Scientific paper

Statistical Analysis of Gibbs Energies of Transfer of Cations and Soft Solvent Parameters

Gerhard Gritzner and Michael Auinger

Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University Linz, A-4040 Linz, Austria

* Corresponding author: E-mail: gerhard.gritzner@jku.at

Received: 15-10-2008

Dedicated to Professor Josef Barthel on the occasion of his 80th birthday

Abstract

Gibbs energies of transfer of the cations Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Tl⁺, Ba²⁺, Cu²⁺, Cd²⁺, Pb²⁺ and Hg²⁺ from water as reference into up to 42 non-aqueous solvents were analyzed by a statistical procedure based on the spectral theorem. The data set had to be separated into three groups. The first group included the alkali metal cations and Ba²⁺, the second Tl⁺, Cd²⁺ and Pb²⁺ and the third group Ag⁺ and Hg²⁺. Analysis of the respective subgroups yielded classification schemes for solvents versus the individual groups of cations. The respective solvent parameters derived from statistical analysis for the subgroups did not depend on each other. Correlations with solvent parameters claiming to account for "solvent softness" were only found for the parameters derived from the subgroup consisting of Ag⁺ and Hg²⁺. A mere separation into "hard and soft solvents" was found to be insufficient to account for the experimental data.

Keywords: Gibbs energies of transfer of cations, *bis*(biphenyl)chromium assumption, "hard and soft solvents", "soft" solvent parameters

1. Introduction

The lack of correlations of thermodynamic, spectroscopic and kinetic data in non-aqueous solvents with macroscopic solvent parameters such as the relative permittivity (Born theory), combinations of the relative permittivity and the dipole moment as developed by Bernal, Fowler, Eley and Evans^{2,3} or Buckingham's expanded model including the quadrupole moment and the induced dipole moment⁴ of solvents led to the proposal of empirical solvent parameters. Examples of such parameters are the Gutmann Donor and Acceptor numbers, ^{5,6} the Kosower Z-value⁷, the Dimroth-Reichardt $E_{\rm T}$ parameter, ^{8,9} the Koppel-Palm parameters or the Kamlet (Abboud) Taft parameters. ^{11–13} Since all of these parameters were subject to extensions in many publications, only the first paper for each parameter is quoted in this manuscript.

In the 1980'ies the "principle of hard and soft acids and bases" entered solution chemistry. This classification proposed by Pearson¹⁴ has its predecessors in concepts developed by Ahrland, Chatt and Davies¹⁵ and to a limited

extend by Schwarzenbach.¹⁶ Ahrland, Chatt and Davies focused on the stability of complexes between cations and various ligands and more or less classified cations according to the complex formation into class (a) and class (b) cations. However, both the concept of class (a) and class (b) cations as well as the "principle of hard and soft acids and bases" suffered from the lack of a unique property, which would allow unambiguous classification of cations and ligands.

In solution chemistry the proposed parameters for quantizing the "solvent softness" were based either on Gibbs energies of transfer of cations, 17,18 or on the shift of the Raman and infrared stretching vibrational frequency of mercury (II) halides (HgBr₂) in different solvents 19 or on the infrared shift of the stretching vibration of C–I of iodoacetylenes and especially of iodine cyanide, I–C \equiv N, ("soft"). 20

Single-ion transfer properties of cations and of anions are excellent probes to learn about solute – solvent interactions. ²¹ Single-ion transfer properties of cations were derived from the respective thermodynamic data for salts from different extra-thermodynamic assumptions.

The most prominent assumptions are based on either a reference electrolyte (e. g. the tetraphenylarsonium tetraphenylborate assumption^{22,23}), a reference redox system (e. g. the *bis*(biphenyl)chromium assumption²⁴) or on the assumption of a negligible diffusion potential between two different liquids (tetraethylammonium picrate assumption²⁵). These assumptions have been discussed in detail in the past. It was shown that good agreement exists between data obtained from different assumptions for many cations and solvents.²¹ This agreement in values derived from different experimental techniques and based on different assumptions strongly supports the concept of single-ion transfer properties. Such data offer an excellent tool to probe ion – solvent interactions and allow a more general understanding of chemical interactions.

In this paper we shall employ a statistical approach without any presumption to analyze whether the principle of "hard and soft acids and bases" and thus solvent parameters describing the softness of solvents is supported by single-ion Gibbs energies of transfer and whether a separation into "hard and soft" solvents only is meaningful. Our approach follows a statistical procedure introduced by Krygowskyi and Fawcett²⁶ to solution chemistry. It differs from the statistical analysis by Marcus²⁷ in as much as the analysis by Marcus already uses solvent parameters for the correlation.

2. Statistical Evaluation

The data set is analyzed without any preconditions following a published procedure.²¹

$$\Delta G_{i,j} = a_i b_j + c_j \tag{1}$$

Within this mathematical model, the Gibbs energy of transfer $\Delta G_{i,j}$ of cation j from water into solvent i scatters around a mean value c_j . This value depends only on the properties of the ion.

$$c_{j} = \frac{1}{n} \sum_{i=1}^{n} \Delta G_{i,j} \tag{2}$$

Specific solvent-solute interaction is taken into account by introducing the product of the ion parameter b_j and the solvent parameter a_i .

$$a_i b_j = \Delta G_{i,j} - c_j \quad \left(= x_{i,j}\right) \tag{3}$$

In order to fit the model with experimental data, one has to optimize:

$$\frac{1}{n} \frac{1}{m} \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\Delta G_{i,j} - \left(a_i b_j + c_j \right) \right)^2 \rightarrow \min$$
 (4)

This can be done by multiplying the reduced data set $(x_{i,j})_{n,m}$ with the transposed matrix $(x_{i,j})_{n,m}^T$ to generate a set of correlated data.

$$\begin{pmatrix}
\sum_{k=1}^{n} x_{k,1} & x_{k,1} & \sum_{k=1}^{n} x_{k,1} & x_{k,2} & \cdots & \sum_{k=1}^{n} x_{k,1} & x_{k,m} \\
\sum_{k=1}^{n} x_{k,2} & x_{k,1} & \sum_{k=1}^{n} x_{k,2} & x_{k,2} & & \vdots \\
\vdots & & \ddots & & \vdots \\
\sum_{k=1}^{n} x_{k,m} & x_{k,1} & \cdots & & \sum_{k=1}^{n} x_{k,m} & x_{k,m}
\end{pmatrix} =$$
(5)

$$= \sum_{k=1}^{n} a_{k}^{2} \begin{pmatrix} b_{1}b_{1} & b_{1}b_{2} & \cdots & b_{1}b_{m} \\ b_{2}b_{1} & b_{2}b_{2} & & \vdots \\ \vdots & & & & \vdots \\ b_{m}b_{1} & \cdots & & b_{m}b_{m} \end{pmatrix}$$

The specific ion parameter $b_{\rm j}$ is obtained by applying the spectral theorem to derive the eigenvector $v_{\rm max}$, corresponding to the biggest eigenvalue $\lambda_{\rm max}$ of this matrix.

$$v = \sum_{k=1}^{n} a_{k}^{2} \left(\frac{b_{1}}{b_{m}}, \frac{b_{2}}{b_{m}}, \frac{b_{3}}{b_{m}}, \dots, \frac{b_{m-1}}{b_{m}}, 1 \right)^{T}$$
 (6)

One data point must be selected in this model. We arbitrarily chose the value of 10 for the ion parameter b_j of Rb⁺ as in our previous publication.²¹

Finally, the specific solvent parameters a_i are calculated by using equations (1) and (4).

$$a_{i} = \frac{\sum_{j=1}^{m} x_{i,j} b_{j}}{\sum_{j=1}^{m} b_{j} b_{j}}$$
(7)

3. Data

The data used for the statistical evaluation are given in table 1. Water was chosen as a reference solvent to allow inclusion of recent data for the solvents tris(ethyl) phospite²⁸ and N,N'-dimethylpropyleneurea.²⁹ The data were derived from solubility measurements and partitioned according to the tetraphenylarsonium tetraphenylborate assumption. All other data were derived from electrochemical measurements based on the bis(biphenyl) chromium assumption.^{30–36}

4. Results

Additional data, which were measured after the publication of the original paper, allow extension of the

Table 1: Molar Gibbs energies of transfer in kJ mol⁻¹ for several cations from water as reference solvent. Unless stated otherwise the data was derived from electrochemical measurements and partitioned via the *bis*(biphenyl)chromium assumption

Water Water WeOH 15 10 10 10 10 10 10 10		Solvents	Abbr.	Γiţ	Na^{+}	\mathbf{K}^{+}	$\mathbf{R}\mathbf{b}^{+}$	cs^{+}	$\mathbf{A}\mathbf{g}^{+}$	Π^{+}	\mathbf{Ba}^{2+}	Cu ²⁺	Cd^{2+}	${ m Pb}^{2+}$	Hg^{2+}
Ethanol McCH -4.3 4.3 5.8 5.7 6.9 2.1 Filthored 1.5 8.7 9.4 8.5 1.0 0.0 Friftoncethanol Triftoncethanol Triftoncethanol 1.0 1.2 1.8 1.4 1.4 2.0 2.0 1Butanol BrOH 8.9 1.60 8 8 1.0 2.0 2.0 2.0 1.2 1.	1	Water	W	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0^{a}
Februaries Eroh 1.5 8.7 9.4 8.5 10.4 0.0	7	Methanol	MeOH	-4.3	4.3	5.8	5.7	6.9	2.1	1.3	3.7	11.0	1.2	4.0-	*
Proper P	3	Ethanol	EtOH	1.5	8.7	9.4	8.5	10.4	-0.2	4.4	18.3	22.2	3.1	10.8	5.8
I-Propanol PrOH 6.9 14.2 15.7 15.9 19.8 20.0 5.6 1-Branol HAOH 8.9 16.0 18.9 19.8 20.0 5.6 1-Lexanol Acetone AC 17.0 1.4 1.4 2.2 5.2 -5.2 1-Lexanol AC AC 1.4 1.4 2.2 5.2 -5.2 1-Lexanol AC AC 1.4 1.4 2.2 5.2 -5.2 1-Lexanol AC AC AC AC AC 4.4 1.4 4.5 5.2 -5.2 2.2 5.2	4	Trifluoroethanol	TFEtOH	*	*	*	*	*	46.8	33.0	*	139.7	127.7	0.86	*
-Buttnool BuOH 96 170 18.9 19.8 20.0 56 -Ethanecol ETDI -1.3 1.4 1.4 2.2 5.2 5.2 -Ethanecol ETDI -1.3 1.4 1.4 2.1 3.7 9.3 -Ethanecol ETDI -1.3 1.4 9.1 8.5 0.0 2.8 -Ethanecol ETDI ETDI -1.3 1.4 9.1 8.5 0.0 2.8 -Ethanecol ETDI ETDI -1.3 1.4 9.1 8.5 0.0 3.1 -Ethanecol ETDI ETDI -1.0 -6.2 3.8 4.1 6.8 -Ethanecol ETDI ETDI -1.1 -6.4 4.8 -3.9 -2.1 -Ethanecol ETDI ETDI -1.1 -6.4 -4.8 -3.9 -2.1 -Ethanecol ETDI ETDI -1.1 -6.4 -4.8 -3.9 -2.1 -Ethanecol ETDI ETDI -1.1 -6.1 -4.8 -3.9 -2.1 -Ethanecol ETDI ETDI -1.0 -3.4 -1.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.8 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.8 -3.4 -3.8 -Ethanecol ETDI ETDI -3.5 -3.8 -3.4 -3.8 -Ethanecol ETDI ETDI -3.8 -3.8 -3.8 -3.8 -3.8 -3.8 -3.8 -Ethanecol ETDI ETDI -3.8 -3.	5	1-Propanol	PrOH	6.9	14.2	15.7	15.9	14.1	5.6	6.5	18.9	24.7	9.5	13.1	*
HyOH 8.9 16.0 8. 6.9 Accorded AC 1.3 1.4 1.4 2.2 5.2 5.2 Tetrahaction AC 9.6 4.1 1.4 0.4 1.7 4.5 Tetrahydrofurane BL 1.5 3.1 3.1 3.1 3.1 3.1 Propylene carbonate BC 2.5.3 18.3 10.3 6.0 7.7 2.3.7 Trinchtyphosphate PC 2.5.3 18.3 10.3 6.0 7.7 2.3.7 N.A.Dimethylormanide DMA -1.5 -5.3 -7.7 -4.4 -4.8 -1.9 N.A.Dimethylormanide DMA -1.8 -1.1 -6.4 -4.8 -3.9 -2.7 -1.2.1 N.A.Dimethylormanide DMA -1.8 -1.0 -7.0 -5.4 -1.8 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.2 -2.3 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.4 -1.8 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.2 -2.3 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.4 -1.8 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.4 -1.8 N.A.Dimethylormanide DMA -1.8 -1.0 -1.0 -5.4 -1.8 N.A.Dimethylormanide DMS -2.0 -1.2 -1.0 -5.4 -1.8 N.A.Dimethylormanide DNS -3.5 -1.3 -1.4 -1.4 -3.5 A.A.Dimethylormanide DNS -3.5 -1.2 -1.0 -5.4 -1.8 Butamitrile BUN 2.5 1.2 -1.4 -1.4 -1.5 -2.0 Phenylacetonitrile BN 3.4 3.1 3.1 -4.4 3.1 3.1 Phenylacetonitrile BN 3.4 3.1 3.1 -4.4 3.1 3.1 Phyrol Phy	9	1-Butanol	BuOH	9.6	17.0	18.9	19.8	20.0	2.6	9.6	24.1	29.3	41.1	28.9	*
1.2-Ethanedio ETDI -1.3 1.4 1.4 2.2 5.2 -5.2 Acctione AC 5.6 4.1 1.4 0.4 1.5 2.8 Butyrolactone BL 15.4 9.1 8.5 0.3 2.8 Butyrolactone BL 15.4 9.1 8.5 0.3 2.8 Butyrolactone BL 15.4 9.1 8.5 0.3 3.7 9.3 Trimethyplosphane TMP -21.3 10.3 6.0 7.7 2.3 Formamide FA 8.1 8.1 8.1 8.6 7.7 1.5 Formamide DMF 1.15 8.0 7.2 6.4 4.5 1.5 N.A-Dinethylformamide DMF 1.19 8.0 7.2 6.4 4.5 1.5 N.A-Dinethylformamide DEF 1.14 6.4 4.8 7.3 7.1 1.0 N.A-Dinethylformamide DEF 1.14 6.4 4.8 7.3 7.3 1.5 1.5 N.A-Dinethylformamide DEF 1.14 6.4 4.8 7.5 6.2 2.3 N.A-Dinethylformamide DEF 1.14 6.4 4.8 7.3 7.3 7.3 1.5 1.5 N.A-Dinethylformamide DEF 1.14 6.4 4.8 7.5 6.5 7.3 4.4 N.A-Dinethylformamide DEF 1.14 6.4 4.4 3.1 3.1 3.4	7	1-Hexanol	HXOH	8.9	16.0	*	*	*	6.9	9.9	11.4	*	24.5	8.3	*
Actione AC 96 41 14 -04 17 45 Ternalydrofurane BL 154 9.1 8.5 -0.9 2.8 Butyolactone BL 154 9.3 2.6 3.1 9.3 Propylene carbonate PC 25.3 18.3 10.3 6.0 7.7 2.3.7 Trimethylposphate FA ** ** ** ** -6.8 NA-Dimethylformamide DMF -1.5 -5.3 -3.7 -4.1 -0.6 -19.1 NA-Dimethylformamide DMF -1.9 -8.0 -7.2 -4 -4.5 -15.1 NA-Dimethylformamide DMA -1.8 -1.0 -7.2 -4 -4.5 -15.1 NA-Dimethylformamide DMA -1.8 -1.0 -7.2 -4 -4.5 -15.1 NA-Dimethylforophoric trimide DMA -1.8 -1.0 -7.2 -4 -2.3 -2.4 -2.3 NA-N-N-A-Terramethylmrea<	∞	1,2-Ethanediol	ETDI	-1.3	1.4	1.4	2.2	5.2	-5.2	-3.1	-12.9	5.4	13.7	-10.8	*
Tetrahydrofunane THF 6.3 1.4 9.1 8.5 -0.9 2.8 Butyolactone BL 15.4 9.3 2.6 3.1 3.7 9.3 Propyclane carbonate PC 25.3 18.3 10.3 6.0 7.7 23.7 Trimethylphosphate FA * * * * * 8.6 -6.8 -4.1 -8.6 N.W. Dimethylformamide DMF -11.5 -5.3 -3.7 -4.1 -6.8 -6.4 -6.8 -6.9 -5.3 -5.1 -15.1 -6.9 -5.3 -15.1 <t< td=""><td>6</td><td>Acetone</td><td>AC</td><td>9.6</td><td>4.1</td><td>1.4</td><td>4.0-</td><td>1.7</td><td>4.5</td><td>3.1</td><td>5.6</td><td>69.1</td><td>52.1</td><td>46.1</td><td>*</td></t<>	6	Acetone	AC	9.6	4.1	1.4	4.0-	1.7	4.5	3.1	5.6	69.1	52.1	46.1	*
Butyrolactone BL 154 93 26 31 37 93 Propyclene carbonate PC 25.3 18.3 10.3 6.0 7.7 23.7 Trimethylphosphate FA -1.3 -1.0 -6.2 -3.8 +1.0 -6.8 Formamide NAME -1.5 -5.3 -3.7 -4.1 -0.6 -19.1 N.W-Dientylpformamide DEF -11.4 -6.4 -4.8 -3.9 -2.7 -15.1 N.W-Dientylformamide DEF -11.4 -6.4 -4.8 -3.9 -2.7 -10.1 N.W-Dientylformamide DEA -25.6 -10.8 -7.6 -4.5 -2.4 -12.1 N.W-Dientylformamide DEA -25.6 -10.4 -5.5 -2.4 -12.1 N.W-Dientylformamide DEA -25.0 -10.4 -5.5 -2.4 -12.1 N.W-Dientylforphosphereura DMPU -25.1 -10.2 -7.0 -2.3 -2.3 -10.2	10	Tetrahydrofurane	THF	6.3	1.4	9.1	8.5	6.0-	2.8	2.9	0.4	-10.6	15.4	8.1	9.3
Propylene carbonate PC 25.3 18.3 10.3 6.0 7.7 23.7 Trimethylbosphate FA -21.3 -10.0 -6.2 -3.8 -4.1 -6.8 Formamide FA -1.3 -10.0 -6.2 -3.8 -4.1 -6.8 N-Methylformamide DMF -11.5 -5.3 -3.7 -4.1 -6.6 -19.1 N/A-Dimethylformamide DMF -11.9 -6.4 -4.8 -15.1 N/A-Dimethylforcamide DMF -11.3 -10.4 -6.5 -5.4 -13.1 N/A-Dimethylforchylfurca DMPO -25.6 -10.8 -7.6 -4.9 -5.2 -2.3.4 N/A-MA/A-Tertamethylfurca DMPU -10.0 -9.7 -10.5 -5.4 -18.8 N/A-Dimethylpropyleneurea DMPU -10.0 -6.7 -5.4 -18.8 N/A-Dimethylpropyleneurea DMPU -11.2 -4.4 -3.2 -2.7 N/A-Dimethylpropyleneurea DMPU -11.2	11	Butyrolactone	BL	15.4	9.3	5.6	3.1	3.7	9.3	3.1	*	49.4	52.3	*	*
Trimethylphosphate TMP -21.3 -10.0 -6.2 -3.8 4.1 -8.6 Formanide FA * * * * * -8.8 N.W.Dimethylformanide DMF -11.9 -8.0 -7.2 -6.4 -4.5 -15.1 N.W.Diethylformanide DBA -11.4 -6.4 -4.9 -5.7 -12.1 N.W.Diethylformanide DBA -18.3 -11.0 -10.4 -5.2 -5.4 -15.1 N.W.Diethylformanide DBA -18.3 -11.0 -10.4 -5.2 -5.4 -13.1 N.W.Diethylformanide DBA -25.6 -10.8 -7.6 -4.9 -5.2 -5.4 -18.3 N.W.Diethylforetamide DBA -1.0 -0.7 -10.4 -5.5 -5.4 -18.3 N.W.Diethylforetamidylpropyleneuera DMBO -1.0 -1.0 -7.2 -1.1 -5.2 -2.3.4 -1.8.8 N.W.Diethylforetamidylpropyleneuera DMBO -1.7 -10	12	Propylene carbonate	PC	25.3	18.3	10.3	0.9	7.7	23.7	12.1	33.8	72.9	79.1	42.8	55.4
Formanide FA * * -6.8 N.W.Dienklylformanide NMF -15.5 -3.7 -4.1 -0.6 -19.1 N.W.Dimethylformanide DMF -11.9 -8.0 -7.2 -6.4 -4.5 -5.4 -2.7 -15.1 N.W.Dimethylformanide DMF -11.4 -6.4 -4.8 -3.9 -2.7 -12.1 N.W.Diethylacetamide DMA -18.3 -11.0 -10.4 -5.5 -5.4 -2.3.4 N.W.Diethylacetamide DMA -19.0 -9.7 -10.6 -5.2 -2.3.3 N.W.Diethylacetamide DMA -2.5 -10.1 -6.7 -4.9 -5.2 -2.3.3 N.W.D.Jonethylacetamide DMPU -2.5 -10.1 -6.7 -4.9 -5.2 -2.3.3 N.W.W.A.P.Tetramethylacetamide DMPU -2.5 -10.1 -6.7 -4.9 -5.2 -2.3.3 N.W.W.A.P.Dimethylacetamide DMPU -2.5 -1.1 -1.4 -1.1 -1.4 <t< td=""><td>13</td><td>Trimethylphosphate</td><td>TMP</td><td>-21.3</td><td>-10.0</td><td>-6.2</td><td>-3.8</td><td>4.1</td><td>9.8–</td><td>-5.7</td><td>-42.3</td><td>11.6</td><td>-5.8</td><td>-23.9</td><td>-5.2</td></t<>	13	Trimethylphosphate	TMP	-21.3	-10.0	-6.2	-3.8	4.1	9.8–	-5.7	-42.3	11.6	-5.8	-23.9	-5.2
N. Methyl fromamide NMF -15.5 -5.3 -3.7 -4.1 -0.6 -19.1 N. W. Dinethyl formamide DMF -11.9 -8.0 -7.2 -6.4 -4.5 -15.1 N. W. Dinethyl formamide DMA -11.9 -8.0 -7.0 -6.4 -4.5 -15.1 N. W. Diethyl formamide DMA -18.3 -11.0 -10.4 -5.5 -5.4 -23.4 N. W. Diethyl forcetamide DEA -25.6 -10.8 -7.0 -5.4 -18.3 N. W. Diethyl forcetamide DMP -19.0 -9.7 -10.5 -7.0 -5.4 -18.8 N. W. W. W. J. Etamethyl forcetamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 -18.8 M. W. W. W. J. Etamethyl forcetamide HMP * -24.9 -13.8 -9.1 -6.7 -6.7 -6.7 -2.2 -2.4 -18.8 M. W. Diethylorophic triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 <td>14</td> <td>Formamide</td> <td>FA</td> <td>*</td> <td>*</td> <td>*</td> <td>*</td> <td>*</td> <td>-6.8</td> <td>1:1</td> <td>*</td> <td>-2.7</td> <td>-16.2</td> <td>-15.8</td> <td>*</td>	14	Formamide	FA	*	*	*	*	*	-6.8	1:1	*	-2.7	-16.2	-15.8	*
N.N-Dimethylformamide DMF -11.9 -8.0 -7.2 -6.4 -4.5 -15.1 N.N-Dimethylformamide DEF -11.4 -6.4 -4.8 -3.9 -2.7 -12.1 N.N-Diethylacoramide DBA -18.4 -1.0 -6.4 -5.2 -2.3.4 N.N-Diethylacoramide DBA -25.6 -10.8 -7.6 -4.9 -5.2 -23.4 N.N-Diethylacoramide NMP -19.0 -9.7 -10.5 -7.0 -5.4 -18.8 N.N-N-N-Tetramethylacoramide HMP -8.7 -10.1 -6.7 -5.2 -23.3 N.N-Dimethylacophoric trainide HMP -8.2 -13.8 -9.1 -6.6 -36.4 Hexamethylacosulfine DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -5.9 Furnachylacosulfine DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -2.4 Accountrile Propamitrile PRN 28.9 14.3 7.0 6.6	15	<i>N</i> -Methylformamide	NMF	-15.5	-5.3	-3.7	4.	9.0-	-19.1	-8.6	-45.2	-28.8	-20.5	-36.3	*
N.W-Diethylformamide DEF -11.4 -64 -4.8 -3.9 -2.7 -12.1 N.W-Diethylformamide DMA -18.3 -11.0 -10.4 -5.5 -5.4 -23.4 N.W-Diethylacetamide DBA -18.3 -11.0 -10.4 -5.5 -5.4 -23.4 N.W-Diethylacetamide DBA -19.0 -9.7 -10.5 -7.0 -5.4 -13.3 N.W.N.M-Tetramethylurea TMU -25.1 -12.2 -10.1 -6.7 * -22.4 N.W.N.M-Tetramethylurea TMU -25.1 -12.2 -10.1 -6.7 * -22.4 H.W.W.N.M-Tetramethylurea TMU -25.1 -12.2 -10.1 -6.7 * -22.4 -18.8 H.W.W.N.M-Tetramethylurea TMN * -13.3 -13.3 -13.4 -36.5 -11.4 -6.6 -36.4 -33.4 -36.4 -33.4 -36.5 -14.4 -36.5 -36.4 -18.8 -2.7 -13.8 -13.4 -36.5 <td>16</td> <td><i>N,N</i>-Dimethylformamide</td> <td>DMF</td> <td>-11.9</td> <td>-8.0</td> <td>-7.2</td> <td>-6.4</td> <td>4.5</td> <td>-15.1</td> <td>-11.3</td> <td>-39.6</td> <td>-32.0</td> <td>-22.0</td> <td>-38.2</td> <td>-33.8</td>	16	<i>N,N</i> -Dimethylformamide	DMF	-11.9	-8.0	-7.2	-6.4	4.5	-15.1	-11.3	-39.6	-32.0	-22.0	-38.2	-33.8
N.N-Dimethylacetamide DMA -18.3 -11.0 -10.4 -5.5 -5.4 -23.4 N.N-Dimethylacetamide DEA -25.6 -10.8 -7.6 -4.9 -5.2 -23.3 N-N-Diethylacetamide NMP -25.6 -10.8 -7.6 -4.9 -5.2 -23.3 N-N-Ly-Etramethylucea TMU -25.1 -12.2 -10.1 -6.7 -5.4 -18.8 N/N-Dimethylprosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 -18.8 N/N-Dimethylprosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 -18.8 Teramethylprosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 -36.5 Teramethylprosphoric triamide DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Ethylene sulfine SN 6.3 -3.4 -1.3 -1.4 -3.5 Acetonitrile B	17	N,N-Diethylformamide	DEF	-11.4	-6.4	4.8	-3.9	-2.7	-12.1	-10.2	*	-29.7	-20.3	-40.3	*
N,N-Diethylacetamide DEA -25.6 -10.8 -7.6 -4.9 -5.2 -23.3 N-Methyl-2-pytrolidone NMP -19.0 -9.7 -10.5 -7.0 -5.4 -18.8 N/N-V-Dimethylpropyleneurea TMU -2.1 -10.1 -6.6 -36.4 -18.8 N/N-Dimethylpropyleneurea TMMP * -24.9 -13.8 -9.1 -6.6 -36.4 Hexamethylpropyleneurea TMMP * -24.9 -13.8 -9.1 -6.6 -36.4 Hexamethylpropyleneurea TMMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tetramethylpropyleneurea TMS 23.2 11.2 4.4 3.1 -6.6 -36.4 Tetramethylprosphoric triamide DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Dimethylsulformamitie AN 28.9 14.3 7.0 -6.6 -3.4 -1.14 -36.5 Acetonitrile AN 28.9 14.3	18	<i>N,N</i> -Dimethylacetamide	DMA	-18.3	-11.0	-10.4	-5.5	-5.4	-23.4	-11.5	*	-28.4	-21.4	-40.5	*
N-Methyl-2-pyrrolidone NMP -19.0 -9.7 -10.5 -7.0 -5.4 -18.8 N/N/N/Tertamethylurea TMU -25.1 -12.2 -10.1 -6.7 * -22.4 N/N/N/Tertamethylurea TMS -25.1 -12.2 -10.1 -6.7 * -22.4 N/N-Dimethylposphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tertamethylensulfone DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Ethylenesulfite ES 60.7 17.8 12.6 * -50.0 Acctonitrile PR AN 28.9 14.3 7.0 6.6 7.8 -23.0 Acctonitrile BUN \$ 27.0 16.8 19.9 17.6 16.2 -19.0 Benzonitrile BN \$ 2.0 1.5 \$ 2.0 18.4 -13.1 9 17.6 16.2 19.0 Benzonitrile <td< td=""><td>19</td><td><i>N,N</i>-Diethylacetamide</td><td>DEA</td><td>-25.6</td><td>-10.8</td><td>9.7-</td><td>4.9</td><td>-5.2</td><td>-23.3</td><td>-11.4</td><td>-48.2</td><td>-26.2</td><td>-25.3</td><td>-38.0</td><td>*</td></td<>	19	<i>N,N</i> -Diethylacetamide	DEA	-25.6	-10.8	9.7-	4.9	-5.2	-23.3	-11.4	-48.2	-26.2	-25.3	-38.0	*
N,N,N,Tetramethylurea TMU -25.1 -12.2 -10.1 -6.7 * -22.4 N,N-N,M-Tetramethylurea DMPU * -18.3 -13.1 -14.3 -11.4 -36.5 M,N-Dimethylproppleneurea HMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tetramethylprosphoric triamide TMS -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Dimethylsulfoxide ES 60.7 17.8 12.6 * 20.6 Ethylenesulfite BN 28.9 14.3 7.0 6.6 7.8 -23.0 Ethylenesulfite BN 28.9 14.3 7.0 6.6 7.8 -20.9 Actonitrile BN 25.7 15.2 9.2 * * -21.8 Butannitrile BUN 25.7 15.2 9.2 * * -21.8 Isobutyronitrile BN 34.6 22.0 13.2 13.0 Bhenylanding	20	<i>N</i> -Methyl-2-pyrrolidone	NMP	-19.0	7.6 -	-10.5	-7.0	-5.4	-18.8	-14.1	-55.2	-18.9	-23.5	-39.2	-38.8
N,N-Dimethylpropyleneurea DMPU * -18.3 -13.1 -14.3 -11.4 -36.5 Hexamethylphosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tetramethylphosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tetramethylphosphoric triamide DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Ethylenesulfite AN 28.9 14.3 7.0 6.6 7.8 -29.0 Acetonitrile AN 25.7 15.2 9.2 * -22.4 Butannitrile BUN * 16.3 * * -21.8 Isobutyronitrile BN 34.6 22.0 13.2 12.0 11.6 -13.8 Isobutyronitrile BN 34.6 22.0 13.2 12.0 11.6 -23.0 Benzonitrile PAN 38.6 22.0 12.0 14.4 38.1 *	21	<i>N,N,N</i> , <i>N</i> –Tetramethylurea	TMU	-25.1	-12.2	-10.1	-6.7	*	-22.4	-15.0	41.9	15.1	1.7	-48.0	*
Hexamethylphosphoric triamide HMP * -24.9 -13.8 -9.1 -6.6 -36.4 Tetramethylphosphoric triamide TMS 23.2 11.2 4.4 3.1 3.7 9.5 Dimethylsulfoxide ES 60.7 17.8 12.6 * 20.9 Ethylenesulfite ES 60.7 17.8 12.6 * 20.9 Acconitrile BN 28.9 14.3 7.0 6.6 7.8 -23.0 Propamitrile BUN 28.9 14.3 7.0 6.6 7.8 -23.0 Butamitrile BUN 27.9 16.8 19.9 17.6 16.2 -19.0 Butamitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Butamitrile BN 34.6 22.0 13.2 12.0 11.6 11.7 Butamitrile BN 34.6 22.0 13.2 12.0 12.1 Benzomitrile BN <td< td=""><td>22</td><td><i>N,N'</i> -Dimethylpropyleneurea</td><td>DMPU</td><td>*</td><td>-18.3</td><td>-13.1</td><td>-14.3</td><td>-11.4</td><td>-36.5</td><td>-9.2_b</td><td>*</td><td>*</td><td>*</td><td>*</td><td>*</td></td<>	22	<i>N,N'</i> -Dimethylpropyleneurea	DMPU	*	-18.3	-13.1	-14.3	-11.4	-36.5	-9.2 _b	*	*	*	*	*
Tetramethylensulfone TMS 23.2 11.2 4.4 3.1 3.7 9.5 Dimethylsulfoxide DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Ethylenesulfite ES 60.7 17.8 12.6 * * 20.6 Acctonitrile PRN 28.9 14.3 7.0 6.6 7.8 -29.0 Butannitrile BUN * 15.2 9.2 * -22.4 Butannitrile BUN * 16.3 * * -22.4 Butannitrile BN * 16.3 * * -22.4 Boutyronitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile BN 38.6 20.9 * * -22.0 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Aniline Aniline ANI 44.4 38.1 <td< td=""><td>23</td><td>Hexamethylphosphoric triamide</td><td>HIMP</td><td>*</td><td>-24.9</td><td>-13.8</td><td>-9.1</td><td>9.9–</td><td>-36.4</td><td>-23.8</td><td>-73.5</td><td>-61.9</td><td>-35.7</td><td>-60.0</td><td>-75.3</td></td<>	23	Hexamethylphosphoric triamide	HIMP	*	-24.9	-13.8	-9.1	9.9–	-36.4	-23.8	-73.5	-61.9	-35.7	-60.0	-75.3
Dimethylsulfoxide DMSO -34.7 -10.0 -8.3 -7.5 -7.0 -29.9 Ethylenesulfite ES 60.7 17.8 12.6 * 20.6 Acetonitrile AN 28.9 14.3 7.0 6.6 7.8 -23.0 Propannitrile BUN 25.7 15.2 9.2 * 2.2.4 Butannitrile BUN 3.7 16.3 17.6 6.6 7.8 -23.0 Bonzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile PAN 38.6 20.9 * * -12.7 Phenylacetonitrile PAN 38.6 20.9 11.6 -15.1 Phyridine PAN 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PY 6.9 6.3 5.8 7.0 -63.4 Aniline ME * * * * * -	24	Tetramethylensulfone	TMS	23.2	11.2	4.4	3.1	3.7	9.5	3.1	18.1	6.69	65.8	33.2	*
Ethylenesulfite ES 60.7 17.8 12.6 * 20.6 Acetonitrile AN 28.9 14.3 7.0 6.6 7.8 -23.0 Propannitrile BUN 25.7 15.2 9.2 * -22.4 Butannitrile BUN * 16.3 * * -21.8 Isobutyronitrile BN 34.6 22.0 13.2 17.6 16.2 -19.0 Benzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phyridine PAN 38.6 20.9 * * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PK 71.5 50.3 51.7 51.6 -12.7 Aniline ME * * * * * -24.4 Aniline ME * * * * * -25.7	25	Dimethylsulfoxide	DMSO	-34.7	-10.0	-8.3	-7.5	-7.0	-29.9	-19.1	49.4	-28.6	-42.5	-56.0	-57.3
Acetonitrile AN 28.9 14.3 7.0 6.6 7.8 -23.0 Propannitrile PRN 25.7 15.2 9.2 * -22.4 Butannitrile BUN * 16.3 * * -21.8 Isobutyronitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PL 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline ME * * * * -36.1 Aniline ME * * * -36.1 Mercaptochanol TTDE * * * * -55.7 Thiophenol TFP * * * * -57.8 Triophenol	56	Ethylenesulfite	ES	60.7	17.8	12.6	*	*	20.6	11.9	*	71.6	62.9	41.7	53.3
Propannitrile PRN 25.7 15.2 9.2 * -22.4 Butannitrile BUN * 16.3 * * -21.8 Isobutyronitrile BUN 27.9 16.8 19.9 17.6 16.2 -19.0 Benzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile PAN 38.6 20.9 * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PL 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline ME * * * * * -36.1 Mercaptochanol ME * * * * * -36.1 Thiophenol TPP * * * * * -55.7 Triophenol TPT * * * * -54.8	27	Acetonitrile	AN	28.9	14.3	7.0	9.9	7.8	-23.0	8.6	42.6	*	42.5	41.9	3.3
Butannitrile BUN * 16.3 * * -21.8 Isobutyronitrile IBUN 27.9 16.8 19.9 17.6 16.2 -19.0 Benzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile PAN 38.6 20.9 * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PL 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline Aniline * * * * * -36.1 Mercaptochanol ME * * * * * -36.1 Thiophenol TP * * * * * -55.7 Thiophenol TPT * * * * * -56.8 N.W-Dimethylthioformamide DMTF 50.8 34.7 26.5	28	Propannitrile	PRN	25.7	15.2	9.2	*	*	-22.4	9.6	35.7	*	34.7	38.6	20.1
Isobutyronitrile IBUN 27.9 16.8 19.9 17.6 16.2 -19.0 Benzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile PAN 38.6 20.9 * * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine PL 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline ANI 44.4 38.1 * * * -36.1 Mercaptochanol ME * * * * * -36.1 Thiophenol TP * * * * * -55.7 Thiophenol TPT * * * * -56.8 N.N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 Hexamethylthiophosphoric triamide HMTP *<	59	Butannitrile	BUN	*	16.3	*	*	*	-21.8	10.7	31.5	*	43.0	41.9	20.8
Benzonitrile BN 34.6 22.0 13.2 12.0 11.6 -15.1 Phenylacetonitrile PAN 38.6 20.9 * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine Anli H 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline Aniline * * * * -36.1 Mercaptocthanol ME * * * * -36.1 Thiophenol TP * * * * * -55.7 Thiophenol TPT * * * * -55.7 Triahydrothiophene THT * * * -55.7 N.Wethyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphite TEP * -0.6 0.6 3.4 1.7 -70.8	30	Isobutyronitrile	IBUN	27.9	16.8	19.9	17.6	16.2	-19.0	8.6	*	*	34.2	36.5	*
Phenylacetonitrile PAN 38.6 20.9 * * -12.7 Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyridine Anli H 44.4 38.1 * * -28.6 Aniline ME * * * -36.1 Mercaptochanol ME * * * * -36.1 Thiophenol TP * * * * -55.7 Thiophenol TP * * * * -55.7 Thiophenol TPT * * * * -54.8 N.N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	31	Benzonitrile	BN	34.6	22.0	13.2	12.0	11.6	-15.1	11.8	38.8	*	57.9	45.5	24.9
Pyridine PY 6.9 6.3 6.3 5.8 7.0 -63.4 Pyrrol Anline ANI 44.4 38.1 * * -28.6 Aniline ME * * * -36.1 Mercaptochanol ME * * * * 2,2°-Thiodiethanol TDE * * * * -55.7 Thiophenol TP * * * * -55.7 Triophenol THT * * * * -56.7 Triaphylorophone THT * * * * -54.8 NN-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	32	Phenylacetonitrile	PAN	38.6	20.9	*	*	*	-12.7	12.5	49.0	*	9.19	8.09	28.9
Pyrrol PL 71.5 50.3 51.7 51.6 51.2 -28.6 Aniline ANI 44.4 38.1 * * -36.1 Mercaptoethanol ME * * * * -36.1 Thiophenol TP * * * * -55.7 Thiophenol TPT * * * -56.0 Tetrahydrothiophene THT * * * -54.8 N.N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	33	Pyridine	ΡΥ	6.9	6.3	6.3	5.8	7.0	-63.4	-13.1	-6.2	*	-40.3	-25.5	-103.4
Aniline ANI 44.4 38.1 * * -36.1 Mercaptoethanol TDE * -90.0 * -90.0 * -90.0 * -54.8 * -54.4 -103.3 * -79.4 * -79.4 *<	34	Pyrrol	PL	71.5	50.3	51.7	51.6	51.2	-28.6	7.9	87.4	*	59.0	37.2	*
Mercaptoethanol ME *	35	Aniline	ANI	44.4	38.1	*	*	*	-36.1	0.7	73.9	*	7.5	3.1	
2,2°-Thiodiethanol TDE * * * * -55.7 Thiophenol TP * * * * -90.0 Tetrahydrothiophene THT * * * * -54.8 N,N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 N-Methyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphoric triamide HMTP * * * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	36	Mercaptoethanol	ME	*	*	*	*	*	*	2.4	*	*	29.1	5.4	-65.6
Thiophenol TP * * * * 90.0 Tetrahydrothiophene THT * * * * -90.0 N,N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 N-Methyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	37	2,2'-Thiodiethanol	TDE	*	*	*	*	*	-55.7	-2.6	*	-90.1	15.2	-5.0	*
Tetrahydrothiophene THT * * * * -54.8 N,N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 N-Methyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * -79.4 Triethylphosphite Triethylphosphite 1.7 -70.8	38	Thiophenol	TP	*	*	*	*	*	-90.0	-23.3	*	*	-56.0	-67.3	*
N.N-Dimethylthioformamide DMTF 50.8 34.7 26.5 20.7 13.6 -97.2 N-Methyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	38	Tetrahydrothiophene	THT	*	*	*	*	*	-54.8	-2.2	*	*	17.0	-15.1	-103.2
N-Methyl-2-thiopyrrolidone NMTP 45.8 31.7 25.6 19.4 14.4 -103.3 Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * * -79.4 Triethylphosphite TEP * -0.6 0.6 3.4 1.7 -70.8	40	N,N-Dimethylthioformamide	DMTF	50.8	34.7	26.5	20.7	13.6	-97.2	-19.8	67.9	*	-35.9	-35.9	-157.8
Hexamethylthiophosphoric triamide HMTP 41.3 44.1 * * -79.4 Triethylphosphite * -0.6 0.6 3.4 1.7 -70.8	41	N-Methyl-2-thiopyrrolidone	NMTP	45.8	31.7	25.6	19.4	14.4	-103.3	-22.1	592	*	-34.9	-38.0	-167-3
TEP * -0.6 0.6 3.4 1.7 -70.8	45	Hexamethylthiophosphoric triamide	HMTP	41.3	4.1	*	*	*	-79.4	-6.5	*	*	2.1	-6.2	-119.6
	43	Triethylphosphite	TEP	*	9.0-	9.0	3.4	1.7	-70.8	-10.8	*	*	*	*	*

 $^{\rm a}$ from ref $^{\rm 34~b}$ The minus sign is missing in the original paper

SP-parameter¹⁸ (Softness Parameter of solvents) according to SP = 25 + $[\Delta_t G^{\circ} Ag^+ \text{ (benzonitrile)} - \Delta_t G^{\circ} Ag^+ \text{ (Solvent)}]$. This calculation differs slightly from the calculation given in Ref. 18, (SP = $|\Delta_t G^{\circ} (Ag^+) \text{ (BN} \rightarrow \text{Solvent)}| + 25$), but the new definition allows the inclusion of data for phenylacetonitrile in a correct manner.

The results are given in Table 2 as SP_n values together with other solvent parameters, which also claim to account for solvent softness. In a few solvents minor changes between the previously published SP values and the

SP_n values were observed. The previously published value for SP of tetrahydrothiophene was incorrectly calculated and should be changed to 65. Thus the SP_n parameters should be considered to be the SP parameters in future.

A plot of the Gibbs energies of transfer of Na⁺ versus Ag⁺ as shown in Figure 1 clearly shows a separation of the data into at least three groups. One such group is formed by the oxygen donor solvents, another one or possibly two by the nitrogen donor solvents and an additional one by the sulfur donor solvents.

Table 2: Solvent parameters proposed to describe "soft" solvent properties.

	Solvents	Abbr.	SP ^a	SP _n	μ ^c	$D_{ m S}^{ m d}$	Δν (C-I) ^e	ΔΔ <i>v</i> (C-I) ^f
1	Water	W	*	*	0	17	*	*
2	Methanol	MeOH	*	*	0.02	18	18	-1
3	Ethanol	EtOH	*	*	0.08	19	20	3
4	Trifluoroethanol	TFEtOH	*	*	-0.12		3	-8
5	1-Propanol	PrOH	*	*	0.16	17	27	6
6	1-Butanol	BuOH	*	*	0.18	19	27	7
7	1-Hexanol	HxOH	*	*	0.12	16	24	2
8	1,2-Ethanediol	ETDI	*	*	-0.03	20	13	-8
9	Acetone	AC	*	*	0.03	15	18	-3
10	Tetrahydrofurane	THF	*	*	0	17	25	-5
11	Butyrolactone	BL	*	*	0.02	14	16	-1
12	Propylene carbonate	PC	*	*	-0.09	12	13	-1
13	Trimethylphosphate	TMP	*	*	0.02	23	26	2
14	Formamide	FA	*	*	0.09	21	11	-12
15	<i>N</i> -Methylformamide	NMF	*	*	0.17	22	27	2
16	<i>N,N</i> -Dimethylformamide	DMF	*	*	0.11	24	30	5
17	<i>N</i> , <i>N</i> -Diethylformamide	DEF	*	*	0.09	23	27	0
18	<i>N</i> , <i>N</i> -Dimethylacetamide	DMA	*	*	0.17	25	28	-2
19	<i>N</i> , <i>N</i> -Diethylacetamide	DEA	*	*	0.17	24	38	8
20	<i>N</i> -Methyl-2-pyrrolidone	NMP	*	*	0.13	27	27	-4
21	<i>N,N,N,N</i> -Tetramethylurea	TMU	*	*	0.14	24	29.5	0
22	<i>N,N</i> '-Dimethylpropyleneurea	DMPU	*	*	*	*	*	*
23	Hexamethylphosphoric triamide	HMP	*	*	0.29	34	34	- 7
24	Tetramethylensulfone	TMS	*	*	*	29	34	-3
25	Dimethylsulfoxide	DMSO	*	*	0.22	28	32	2
26	Ethylenesulfite	ES	*	*	*	*	*	*
27	Acetonitrile	AN	32	33	0.34	12	17	2
28	Propannitrile	PRN	33	32	0.36	14	13	-1
29	Butannitrile	BUN	30	32	0.37	13	13	-1
30	Isobutyronitrile	IBUN	*	29	0.41	14	*	*
31	Benzonitrile	BN	25	25	0.36	12	23	0
32	Phenylacetonitrile	PAN	*	23	0.38	18	13	0
33	Pyridine	PY	73	73	0.66	38	57	16
34	Pyrrol	PL	*	39	0.81	20	20	*
35	Aniline	ANI	*	46	0.75	*	*	18
36	Mercaptoethanol	ME	51	*	*	*	*	*
37	2,2'-Thiodiethanol	TDE	66	66	0.68^{g}	39	*	*
38	Thiophenol	TP	*	100	*	*	*	*
38	Tetrahydrothiophene	THT	73 ^h	65	0.8	43	50	28
40	N,N-Dimethylthioformamide	DMTF	107	107	1.33	52	69	47
41	<i>N</i> -Methyl-2-thiopyrrolidone	NMTP	115	113	1.36	56	*	*
42	Hexamethylthiophosphoric triamide	HMTP	89	89	$1.57^{g,i}$	54	*	*
43	Triethylphosphite	TEP	*	81	*	*	*	*

^a SP Softness parameter of solvents Ref. ^{18 b} SP_n Softness parameter of solvents calculated in this study. ^c μ -parameter Ref. ¹⁷, ^d $D_{\rm S}$ parameter Ref. ¹⁹, ^e B_s parameter Refs. ^{20,40}, ^f Ref. ⁴⁰, ^g added as suggested by one of the referees, Ref ⁴⁶, ^h erroneous calculation in the original publication, correct value 65 ⁱ differs from the value given in Refs. ¹⁷ and ⁴⁰

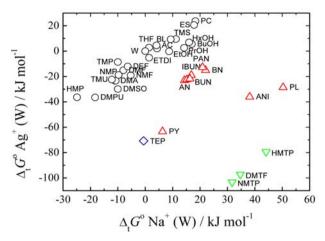


Figure 1. Molar Gibbs energies of transfer in kJ mol $^{-1}$ of Na $^{+}$ ($\Delta_l G^o$ Na $^{+}$ (W)) versus Ag $^{+}$ ($\Delta_l G^o$ Ag $^{+}$ (W)) from water as reference solvent

Gibbs energies of transfer from water into *N*,*N*'-dimethylpropyleneurea show that this solvent is a strong oxygen donor solvent, comparable to hexamethylphosphoric triamide and slightly stronger than dimethylsulfoxide. The data point is on the line for oxygen donor solvents in the plot of Gibbs energies of transfer of Na⁺ versus Ag⁺ (Figure 1).

Tris(ethyl)phosphite, [(C₂H₅O)₃P] better be named tris(ethoxy)phosphane has two possible donor atoms in the molecule, namely phosphorus and oxygen. Coordination via the phosphorus atom occurs towards Cu^{+ 37} and it is expected that coordination towards Ag⁺ also occurs via phosphorous. But it is very likely that the alkali metal cations prefer the oxygen atoms in the molecule. Towards alkali metal cations *tris*(ethoxy)phosphane is about as strong a donor solvent as water (Figure 2). The possibility that a solvent can have more than one donor site to interact with cations was already pointed out during studies in the solvents 2,2'-thiodiethanol38 and mercaptoethanol.39 Since Gibbs energies of transfer are only available for tris(ethoxy)phosphane as a phosphorus donor, it is not possible from these data alone to elucidate whether phosphorus donor solvents form an additional group.

In the previous publication²¹ we focused on solvent groups, in this paper we analyze the grouping of solvents versus cations. As observed before, statistical analysis of the Gibbs energies of transfer of the cations cannot be carried out for the complete data set.²¹ Figure 3 exemplifies this situation with respect to the Gibbs energies of transfer of Ag⁺ and Cd²⁺. Thus we searched and found subgroups, (*i*) the alkali metal cations and Ba²⁺ (Figure 2), (*ii*) Tl⁺, Cd²⁺ and Pb²⁺ (Figure 4) and (*iii*) Ag⁺ and Hg²⁺ (Figure 5). Since we need a complete set of data in the matrix we had to delete some solvents. In addition the data set for Li⁺ and Ba²⁺ is limited and was excluded in the analysis given in Table 3. The linear dependence of the Gibbs energies of transfer for Li⁺ and Ba²⁺ versus the Gibbs energies of

transfer of Na⁺, however, was proven for the solvents for which data are available. The results of the statistical analysis of the three subgroups are given in Table 3.

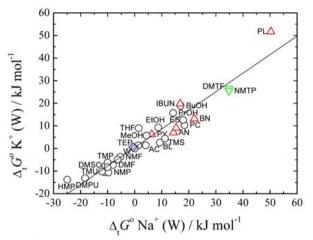


Figure 2: Molar Gibbs energies of transfer in kJ mol⁻¹ of Na⁺ ($\Delta_i G^o$ Na⁺ (W)) versus K⁺ ($\Delta_i G^o$ K⁺ (W)) from water as reference solvent.

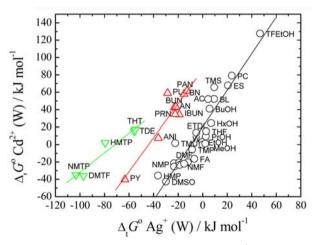


Figure 3: Molar Gibbs energies of transfer in kJ mol⁻¹ of $Ag^+(\Delta_i G^0 \times Ag^+(W))$ versus $Cd^{2+}(\Delta_i G^0 \times Cd^{2+}(W))$ from water as reference solvent.

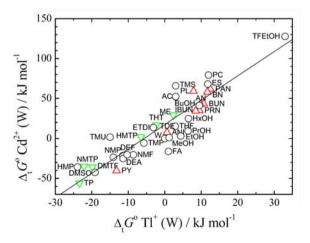


Figure 4: Molar Gibbs energies of transfer in kJ mol⁻¹ of Tl⁺ ($\Delta_i G^o$ Tl⁺ (W)) versus Cd²⁺ ($\Delta_i G^o$ Cd²⁺ (W)) from water as reference solvent.

Table 3: a_i parameters of the solvents from different statistical analyses.

	Solvents	Abbr.	$a_{i}(A)^{a}$	$a_{i}(B)^{b}$	$a_{i}(C)^{c}$
1	Water	W	-0.461	-0.212	2.944
2	Methanol	MeOH	0.05	-0.191	*
3	Ethanol	EtOH	0.383	0.048	3.309
4	Trifluoroethanol	TFEtOH	*	3.864	*
5	1-Propanol	PrOH	0.913	0.21	*
6	1-Butanol	BuOH	1.264	1.05	*
7	1-Hexanol	HxOH	*	0.394	*
8	1,2-Ethanediol	ETDI	-0.242	-0.17	*
9	Acetone	AC	-0.292	1.5	*
10	Tetrahydrofurane	THF	-0.042	0.211	3.63
11	Butyrolactone	BL	-0.009	*	*
12	Propylene carbonate	PC	0.559	1.967	7.257
13	Trimethylphosphate	TMP	-1.042	-0.748	2.334
14	Formamide	FA	*	-0.759	*
15	<i>N</i> -Methylformamide	NMF	-0.793	-1.231	*
16	<i>N,N</i> -Dimethylformamide	DMF	-1.075	-1.304	0.291
17	<i>N</i> , <i>N</i> -Diethylformamide	DEF	-0.886	-1.303	*
18	<i>N,N</i> -Dimethylacetamide	DMA	-1.231	-1.333	*
19	<i>N,N</i> -Diethylacetamide	DEA	-1.142	-1.359	*
20	<i>N</i> -Methyl-2-pyrrolidone	NMP	-1.23	-1.362	-0.149
21	<i>N,N,N,N</i> -Tetramethylurea	TMU	*	-1.071	*
22	<i>N,N</i> '-Dimethylpropyleneurea	DMPU	-1.798	*	*
23	Hexamethylphosphoric triamide	HMP	-1.798	-1.978	-3.055
24	Tetramethylensulfone	TMS	0.086	1.523	*
25	Dimethylsulfoxide	DMSO	-1.228	-2.006	-1.692
26	Ethylenesulfite	ES	*	1.75	7.023
27	Acetonitrile	AN	0.387	1.295	2.416
28	Propannitrile	PRN	*	1.101	3.512
29	Butannitrile	BUN	*	1.308	3.576
30	Isobutyronitrile	IBUN	1.161	1.051	*
31	Benzonitrile	BN	0.933	1.637	4.054
32	Phenylacetonitrile	PAN	*	1.796	4.388
33	Pyridine	PY	0.12	-1.421	-5.724
34	Pyrrol	PL	4.237	1.496	*
35	Aniline	ANI	*	-0.024	*
36	Mercaptoethanol	ME	*	0.404	*
37	2,2'-Thiodiethanol	TDE	*	-0.043	*
38	Thiophenol	TP	*	-2.456	*
38	Tetrahydrothiophene	THT	*	-0.179	-5.435
40	<i>N,N</i> -Dimethylthioformamide	DMTF	1.82	-1.554	-10.299
41	<i>N</i> -Methyl-2-thiopyrrolidone	NMTP	1.705	-1.584	-11.104
42	Hexamethylthiophosphoric triamide	HMTP	*	-0.314	-7.277
43	Triethylphosphite	TEP	-0.358	*	*

 $^aa_i(A)$ values derived for the alkali metal cations Na $^+$, K $^+$, Rb $^+$, Cs $^+$. $^ba_i(B)$ values for Tl $^+$, Cd $^{2+}$ and Pb $^{2+}$. $^ca_i(C)$ values for Ag $^+$ and Hg $^{2+}$.

5. Discussion

The grouping of solvents and cations, respectively, observed by the statistical analysis in this paper and in a previous publication²¹ deserves some discussion about our underlying model for ion – solvent interactions. We consider the interaction of cations with solvents as chemical bonding between the ion and the solvent molecule. Depending on the exchange rate of the solvent molecules this chemical bond may be short lived or last for some time. The nature of chemical bonding, we feel, is too complex

to be classified into two groups only, namely "hard – hard" or "soft – soft" interactions. Thus arranging solvents into "hard" and "soft" donor solvents only is misleading. 40 The lack of a clear parameter to distinguish between "hard" and "soft" donor and acceptor properties was already apparent at the publication of the principle in 1963. 14 Polarizability was implicitly considered by Pearson to be the main property for grouping into "hard and soft acids and bases", with the caveat of borderline acceptors and donors. Myers, however, showed that polarizability

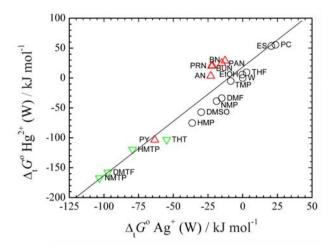


Figure 5: Molar Gibbs energies of transfer in kJ mol⁻¹ of $Ag^+(\Delta_l G^o Ag^+(W))$ versus $Hg^{2+}(\Delta_l G^o Hg^{2+}(W))$ from water as reference solvent

lity (hard species have low polarizability, soft species have high polarizability) is by no means suitable to differentiate between "hard" and "soft" donors and acceptors (Lewis acids and bases).⁴¹

Laurence et al. ²⁰ elaborated scales for "hard and soft basicities". Plotting the data of their B_h (hard basicity) versus their B_s (soft basicity) scales yielded a clear separation into oxygen, nitrogen and sulphur donor solvents. Unfortunately this observation was not followed up and the authors tried to account for their results only within the framework of "hard and soft acids and bases". Chen, Hefter and Marcus⁴⁰ in their effort trying to unify solvent softness scales further enforced this way of thinking, ignoring the chemistry of ion – solvent interactions.

One reason for this behavior may be the overextension of the Lewis acid – base concept. Lewis originally stated that "a basic substance is one which has a lone pair of electrons, which may be used to complete a stable group in another atom, and that an acid substance is one which can employ a lone pair from another molecule in completing a stable group of its own. In other words, the basic substance furnishes a pair of electrons for a chemical bond, an acid substance accepts such a pair". 42 Chatt pointed to the possibility that both partners in a reaction may contribute electrons for the formation of a chemical bond (π -back donation), ^{43,44} but this concept did not receive the attention it deserves. Efforts were made to introduce the possibility of chemical bond formation between cations and solvent molecules where both the cation and the solvent molecule contribute to a chemical bond were made⁴⁵ in order to account for the different behavior of cations towards oxygen, nitrogen and sulfur containing solvents. This first approach was limited to arrange the data within the concept of "hard and soft acids and bases". In view of the current analysis it is obvious that this classification is too crude to account for all data for cation - solvent interactions. More subtle separations according to the nature of the cations and the atomic sites in the solvent molecules interacting with the cations are necessary.

The a_i parameters given in Table 3 are the result of the statistical analysis of the respective subgroups. The $a_i(A)$ values are derived from the Gibbs energies of transfer of Na⁺, K⁺, Rb⁺ and Cs⁺. The $a_i(B)$ values from the Gibbs energies of transfer of Tl⁺, Cd²⁺ and Pb²⁺ and the $a_i(C)$ from the Gibbs energies of transfer of Ag⁺ and Hg²⁺. This grouping is not in line with the classification of hard, borderline and soft Lewis acids as published by Pearson. While Pb²⁺ is considered to be a borderline Lewis acid, Tl⁺, Cs⁺ and Cd²⁺ were classified as soft Lewis acids.

No correlations were found between the $a_i(A)$, $a_i(B)$ and $a_i(C)$ values, respectively. Thus interactions of these three groups of cations with solvent molecules are of different nature.

In this paper we shall concentrate on the $a_i(C)$ values, neglecting the information in $a_i(A)$ and $a_i(B)$ for the time being. These values were derived from the Gibbs energies of transfer of Ag^+ and Hg^{2+} . They were correlated with parameters, which claim to account for solvent softness. Good correlations were observed for the SP-parameter, the D_S parameter¹⁹ and the B_S parameter²⁰ (Table 4).

As a reminder, the SP parameter was derived from the Gibbs energies of transfer of the Ag^+ cation from butanenitrile into nitriles, nitrogen and sulfur donor solvents. A selection of solvents was already made at the time of the proposal of the SP-parameter including only solvents considered to be soft donor solvents. The D_S parameter is based on the vibrational spectroscopy (infrared and Raman stretching shift) of HgBr_2 in vacuum and solvents and defined as the difference between the symmetric Hg – Br stretching frequency of the neutral mercuric bromide complex in the gaseous phase and in saturated solution of the studied solvent and calculated as follows:

$$D_{\rm S} = v_{\rm (HgBr_2)}({\rm gas}) - v_{\rm (HgBr_2)}({\rm solvent})$$

The μ -parameter (malakos-parameter) is based on the Gibbs energies of transfer of Na⁺, K⁺ and Ag⁺ according to:

$$\begin{split} \mu = & \left\{ \frac{1}{2} \left[\Delta_{\tau} G^{\circ} \left(N a^{+}, W \rightarrow S \right) + \Delta_{\tau} G^{\circ} \left(K^{+}, W \rightarrow S \right) \right] - \right. \\ & \left. \Delta_{\tau} G^{\circ} \left(A g^{+}, W \rightarrow S \right) \right\} / 100 \end{split}$$

Very good correlations were obtained for the SP, the $D_{\rm S}$ and the B $_{\rm S}$ [Δv (C–I)] parameter. Correlations with the μ -parameter and the $\Delta \Delta v$ (C–I) parameter are less than satisfying. The lack of an acceptable correlation between the $D_{\rm S}$ and the μ parameter was pointed out and implicitly acknowledged in a later publication. An explanation could be the fact that the μ -parameter was derived from three single-ion transfer properties, namely the

Table 4: Correlations between the $a_i(C)$ solvent parameters and "solvent softness parameters" $(a_i(C) = A + B x)$

×	A	В	Rª	SDb	n°
SP^d	47.3	-5.42	0.988	5.59	10
μ^e	0.407	-0.0788	0.852	0.265	19
$D_{\rm S}^{\rm f}$	X	-2.72	0.969	3.79	19
Δv (C–I) / B_s^g	30.0	-3.54	0.962	4.79	16
$\Delta\Delta\nu(C-I)^h$	6.61	-2.36	0.785	8.95	16

 $^{^{\}rm a}$ regression coefficient, $^{\rm b}$ standard deviation of parameter x, $^{\rm c}$ number of solvents, $^{\rm d}$ Gritzner Softness parameter of solvents Ref. $^{18}, \,^{\rm e}$ Marcus µ-parameter Ref. $^{17}, \,^{\rm f}$ Persson $D_{\rm S}$ -parameter Ref. $^{19}, \,^{\rm g}$ B $_{\rm s}$ -parameter Refs. $^{20,40}, \,^{\rm h}\Delta\Delta v(\text{C-I})$ Ref. 40

Gibbs energies of transfer of Na⁺, K⁺ and Ag⁺ taken from a computer averaged data base and thus includes uncertainties in all of these three transfer properties.

The very poor correlation between both the $a_i(C)$ values and the D_S -parameter, respectively, with the $\Delta \Delta v$ (C–I) values may serve as an indication that the softness parameter (B_s) cannot be improved by deduction of a so-called "hard" contribution⁴⁰. Chemical bonding is more than a linear combination of "hard" and "soft" contributions.

Thus we must conclude in saying that the currently proposed solvent parameters which claim to account for "soft" donor properties of solvents are not generally applicable. Only interaction between Ag⁺ and Hg²⁺ and possible other cations such as Au⁺ or platinum group cations in low valency, for which currently no Gibbs energies of transfer are available, may be accounted for by these parameters.

5. Summary

Statistical analysis without any preconditions of Gibbs energies of transfer of nine cations into solvents containing oxygen, nitrogen and sulfur showed that a separation of solvents into hard and soft donor solvents is too crude to account for the data. Subgroups for the (*i*) alkali metal cations and Ba²⁺, (*ii*) for Tl⁺, Cd²⁺ and Pb²⁺ and for (*iii*) Ag⁺ and Hg²⁺ are necessary.

Statistical analysis yielded information on the strength of interaction of the solvents within each group. Currently proposed "soft" solvent parameters reflect only the behavior of Ag⁺ and Hg²⁺ of the cations studied. Tl⁺, Cd²⁺ as well as Pb²⁺ on one hand and the alkali metal cations on the other form separate groups with different solvent interactions.

6. References

- 1. M. Born, Z. Phys. 1920, 1, 45-48.
- 2. J. D. Bernal, R. H. Fowler, J. Chem. Phys. 1933, 1, 515–548.
- D. O. Eley, M. G. Evans, Trans. Faraday Soc. 1938, 34, 1093–1112.

- 4. A. D. Buckingham, *Disc. Faraday Soc.* **1957**, *24*, 151–157
- V. Gutmann, E. Wychera, *Inorg. Nucl. Chem. Lett.* 1966, 2, 257–260.
- U. Mayer, V. Gutmann, G. Gerger, Monatsh. Chem. 1975, 106, 1235–1257.
- 7. E. Kosower, J. Am. Chem. Soc. 1958, 80, 3253-3260.
- 8. K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, *Liebigs Ann. Chem.* **1963**, *661*, 1–37.
- 9. C. Reichardt, Angew. Chem., Int. Ed. Engl. 1965, 4, 29-40.
- I. A. Koppel, V. A. Palm, in Advances in Linear Free Energy Relationships, N. B. Chapman and J. Shorter, Eds., Plenum, London 1972 Chapter 5, p. 20.
- M. J. Kamlet, R. W. Taft, J. Am. Chem. Soc. 1976, 98, 377–383.
- M. J. Kamlet, R. W. Taft, J. Am. Chem. Soc. 1976, 98, 2886– 2894.
- M. J. Kamlet. J. L. Abboud, R. W. Taft, J Am. Chem. Soc. 1977, 99, 6027–6038.
- 14. R. Pearson, J. Am. Chem. Soc., 1963, 85, 3533-3539.
- S. Ahrland, J. Chatt, N. R. Davies, *Quart. Rev. Chem. Soc.* 1958, 12, 265–276.
- 16. G. Schwarzenbach, Experientia Suppl. 1956, 5, 162–192.
- 17. Y. Marcus, J. Phys. Chem. 1987, 91, 4422-4428.
- G. Gritzner, Z. Phys. Chemie, (München) 1988, 158, 99– 107.
- I. Persson, M. Sandström, P. L. Goggin, *Inorg. Chim. Acta* 1987, 129, 183–197.
- 20. C. Laurence, M. Queignec-Cabanetos, T. Dziembowska, R. Queignec, B. Wojtkowiak, *J. Am. Chem. Soc.* **1981**, *103*, 2567–2573.
- 21. G. Gritzner, R. Takacs, M. Auinger, *Russian J. Electrochem.* **2008**, *44*, 7–15.
- 22. E. M. Arnett, D. R. McKelvey, J. Am. Chem. Soc. 1966, 88, 2598–2599.
- R. Alexander, A. J. Parker, J. Am. Chem. Soc. 1967, 89, 5549–5551.
- 24. G. Gritzner, Inorg. Chim. Acta 1977, 24, 12.
- J. W. Diggle, A. J. Parker, *Electrochim. Acta* 1973, 18, 975–979.
- W. R. Fawcett, T. M. Krygowski, Canadian J. Chem. 1976, 54, 3283–3292.
- Y. Marcus, M. J. Kamlet, R. W. Taft, J. Phys. Chem. 1988, 92, 3613–3622.
- P. Smirnov, I. Persson, J Molecular Liq. 2003, 102, 241– 250.
- P. Smirnov, L. Weng, I. Persson, *Phys. Chem. Chem. Phys.* 2001, 3, 5248–5254.
- 30. G. Gritzner, J. Phys. Chem. 1986, 90, 5478–5485.
- 31. G. Gritzner, Pure Appl. Chem. 1990, 62, 1839-1858.
- 32. G. Gritzner, A. Lewandowski, *J. Chem. Soc, Faraday Trans.* **1991**, 87, 2599–2602.
- 33. F. Hörzenberger, G. Gritzner, *J. Chem. Soc, Faraday Trans.* **1992**, *88*, 695–697.
- 34. G. Gritzner, F. Hörzenberger, *J. Chem. Soc, Faraday Trans.* **1992**, *88*, 3013–3017.

- 35. G. Gritzner, A. Lewandowski, *J. Chem. Soc, Faraday Trans.* **1993**, 89, 3553–3556.
- 36. F. Hörzenberger, G. Gritzner, *J. Chem. Soc, Faraday Trans.* **1993**, *89*, 3557–3564.
- 37. K. B. Nilsson, I. Persson, *Dalton Trans.* **2004**, 1312–1319.
- 38. G. Gritzner, P. Rechberger, *J. Electroanal. Chem.* **1980**, *109*, 333–339.
- 39. S. Sperker, G. Gsaller, H. Marek, G. Gritzner, *J. Solution Chem.* **1988**, *17*, 35–46.
- 40. T. Chen, G. Hefter, Y. Marcus, *J. Solution Chem.* **2000**, *29*, 201–216.

- 41. R. T. Myers, Inorg. Chem. 1974, 8, 2040-2041.
- G. N. Lewis, Valence and the Structure of Atoms and Molecules, The Chemical CatalogCo., New York, 1923 quoted in W. B. Jensen, The Lewis-Acid Base Concepts (John Wiley & Sons 1980) p. 58
- 43. J. Chatt, Nature 1950, 165, 637-638, 1956, 177, 852-853.
- 44. J. Chatt, L. A. Duncanson, L. M. Venanzi, *J. Chem. Soc.*, **1955**, 4456–4460.
- 45. G. Gritzner, J. Mol. Liq. 1997, 73/74, 487-500.
- 46. Y. Marcus: The Properties of Solvents, Wiley, Chichester, 1998, pp. 150–152.

Povzetek

S statistično metodo, osnovano na spektralnem teoremu, smo analizirali Gibbsovo prosto energijo prenosa Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Tl⁺, Ba²⁺, Cu²⁺, Cd²⁺, Pb²⁺ in Hg²⁺ iz vode kot referenčnega topila v 42 nevodnih topil. Izkazalo se je, da vrednosti lahko razdelimo v tri skupine: v prvo spadajo kationi alkalijskih kovin ter Ba²⁺, v drugo Tl⁺, Cd²⁺ in Pb²⁺ ter v tretjo Ag⁺ in Hg²⁺. Statistična analiza eksperimentalnih podatkov za posamezne skupine omogoča tudi klasifikacijo topil, ki kaže, da je delitev topil le na »soft« in »hard« pomanjkljiva in nezadostna.