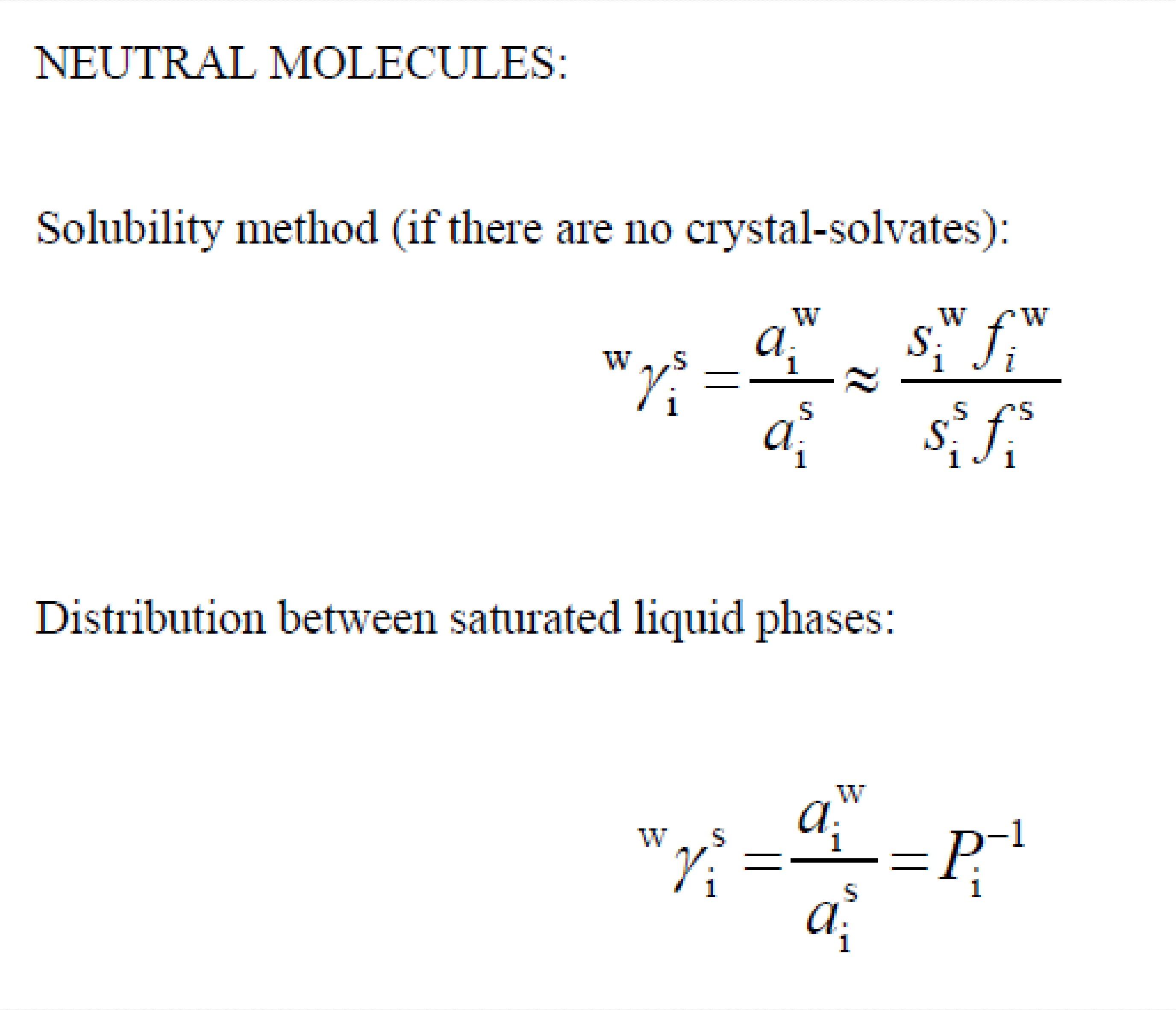
$$\mathrm{p}a_{\mathrm{H}}^{*} = \mathrm{p}K_{\mathrm{a}} + \log \frac{c_s}{c_a} + \log f_1$$

Dependence of the $\mathrm{p}a^{*}_{\mathrm{H}^+}$ values of buffer solutions on the logarithm of acid/salt analytic concentrations ratio: without (1) and with (2) homoassociation.

Transfer activity coefficients

$$\Delta \mathrm{p}K_{\mathrm{a}} - \log {}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{H}^{+}} = \log {}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{A}} - \log {}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{HA}}$$

METHODS OF DETERMINATION OF THE TRANSFER ACTIVITY COEFFICIENTS



NEUTRAL MOLECULES:

Solubility method (if there are no crystal-solvates):

$${}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{a_{\mathrm{i}}^{\mathrm{w}}}{a_{\mathrm{i}}^{\mathrm{s}}} \approx \frac{s_{\mathrm{i}}^{\mathrm{w}} f_{i}^{\mathrm{w}}}{s_{\mathrm{i}}^{\mathrm{s}} f_{\mathrm{i}}^{\mathrm{s}}}$$

Distribution between saturated liquid phases:

$${}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{a_{\mathrm{i}}^{\mathrm{w}}}{a_{\mathrm{i}}^{\mathrm{s}}} = P_{\mathrm{i}}^{-1}$$

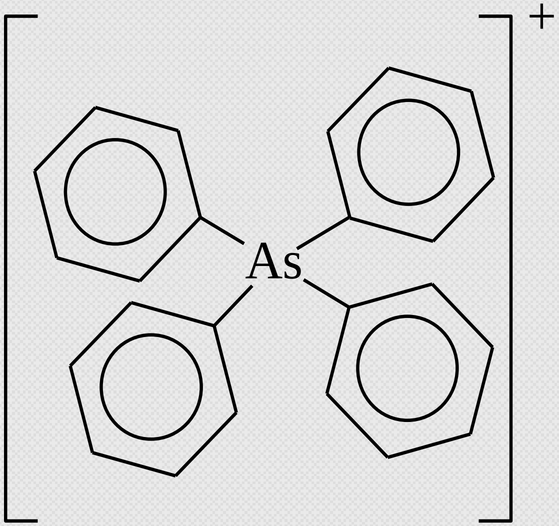
Estimation of the γ_i values of ions

Solubility. $\mathrm{Ct}^+ + \mathrm{An}^- \Leftrightarrow \mathrm{CtAn}\downarrow;\ K_{\mathrm{sp}}$ (solubility product)

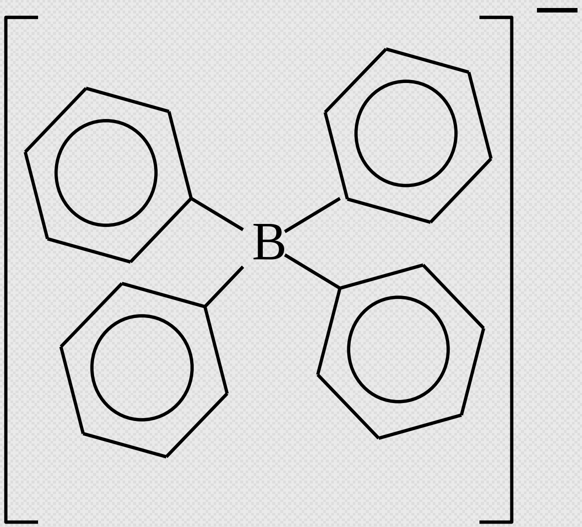
$$\gamma_+\gamma_- = \frac{K_{\mathrm{sp}}^{\mathrm{w}}}{K_{\mathrm{sp}}^{\mathrm{s}}}$$

This approach works for limitedly soluble salts.

γ_{tr}



$=\gamma_{\mathrm{tr}}$



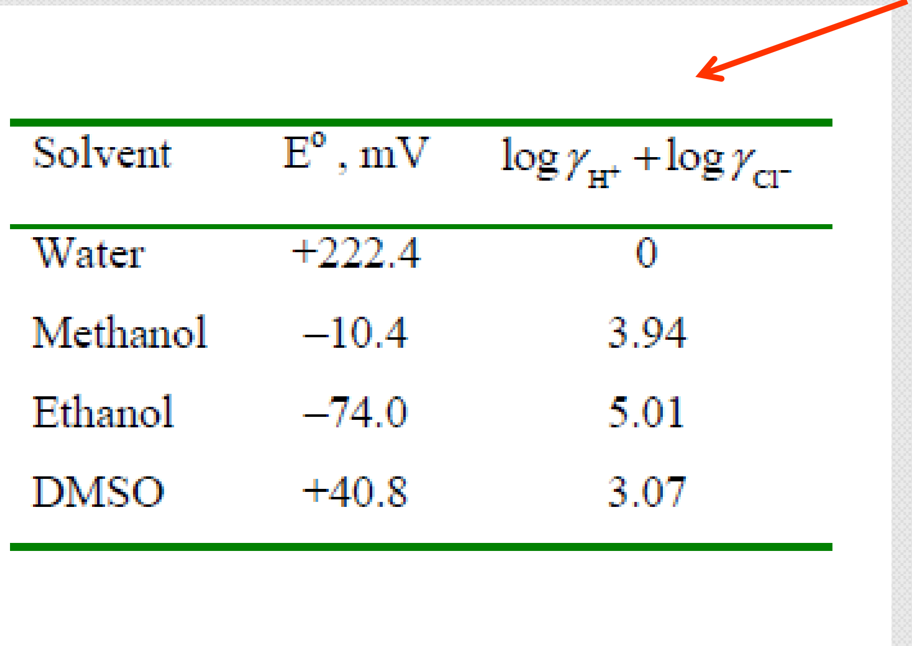
Electrochemical cells.

$$\mathrm{Pt}\left|\mathrm{H_2}\right|\,\mathrm{H^+},\mathrm{Cl^-}\left|\mathrm{AgCl}\right|\mathrm{Ag}$$

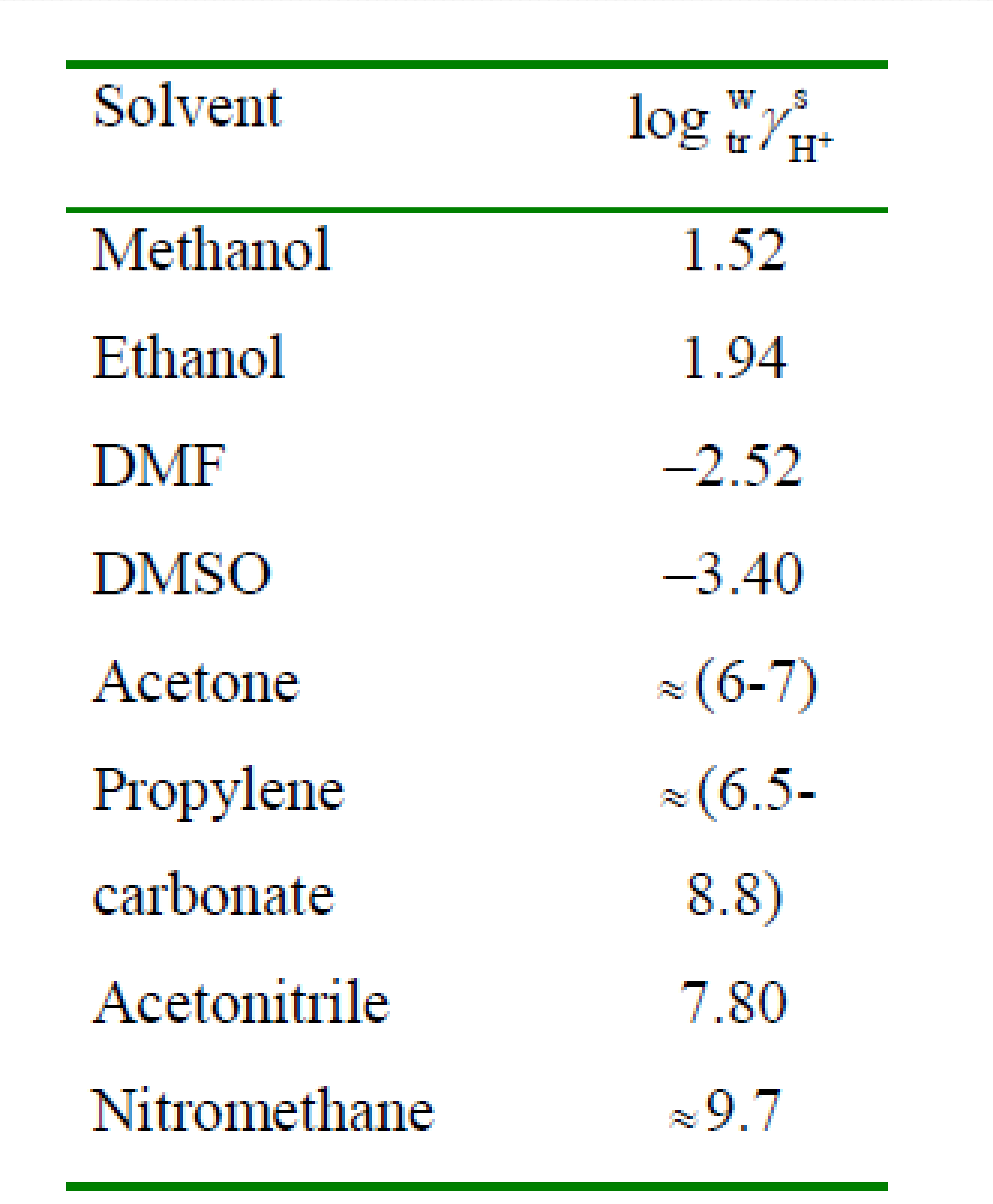
$$\frac{1}{2}\mathrm{H_2}+\mathrm{AgCl}\Leftrightarrow \mathrm{Ag}+\mathrm{H^+}+\mathrm{Cl^-};$$

$$E=E^0-\frac{RT}{F}\ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})$$

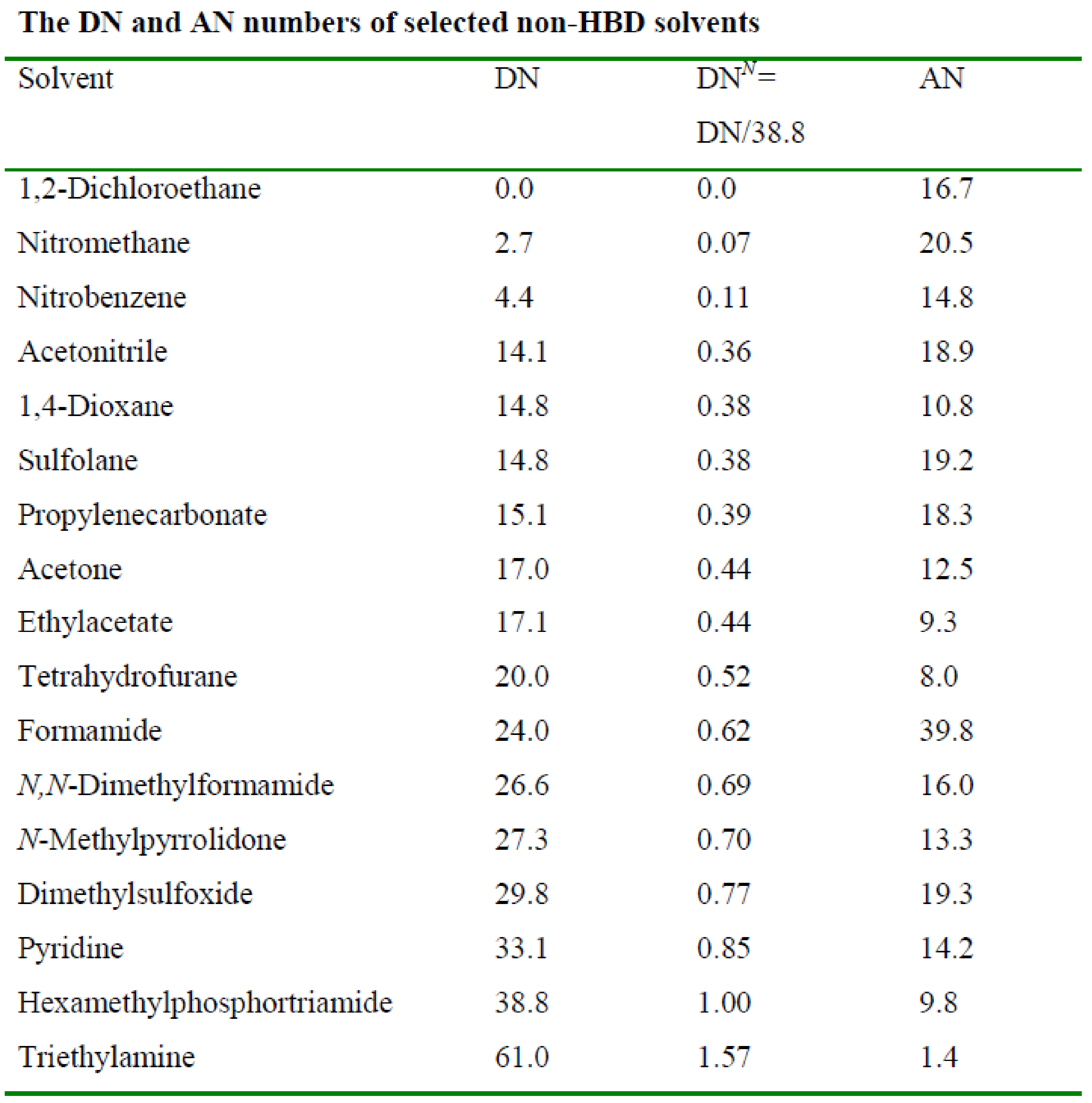
$$\log\gamma_{\mathrm{H^+}}+\log\gamma_{\mathrm{Cl^-}}=\frac{E^{0\mathrm{w}}-E^{0\mathrm{s}}}{59.16}$$



Solvent	E°, mV	$\log\gamma_{\mathrm{H^+}}+\log\gamma_{\mathrm{Cl^-}}$
Water	+222.4	0
Methanol	–10.4	3.94
Ethanol	–74.0	5.01
DMSO	+40.8	3.07



Solvent	$\log {}^{w}_{tr}\gamma^{s}_{H^+}$
Methanol	1.52
Ethanol	1.94
DMF	–2.52
DMSO	–3.40
Acetone	≈(6-7)
Propylene carbonate	≈(6.5-8.8)
Acetonitrile	7.80
Nitromethane	≈9.7



The DN and AN numbers of selected non-HBD solvents

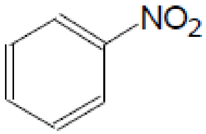
Solvent	DN	$DN^N =$ DN/38.8	AN
1,2-Dichloroethane	0.0	0.0	16.7
Nitromethane	2.7	0.07	20.5
Nitrobenzene	4.4	0.11	14.8
Acetonitrile	14.1	0.36	18.9
1,4-Dioxane	14.8	0.38	10.8
Sulfolane	14.8	0.38	19.2
Propylenecarbonate	15.1	0.39	18.3
Acetone	17.0	0.44	12.5
Ethylacetate	17.1	0.44	9.3
Tetrahydrofurane	20.0	0.52	8.0
Formamide	24.0	0.62	39.8
N,N-Dimethylformamide	26.6	0.69	16.0
N-Methylpyrrolidone	27.3	0.70	13.3
Dimethylsulfoxide	29.8	0.77	19.3
Pyridine	33.1	0.85	14.2
Hexamethylphosphortriamide	38.8	1.00	9.8
Triethylamine	61.0	1.57	1.4

Polar non HBD-solvents

Nitromethane

H_3C-NO_2

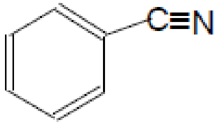
Nitrobenzene



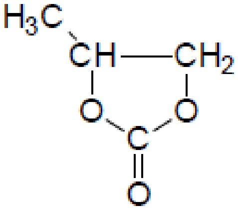
Acetonitrile

$H_3C-C\equiv N$

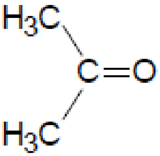
Benzonitrile



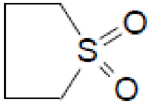
Propylenecarbonate (4-methyl-1,3-dioxolane-2-one)



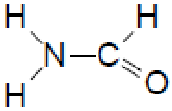
Acetone



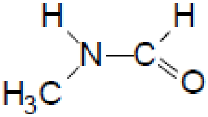
Sulfolane



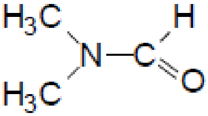
Formamide



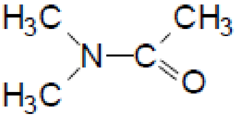
N-Methylformamide



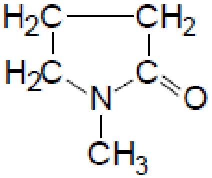
N,N-Dimethylformamide



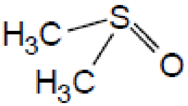
N,N-Dimethylacetamide



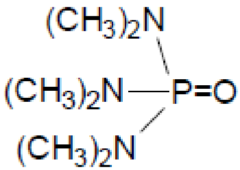
N-Methylpyrrolidone



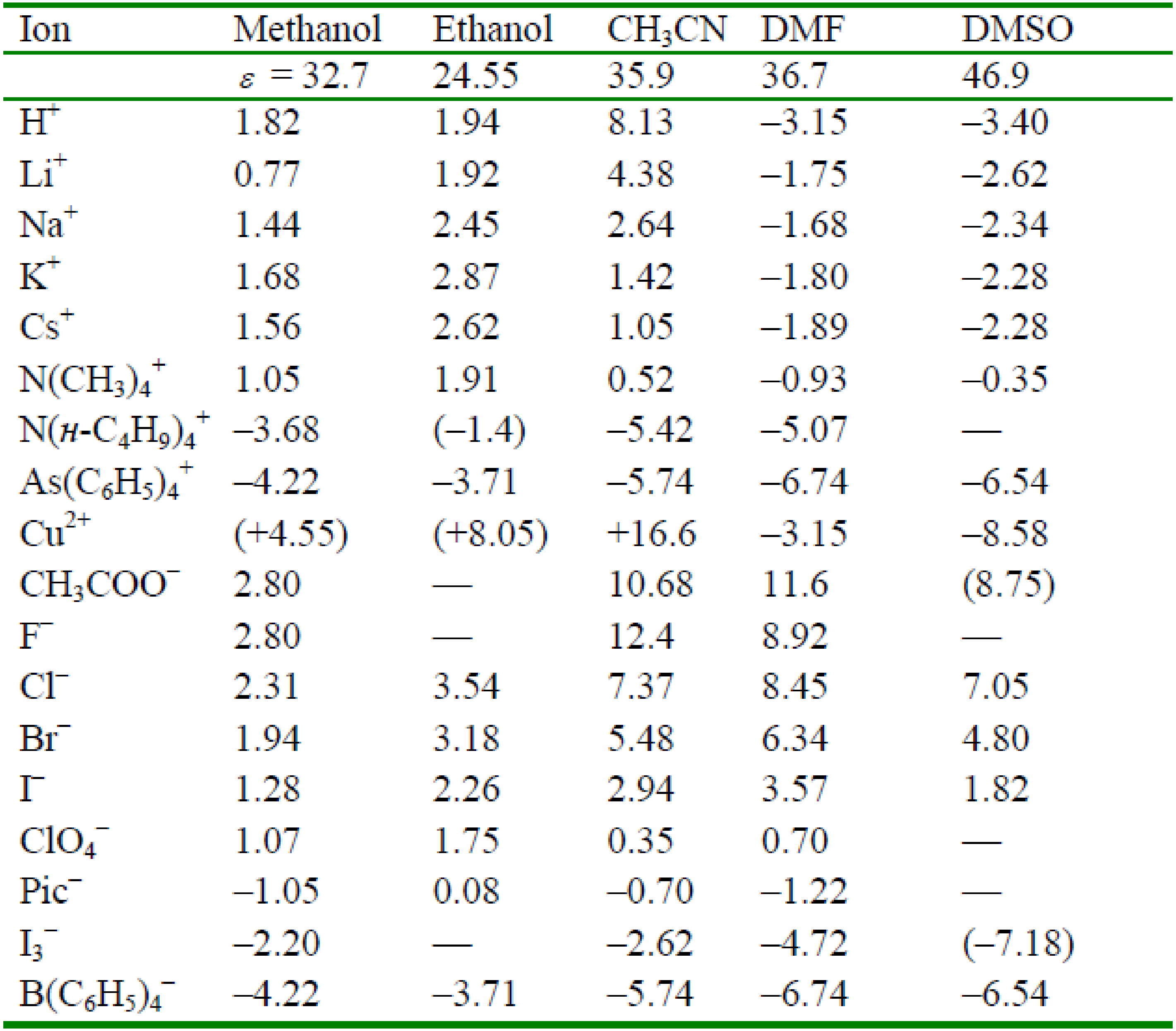
Dimethylsulfoxide



Hexamethylphosphortriamide

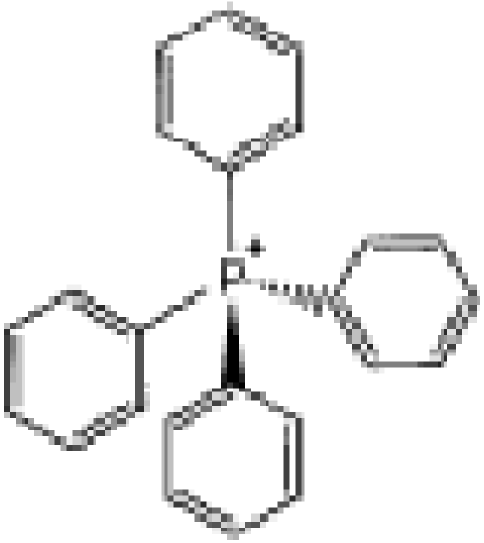


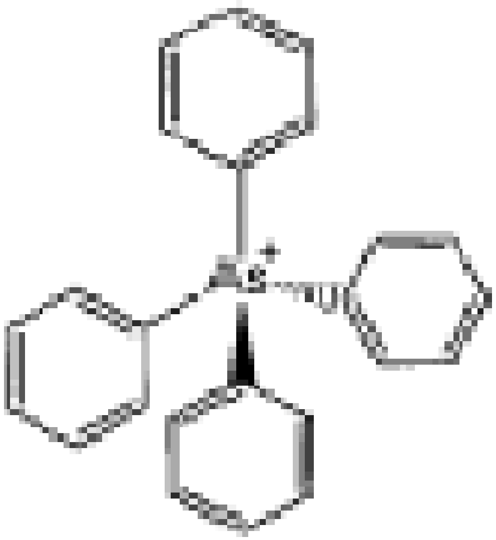
The $\log {}^{w}_{tr}\gamma^{s}_{i}$ values determined by the tetraphenylborate hypothesis

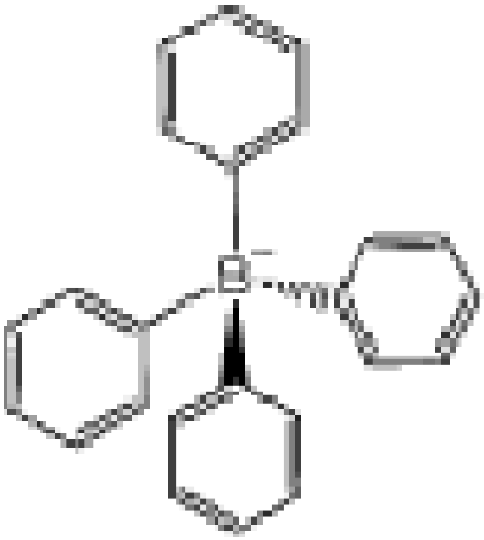


Ion	Methanol	Ethanol	CH_3CN	DMF	DMSO
	ε = 32.7	24.55	35.9	36.7	46.9
H^+	1.82	1.94	8.13	–3.15	–3.40
Li^+	0.77	1.92	4.38	–1.75	–2.62
Na^+	1.44	2.45	2.64	–1.68	–2.34
K^+	1.68	2.87	1.42	–1.80	–2.28
Cs^+	1.56	2.62	1.05	–1.89	–2.28
$N(CH_3)_4{}^+$	1.05	1.91	0.52	–0.93	–0.35
$N(n\text{-}C_4H_9)_4{}^+$	–3.68	(–1.4)	–5.42	–5.07	—
$As(C_6H_5)_4{}^+$	–4.22	–3.71	–5.74	–6.74	–6.54
Cu^{2+}	(+4.55)	(+8.05)	+16.6	–3.15	–8.58
CH_3COO^-	2.80	—	10.68	11.6	(8.75)
F^-	2.80	—	12.4	8.92	—
Cl^-	2.31	3.54	7.37	8.45	7.05
Br^-	1.94	3.18	5.48	6.34	4.80
I^-	1.28	2.26	2.94	3.57	1.82
$ClO_4{}^-$	1.07	1.75	0.35	0.70	—
Pic^-	–1.05	0.08	–0.70	–1.22	—
$I_3{}^-$	–2.20	—	–2.62	–4.72	(–7.18)
$B(C_6H_5)_4{}^-$	–4.22	–3.71	–5.74	–6.74	–6.54

$$ {}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{AsPh}_4^+} = {}^{\mathrm{w}}\gamma^{\mathrm{s}}_{\mathrm{BPh}_4^-} $$







A POSSIBLE CLASSIFICATION OF SOLVENTS

WATER

WATER-LIKE MEDIA: Alcohols
Water-organic mixtures

POLAR non-HBD (“APROTIC”): Protophilic (DMSO, etc.)
$\Delta G_{\mathrm{H^+}}(w \rightarrow s) < 0, \ DN > 20$
$(\varepsilon_r > 20)$

Protophobic (CH_3CN, etc.)

$\Delta G_{\mathrm{H^+}}(w \rightarrow s) > 0, \ DN < 20$

LOW-POLARITY SOLVENTS: Benzene, toluene, etc.

LOW-TEMPERATURE IONIC LIQUIDS: Aprotic IL

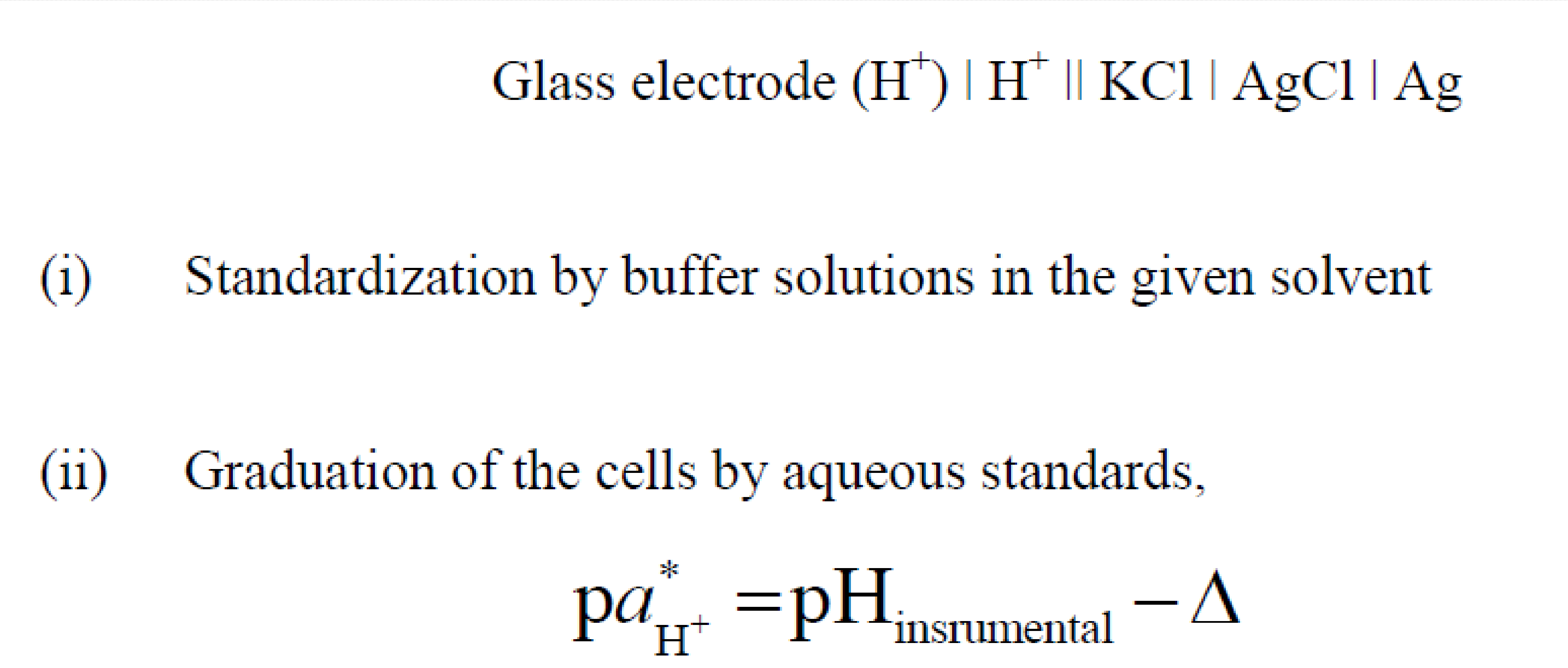
Protic IL

ACIDIC MEDIA: CH_3COOH, CF_3COOH, $HCOOH$, H_2SO_4

SUPERACIDIC MEDIA: $HF + SbCl_5$, $FSO_3H + SbCl_5$

BASIC AND SUPERBASIC MEDIA: NH_3, $H_2N–NH_2$, DMSO + KOH

pH STANDARDIZATION IN NON-AQUEOUS SOLUTIONS

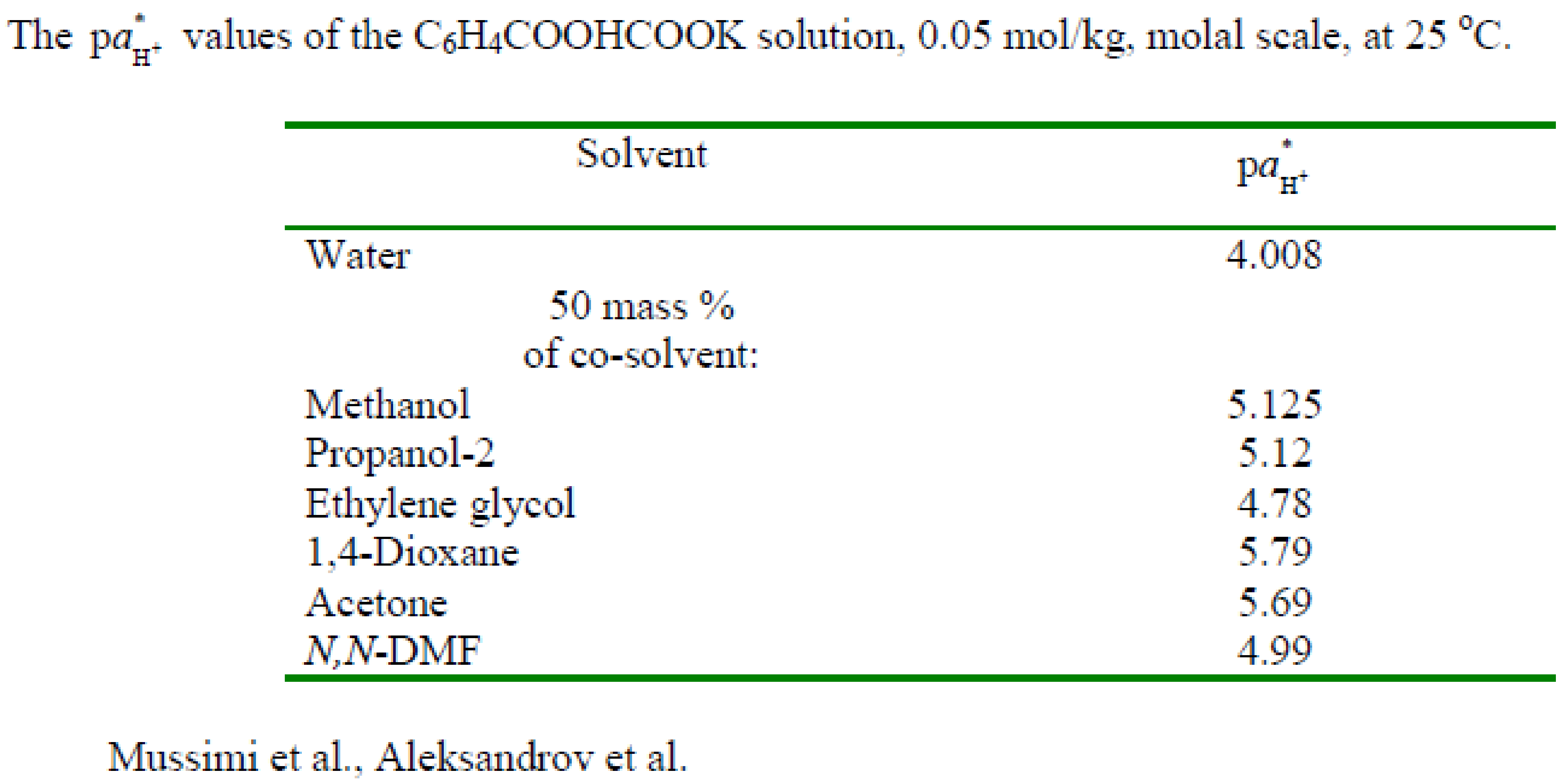


Glass electrode (H^+) | H^+ || KCl | AgCl | Ag

(i) Standardization by buffer solutions in the given solvent

(ii) Graduation of the cells by aqueous standards,

$$pa^{*}_{\mathrm{H}^{+}} = \mathrm{pH}_{\mathrm{insrumental}} - \Delta$$



The $pa^*_{H^+}$ values of the $C_6H_4COOHCOOK$ solution, 0.05 mol/kg, molal scale, at 25 °C.

Solvent	$pa^*_{H^+}$
Water	4.008
50 mass % of co-solvent:	
Methanol	5.125
Propanol-2	5.12
Ethylene glycol	4.78
1,4-Dioxane	5.79
Acetone	5.69
N,N-DMF	4.99

Mussimi et al., Aleksandrov et al.

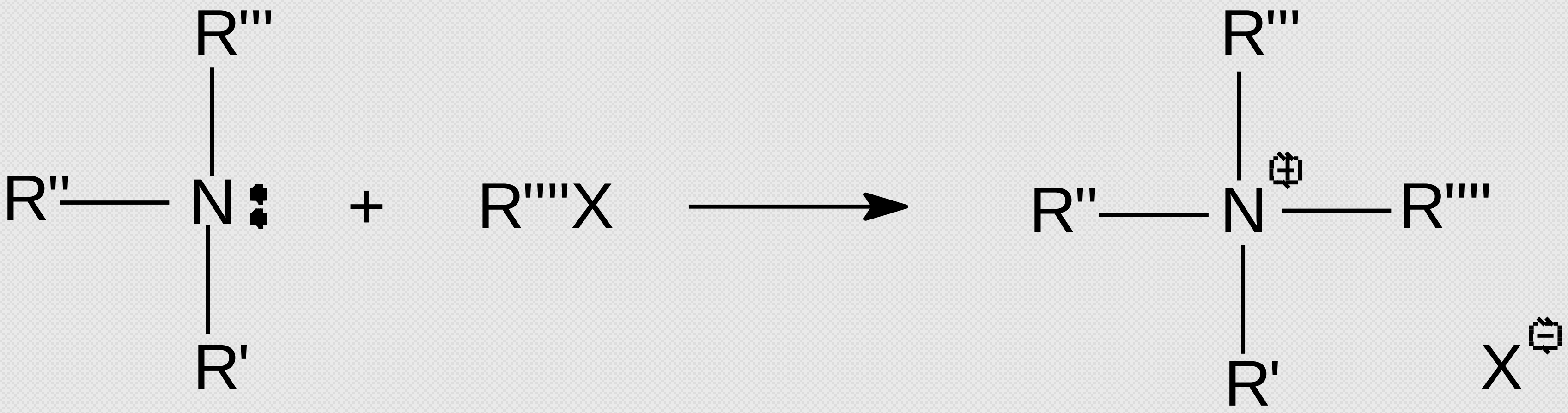
Validation of the hydrogen function of a glass electrode in an organic solvent

$$\mathrm{Pt}\left|\mathrm{H_2}\right|\mathrm{H^+}\left|\text{glass electrode}\right.$$

Measurements of E.M.F. at different pH within a wide range.

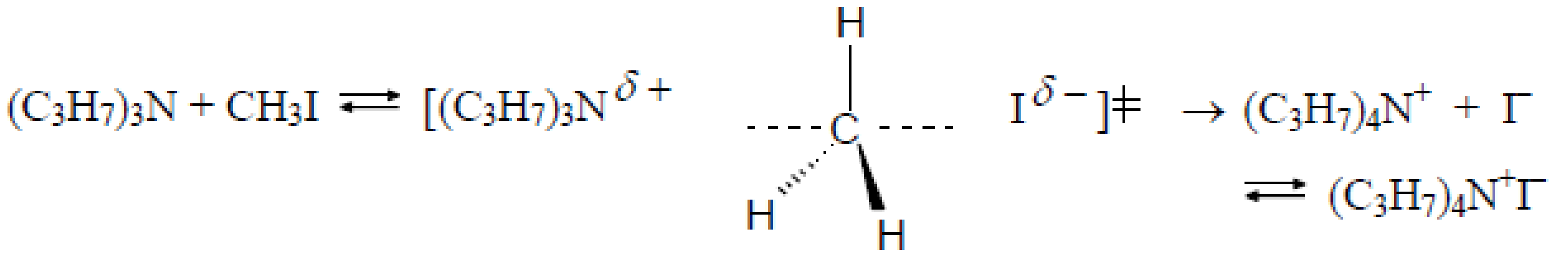
Knowing accurate pH values is unnecessary,
but the E.M.F. value must be constant.

The influence of the solvent on the reaction rate: the Menshutkin reaction



The role of solvent polarity

Quaternization reaction:



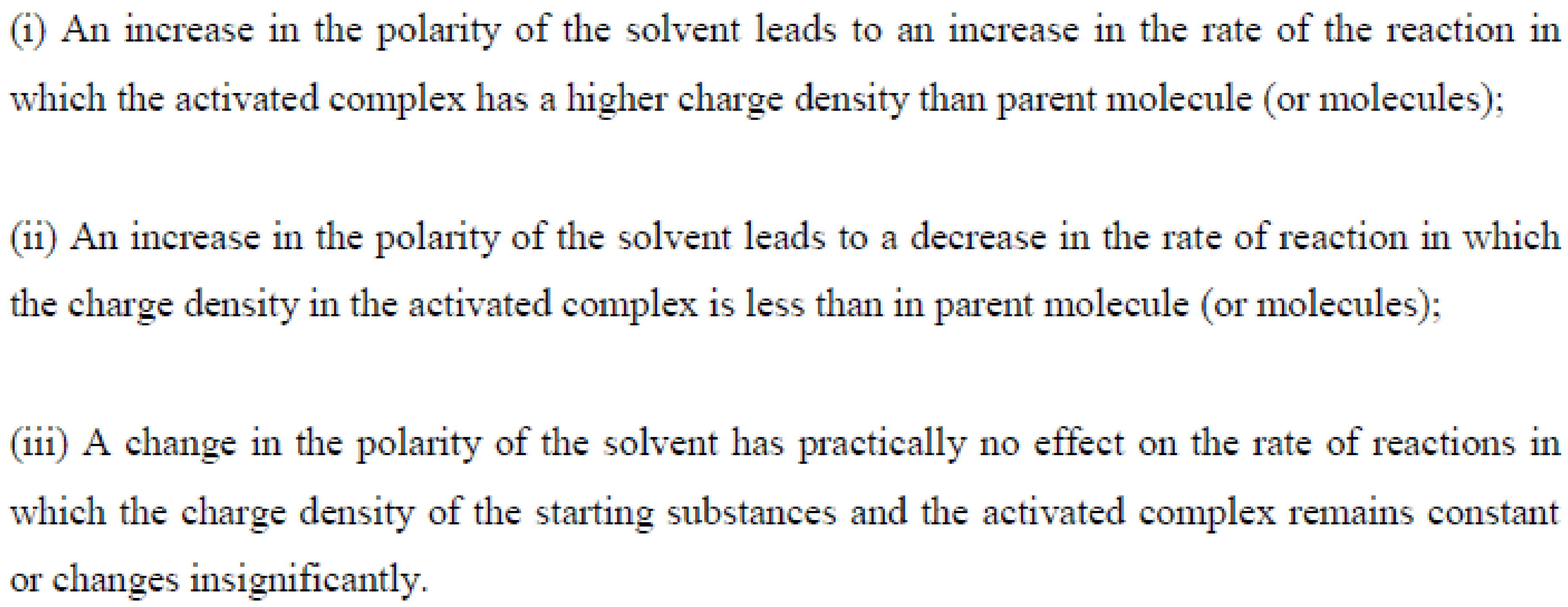
$$(C_3H_7)_3N + CH_3I \rightleftharpoons [(C_3H_7)_3N^{\delta+} \cdots \overset{H}{\underset{H\quad H}{C}} \cdots I^{\delta-}]^{\ddagger} \rightarrow (C_3H_7)_4N^{+} + I^{-} \rightleftharpoons (C_3H_7)_4N^{+}I^{-}$$

$(C_3H_7)_3N$:	$\mu = 0.70\ D$
CH_3I:	$\mu = 1.64\ D$
Activated complex:	$\mu = 8.7\ D$

At 20 °C, the reaction in **diethyl ether** is accelerated **120 times** as compared with *n*-hexane

in **$CHCl_3$**	**13 000 times**
in **CH_3NO_2**	**110 000 times**

Huges - Ingold rules



(i) An increase in the polarity of the solvent leads to an increase in the rate of the reaction in which the activated complex has a higher charge density than parent molecule (or molecules);

(ii) An increase in the polarity of the solvent leads to a decrease in the rate of reaction in which the charge density in the activated complex is less than in parent molecule (or molecules);

(iii) A change in the polarity of the solvent has practically no effect on the rate of reactions in which the charge density of the starting substances and the activated complex remains constant or changes insignificantly.

Scatchard reaction:

$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{kTR}\left(\frac{1}{\varepsilon} - 1\right).$$

Decrease in the relative permittivity on the reaction rate:

Acceleration of the reaction between cation and anion

Deceleration of the reactions of cation + cation
or anion + anion

Some factors besides the solvent polarity are important

Specific solvation; poor solvation

$$\mathrm{F^- + CH_3I \rightarrow CH_3F + I^-}$$

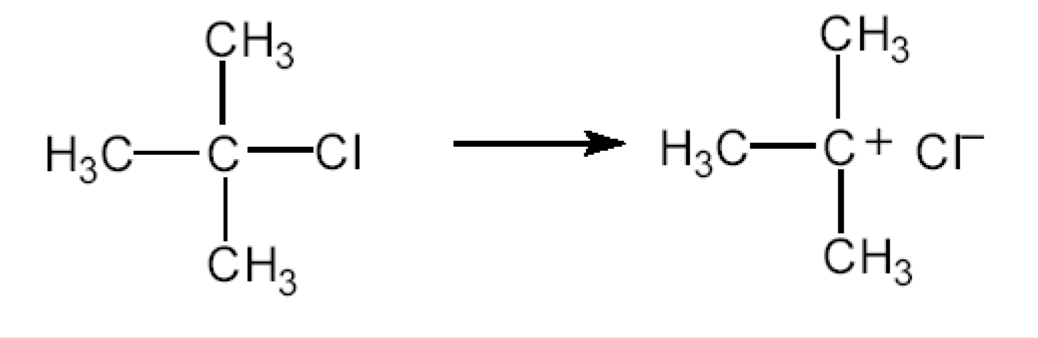
In DMSO the rate is 10^7 times higher than in alcohols

In contrast, the rupture of the Carbon–Halogen bond in triarylhalogenmethanes becomes easier in water and alcohols because of solvation of the activated complex and the halogen ion X^-

$$\mathrm{R{-}X + HO{-}R' \rightarrow [R^{\delta+} \cdots X^{\delta-} \cdots HO{-}R'] \rightarrow R^+ + X^- \cdots HO{-}R'}$$

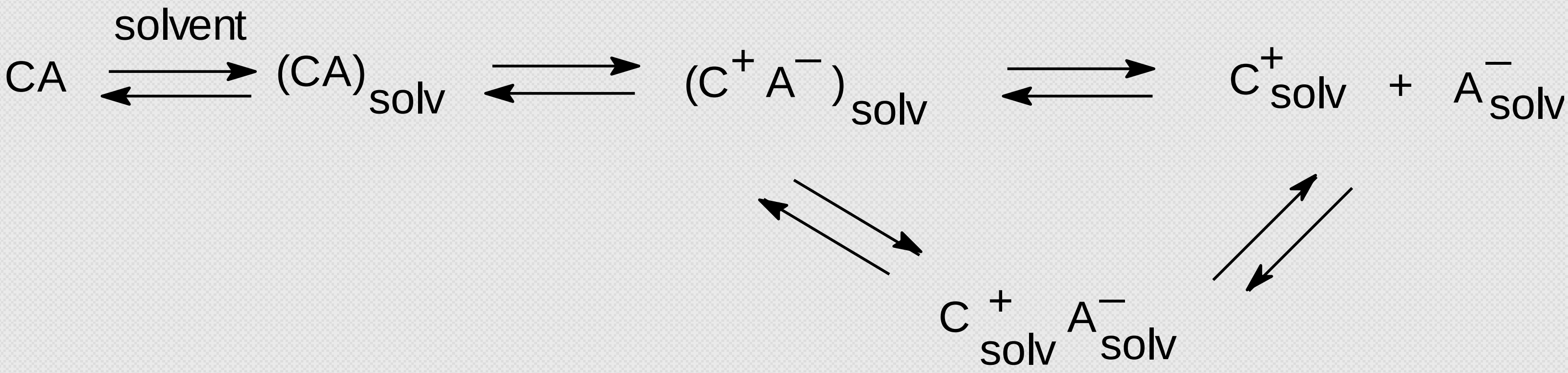
The solvolysis reaction rate

and the ionizing power of the solvent



Ionizing power of the solvent

The role of ionic associates



$$\begin{tikzcd}
\mathrm{CA} \arrow[r, shift left, "\text{solvent}"] & (\mathrm{CA})_{\mathrm{solv}} \arrow[l, shift left] \arrow[r, shift left] & (\mathrm{C}^{+}\,\mathrm{A}^{-})_{\mathrm{solv}} \arrow[l, shift left] \arrow[r, shift left] \arrow[dr, shift left] & & \mathrm{C}^{+}_{\mathrm{solv}} + \mathrm{A}^{-}_{\mathrm{solv}} \arrow[ll, shift left] \arrow[dl, shift left] \\
 & & & \mathrm{C}^{+}_{\mathrm{solv}}\;\mathrm{A}^{-}_{\mathrm{solv}} \arrow[ul, shift left] \arrow[ur, shift left] &
\end{tikzcd}$$

Two types of ionic pairs

Лупи А., Чубар Б. Солевые эффекты в органической и металлоорганической химии. М.: Мир, 1991. 376.

The E^o values in different solvents in respect to the E^o of the hydrogen electrode, ($H^+|H_2$) in the given solvent, taken as 0 at 25 °C, determines the "activity row of metals" in the given solvent.

In water: $E^o(Cu^+|Cu) = +520$ mV; $E^o(Cu^{2+}|Cu) = +340$ mV;

In acetonitrile: $E^o(Cu^+|Cu) = -360$ mV; $E^o(Cu^{2+}|Cu) = -260$ mV

In water, E^o ($Pb^{2+}|Pb$) $= -130$ mV,

In NH_3: $+ 320$ mV.

Cu_2S is insoluble in water even on high acid concentrations.

$$Cu_2S + HNO_3 \rightarrow Cu^{2+} + S\downarrow + NO_2\uparrow \text{ , or}$$

$$Cu_2S + HNO_3 \xrightarrow{t,\ ^\circ C} Cu^{2+} + HSO_4^- + NO_2\uparrow$$

Parker, 1972: **in acetonitrile** with small addition of sulfuric acid:

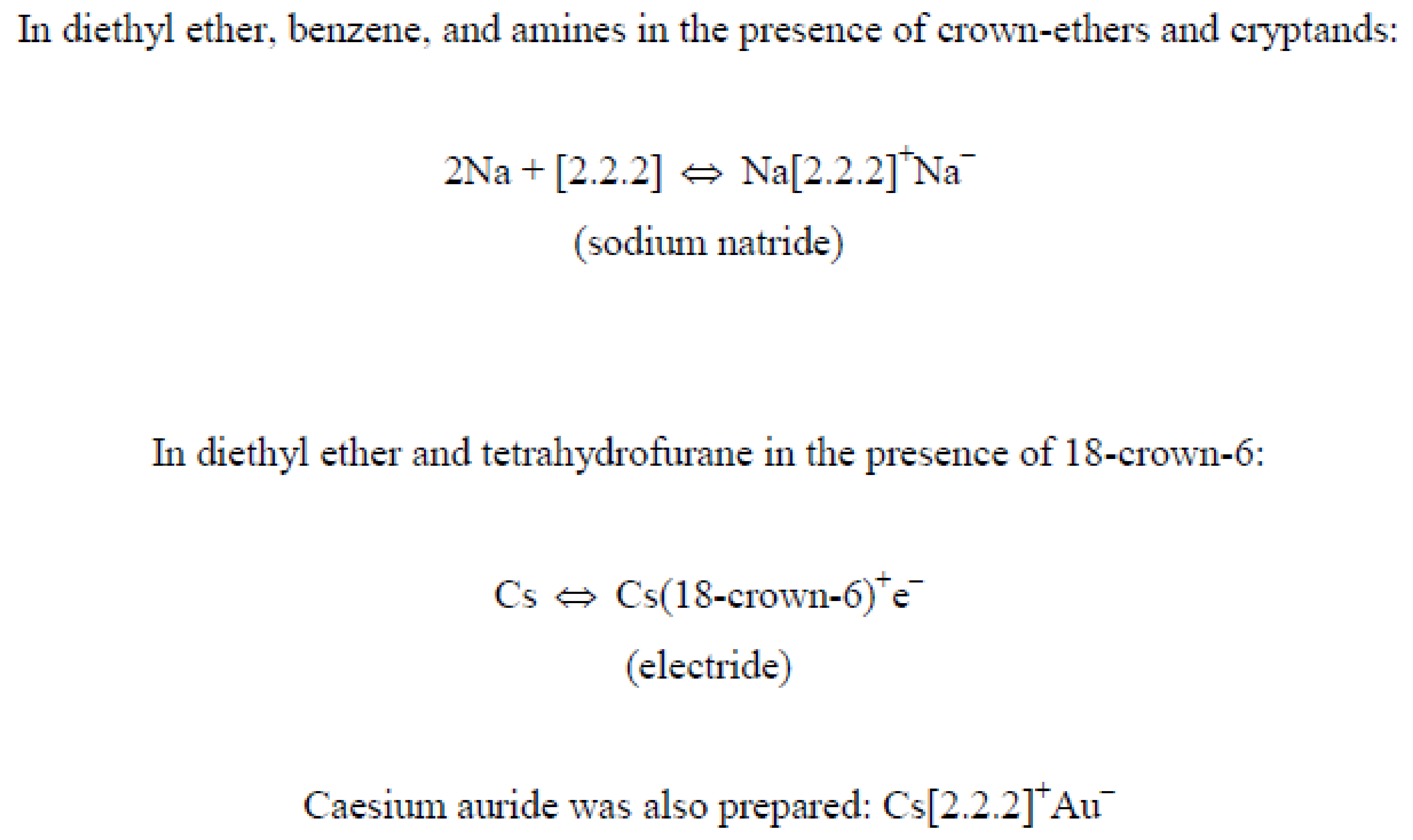
$$Cu_2S + 2H^+ \rightarrow 2Cu^+ + H_2S\uparrow$$

The reason is good solvation of Cu^+ and poor solvation of H^+.

The Cu^+ ion is colorless; H_2S slowly evaporates.

After adding water and evaporating of acetonitrile, the disproportionation takes place:

$$2Cu^+ \rightarrow \mathbf{Cu^{2+}} + \mathbf{Cu}\downarrow$$



In diethyl ether, benzene, and amines in the presence of crown-ethers and cryptands:

$$2Na + [2.2.2] \Leftrightarrow Na[2.2.2]^{+}Na^{-}$$

(sodium natride)

In diethyl ether and tetrahydrofurane in the presence of 18-crown-6:

$$Cs \Leftrightarrow Cs(18\text{-crown-}6)^{+}e^{-}$$

(electride)

Caesium auride was also prepared: $Cs[2.2.2]^{+}Au^{-}$