Scientific paper

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

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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^+, Ba^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+} 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 Ba^{2+}, the second Tl^+, Cd^{2+} and Pb^{2+} and the third group Ag^+ and Hg^{2+}. 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 Hg^{2+}. 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[1] (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 moment[4] 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-value[7], the Dimroth-Reichardt E_T parameter,[8,9] the Koppel-Palm parameters[10] 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 Pearson[14] has its predecessors in concepts developed by Ahrland, Chatt and Davies[15] 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 ($HgBr_2$) 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≡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 assumption[24]) or on the assumption of a negligible diffusion potential between two different liquids (tetraethylammonium picrate assumption[25]). 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 Fawcett[26] to solution chemistry. It differs from the statistical analysis by Marcus[27] 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]

$$\Delta G_{\mathrm{i,j}} = a_{\mathrm{i}}\, b_{\mathrm{j}} + c_{\mathrm{j}} \tag{1}$$

Within this mathematical model, the Gibbs energy of transfer $\Delta G_{\mathrm{i,j}}$ 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.

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

Specific solvent-solute interaction is taken into account by introducing the product of the ion parameter b_{j} and the solvent parameter a_{i}.

$$a_{\mathrm{i}}\, b_{\mathrm{j}} = \Delta G_{\mathrm{i,j}} - c_{\mathrm{j}} \quad \left(= x_{\mathrm{i,j}} \right) \tag{3}$$

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

$$\frac{1}{\mathrm{n}} \frac{1}{\mathrm{m}} \sum_{\mathrm{i}=1}^{\mathrm{n}} \sum_{\mathrm{j}=1}^{\mathrm{m}} \left(\Delta G_{\mathrm{i,j}} - \left(a_{\mathrm{i}} b_{\mathrm{j}} + c_{\mathrm{j}} \right) \right)^2 \rightarrow \min \tag{4}$$

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

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

$$= \sum_{\mathrm{k}=1}^{\mathrm{n}} a_{\mathrm{k}}^2 \begin{pmatrix} b_1 b_1 & b_1 b_2 & \cdots & b_1 b_{\mathrm{m}} \\ b_2 b_1 & b_2 b_2 & & \vdots \\ \vdots & & & \\ b_{\mathrm{m}} b_1 & \cdots & & b_{\mathrm{m}} b_{\mathrm{m}} \end{pmatrix}$$

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

$$v = \sum_{\mathrm{k}=1}^{\mathrm{n}} a_{\mathrm{k}}^2 \left(\frac{b_1}{b_{\mathrm{m}}}, \frac{b_2}{b_{\mathrm{m}}}, \frac{b_3}{b_{\mathrm{m}}}, \ldots, \frac{b_{\mathrm{m}-1}}{b_{\mathrm{m}}}, 1 \right)^{\mathrm{T}} \tag{6}$$

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).

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

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) phospite[28] 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

	Solvents	**Abbr.**	**Li$^+$**	**Na$^+$**	**K$^+$**	**Rb$^+$**	**Cs$^+$**	**Ag$^+$**	**Tl$^+$**	**Ba^{2+}**	**Cu^{2+}**	**Cd^{2+}**	**Pb^{2+}**	**Hg^{2+}**
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]
2	Methanol	MeOH	–4.3	4.3	5.8	5.7	6.9	2.1	1.3	3.7	11.0	1.2	–0.4	*
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
4	Trifluoroethanol	TFEtOH	*	*	*	*	*	46.8	33.0	*	139.7	127.7	98.0	*
5	1-Propanol	PrOH	6.9	14.2	15.7	15.9	14.1	2.6	6.5	18.9	24.7	9.5	13.1	*
6	1-Butanol	BuOH	9.6	17.0	18.9	19.8	20.0	5.6	9.6	24.1	29.3	41.1	28.9	*
7	1-Hexanol	HxOH	8.9	16.0	*	*	*	6.9	6.6	11.4	*	24.5	8.3	*
8	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	*
9	Acetone	AC	9.6	4.1	1.4	–0.4	1.7	4.5	3.1	5.6	69.1	52.1	46.1	*
10	Tetrahydrofurane	THF	6.3	1.4	9.1	8.5	–0.9	2.8	2.9	0.4	–10.6	15.4	8.1	9.3
11	Butyrolactone	BL	15.4	9.3	2.6	3.1	3.7	9.3	3.1	*	49.4	52.3	*	*
12	Propylene carbonate	PC	25.3	18.3	10.3	6.0	7.7	23.7	12.1	33.8	72.9	79.1	42.8	55.4
13	Trimethylphosphate	TMP	–21.3	–10.0	–6.2	–3.8	–4.1	–8.6	–5.7	–42.3	11.6	–5.8	–23.9	–5.2
14	Formamide	FA	*	*	*	*	*	–6.8	1.1	*	–2.7	–16.2	–15.8	*
15	*N*-Methylformamide	NMF	–15.5	–5.3	–3.7	–4.1	–0.6	–19.1	–8.6	–45.2	–28.8	–20.5	–36.3	*
16	*N*,*N*-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
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	*
18	*N*,*N*-Dimethylacetamide	DMA	–18.3	–11.0	–10.4	–5.5	–5.4	–23.4	–11.5	*	–28.4	–21.4	–40.5	*
19	*N*,*N*-Diethylacetamide	DEA	–25.6	–10.8	–7.6	–4.9	–5.2	–23.3	–11.4	–48.2	–26.2	–25.3	–38.0	*
20	*N*-Methyl-2-pyrrolidone	NMP	–19.0	–9.7	–10.5	–7.0	–5.4	–18.8	–14.1	–55.2	–18.9	–23.5	–39.2	–38.8
21	*N*,*N*,*N*,*N*–Tetramethylurea	TMU	–25.1	–12.2	–10.1	–6.7	*	–22.4	–15.0	–41.9	15.1	1.7	–48.0	*
22	*N*,*N*’-Dimethylpropyleneurea	DMPU	*	–18.3	–13.1	–14.3	–11.4	–36.5	–9.2[b]	*	*	*	*	*
23	Hexamethylphosphoric triamide	HMP	*	–24.9	–13.8	–9.1	–6.6	–36.4	–23.8	–73.5	–61.9	–35.7	–60.0	–75.3
24	Tetramethylensulfone	TMS	23.2	11.2	4.4	3.1	3.7	9.5	3.1	18.1	69.9	65.8	33.2	*
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
26	Ethylenesulfite	ES	60.7	17.8	12.6	*	*	20.6	11.9	*	71.6	67.9	41.7	53.3
27	Acetonitrile	AN	28.9	14.3	7.0	6.6	7.8	–23.0	9.8	42.6	*	42.5	41.9	3.3
28	Propannitrile	PRN	25.7	15.2	9.2	*	*	–22.4	9.6	35.7	*	34.7	38.6	20.1
29	Butannitrile	BUN	*	16.3	*	*	*	–21.8	10.7	31.5	*	43.0	41.9	20.8
30	Isobutyronitrile	IBUN	27.9	16.8	19.9	17.6	16.2	–19.0	8.6	*	*	34.2	36.5	*
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
32	Phenylacetonitrile	PAN	38.6	20.9	*	*	*	–12.7	12.5	49.0	*	61.6	50.8	28.9
33	Pyridine	PY	6.9	6.3	6.3	5.8	7.0	–63.4	–13.1	–6.2	*	–40.3	–25.5	–103.4
34	Pyrrol	PL	71.5	50.3	51.7	51.6	51.2	–28.6	7.9	87.4	*	59.0	37.2	*
35	Aniline	ANI	44.4	38.1	*	*	*	–36.1	0.7	73.9	*	7.5	3.1	
36	Mercaptoethanol	ME	*	*	*	*	*	*	2.4	*	*	29.1	5.4	–65.6
37	2,2’-Thiodiethanol	TDE	*	*	*	*	*	–55.7	–2.6	*	–90.1	15.2	–5.0	*
38	Thiophenol	TP	*	*	*	*	*	–90.0	–23.3	*	*	–56.0	–67.3	*
38	Tetrahydrothiophene	THT	*	*	*	*	*	–54.8	–2.2	*	*	17.0	–15.1	–103.2
40	*N*,*N*-Dimethylthioformamide	DMTF	50.8	34.7	26.5	20.7	13.6	–97.2	–19.8	62.9	*	–35.9	–35.9	–157.8
41	*N*-Methyl-2-thiopyrrolidone	NMTP	45.8	31.7	25.6	19.4	14.4	–103.3	–22.1	56.5	*	–34.9	–38.0	–167–3
42	Hexamethylthiophosphoric triamide	HMTP	41.3	44.1	*	*	*	–79.4	–6.5	*	*	2.1	–6.2	–119.6
43	Triethylphosphite	TEP	*	–0.6	0.6	3.4	1.7	–70.8	–10.8	*	*	*	*	*

[a] from ref ,[34] [b] The minus sign is missing in the original paper

SP-parameter[18] (Softness Parameter of solvents) according to SP = 25 + [$\Delta_t G^o$ Ag^+ (benzonitrile) – $\Delta_t G^o$ Ag^+ (Solvent)]. This calculation differs slightly from the calculation given in Ref. 18, (SP = |$\Delta_t G^o$ (Ag^+) (BN → 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[b]	μ[c]	D_S[d]	Δν (C-I)[e]	ΔΔν (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	*N*-Methylformamide	NMF	*	*	0.17	22	27	2
16	*N*,*N*-Dimethylformamide	DMF	*	*	0.11	24	30	5
17	*N*,*N*-Diethylformamide	DEF	*	*	0.09	23	27	0
18	*N*,*N*-Dimethylacetamide	DMA	*	*	0.17	25	28	–2
19	*N*,*N*-Diethylacetamide	DEA	*	*	0.17	24	38	8
20	*N*-Methyl-2-pyrrolidone	NMP	*	*	0.13	27	27	–4
21	*N*,*N*,*N*,*N*-Tetramethylurea	TMU	*	*	0.14	24	29.5	0
22	*N*,*N*'-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	*N*-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_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]

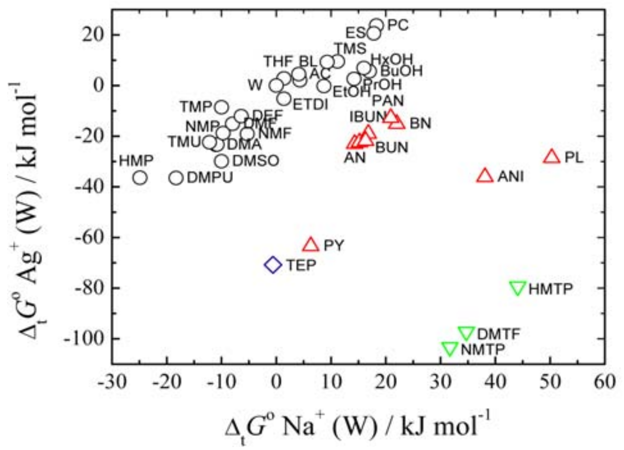

Figure 1. Molar Gibbs energies of transfer in kJ mol^{-1} of Na^+ ($\Delta_t G^o$ Na^+ (W)) versus Ag^+ ($\Delta_t G^o$ Ag^+ (W)) from water as reference solvent

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, $[(C_2H_5O)_3P]$ 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'-thiodiethanol[38] 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 publication[21] 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 Cd^{2+}. Thus we searched and found subgroups, (*i*) the alkali metal cations and Ba^{2+} (Figure 2), (*ii*) Tl^+, Cd^{2+} and Pb^{2+} (Figure 4) and (*iii*) Ag^+ and Hg^{2+} (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 Ba^{2+} is limited and was excluded in the analysis given in Table 3. The linear dependence of the Gibbs energies of transfer for Li^+ and Ba^{2+} 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.

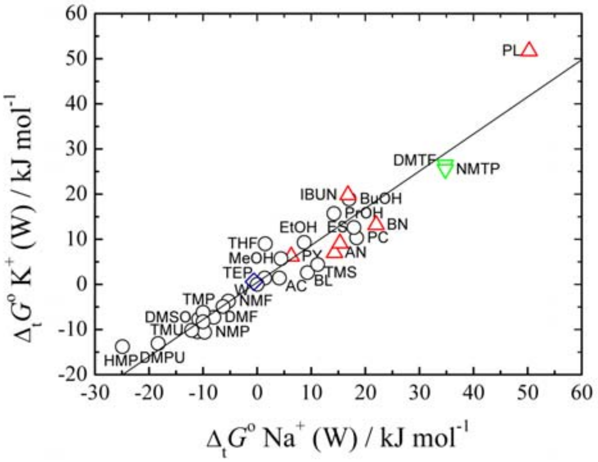

Figure 2: Molar Gibbs energies of transfer in kJ mol^{-1} of Na^+ ($\Delta_t G^o$ Na^+ (W)) versus K^+ ($\Delta_t G^o$ K^+ (W)) from water as reference solvent.

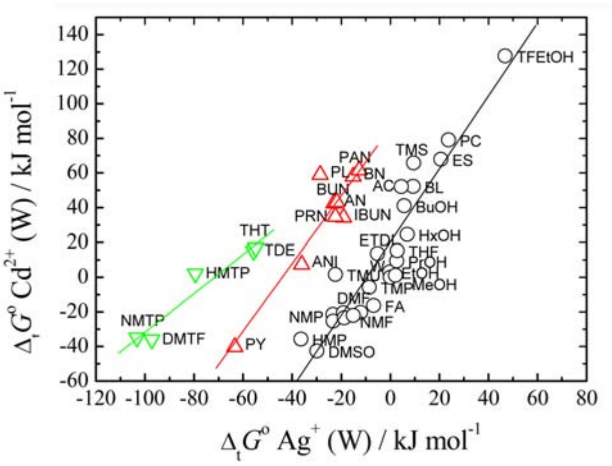

Figure 3: Molar Gibbs energies of transfer in kJ mol^{-1} of Ag^+ ($\Delta_t G^o$ Ag^+ (W)) versus Cd^{2+} ($\Delta_t G^o$ Cd^{2+} (W)) from water as reference solvent.

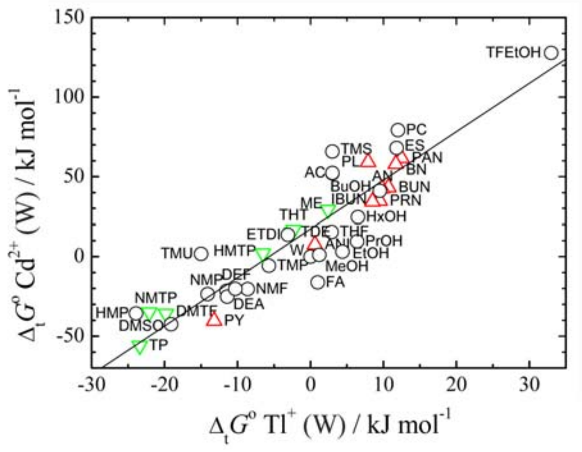

Figure 4: Molar Gibbs energies of transfer in kJ mol^{-1} of Tl^+ ($\Delta_t G^o$ Tl^+ (W)) versus Cd^{2+} ($\Delta_t G^o$ Cd^{2+} (W)) from water as reference solvent.

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	*N*-Methylformamide	NMF	–0.793	–1.231	*
16	*N*,*N*-Dimethylformamide	DMF	–1.075	–1.304	0.291
17	*N*,*N*-Diethylformamide	DEF	–0.886	–1.303	*
18	*N*,*N*-Dimethylacetamide	DMA	–1.231	–1.333	*
19	*N*,*N*-Diethylacetamide	DEA	–1.142	–1.359	*
20	*N*-Methyl-2-pyrrolidone	NMP	–1.23	–1.362	–0.149
21	*N*,*N*,*N*,*N*-Tetramethylurea	TMU	*	–1.071	*
22	*N*,*N*’-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	*N*,*N*-Dimethylthioformamide	DMTF	1.82	–1.554	–10.299
41	*N*-Methyl-2-thiopyrrolidone	NMTP	1.705	–1.584	–11.104
42	Hexamethylthiophosphoric triamide	HMTP	*	–0.314	–7.277
43	Triethylphosphite	TEP	–0.358	*	*

$^a a_i$(A) values derived for the alkali metal cations Na^+ , K^+, Rb^+, Cs^+. $^b a_i$(B) values for Tl^+, Cd^{2+} and Pb^{2+}. $^c a_i$(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 publication[21] 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 polarizabi-

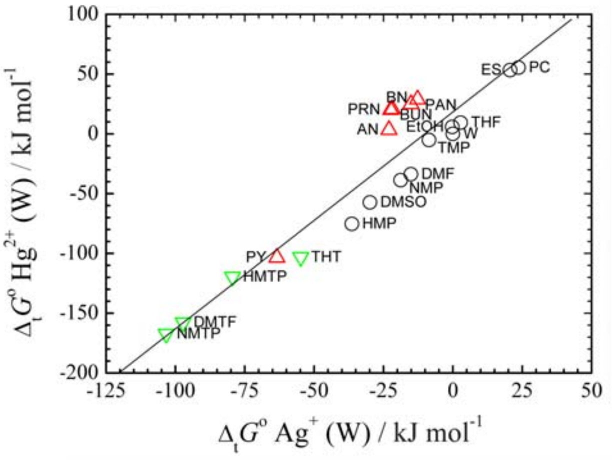

Figure 5: Molar Gibbs energies of transfer in kJ mol^{-1} of Ag$^+$ ($\Delta_t G^o$ Ag$^+$ (W)) versus Hg^{2+} ($\Delta_t G^o$ Hg^{2+} (W)) from water as reference solvent

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 Marcus[40] 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 made[45] 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$^+$, Cd^{2+} and Pb^{2+} and the a_i(C) from the Gibbs energies of transfer of Ag$^+$ and Hg^{2+}. This grouping is not in line with the classification of hard, borderline and soft Lewis acids as published by Pearson.[14] While Pb^{2+} is considered to be a borderline Lewis acid, Tl$^+$, Cs$^+$ and Cd^{2+} 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 parameter[19] and the B_s parameter[20] (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:

$$D_S = \nu_{(HgBr_2)}(\text{gas}) - \nu_{(HgBr_2)}(\text{solvent})$$

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

$$\mu = \left\{ \frac{1}{2}\left[\Delta_t G^o\left(\text{Na}^+, \text{W} \rightarrow \text{S}\right) + \Delta_t G^o\left(\text{K}^+, \text{W} \rightarrow \text{S}\right)\right] - \Delta_t G^o\left(\text{Ag}^+, \text{W} \rightarrow \text{S}\right) \right\} / 100$$

Very good correlations were obtained for the SP, the D_S and the B_s [$\Delta\nu$ (C–I)] parameter. Correlations with the μ-parameter[17] and the $\Delta\Delta\nu$ (C–I) parameter[40] are less than satisfying. The lack of an acceptable correlation between the D_S and the μ parameter was pointed out[45] and implicitly acknowledged in a later publication.[40] 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	B	R[a]	SD[b]	n[c]
SP[d]	47.3	–5.42	0.988	5.59	10
μ[e]	0.407	–0.0788	0.852	0.265	19
D_S[f]	x	–2.72	0.969	3.79	19
$\Delta\nu$ (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

[a] regression coefficient, [b] standard deviation of parameter x, [c] number of solvents, [d] Gritzner Softness parameter of solvents Ref. [18], [e] Marcus μ-parameter Ref. [17], [f] Persson D_S-parameter Ref. [19], [g] B_s-parameter Refs. [20,40], [h] $\Delta\Delta\nu$(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 $\Delta\Delta\nu$ (C–I) values may serve as an indication that the softness parameter (B_s) cannot be improved by deduction of a so-called "hard" contribution[40]. 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 Hg^{2+} 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 Ba^{2+}, (*ii*) for Tl^+, Cd^{2+} and Pb^{2+} and for (*iii*) Ag^+ and Hg^{2+} 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 Hg^{2+} of the cations studied. Tl^+, Cd^{2+} as well as Pb^{2+} on one hand and the alkali metal cations on the other form separate groups with different solvent interactions.

6. References

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Povzetek

S statistično metodo, osnovano na spektralnem teoremu, smo analizirali Gibbsovo prosto energijo prenosa Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Ba^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} in Hg^{2+} 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 Ba^{2+}, v drugo Tl^+, Cd^{2+} in Pb^{2+} ter v tretjo Ag^+ in Hg^{2+}. 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.