Molar Gibbs (Free) Energies of Transfer for Barium(II) and Mercury(II) from Acetonitrile into Nonaqueous Solvents

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Abstract

Molar Gibbs energies of transfer for Ba^{2+} and Hg^{2+} were calculated from electrochemical data on the basis of the bis(biphenyl)chromium assumption for 21 solvents. The transfer data obtained for these cations could be separated into two groups according to the HSAB principle. One group consisted of systems, where both cation and solvent were capable of undergoing soft–soft interactions, the other group of systems where either the solvent or the cation or both lacked the ability for soft interactions. Within each of these two groups it was found that the Gibbs energies of transfer for Ba^{2+} and Hg^{2+} depended on each other as well as on the Gibbs energies of transfer of Ag^+. A variety of solvent parameters were evaluated with respect to their ability to account for the Gibbs energies of transfer for Ba^{2+} and Hg^{2+} into hard and soft solvents. For solvent systems, which exclude soft–soft interactions, the Gibbs energies of transfer for Ba^{2+} and Hg^{2+} can be correlated with traditional solvent parameters such as the donor number, the B and the β parameter. Soft–soft interactions between cations and solvents can be represented by the *SP* parameter. A linear correlation between the Gibbs energies of transfer of the soft Hg^{2+} ion and the shifts in the Hg–Br stretching frequencies (D_s parameter) was observed for all solvents.

Introduction

Gibbs energies of transfer for single ions are derived from the Gibbs energies of transfer of salts upon application of an extrathermodynamic assumption. Numerous such extrathermodynamic assumptions have been proposed [1, 2]. The largest number of data for Gibbs energies of transfer published are based on either one of the following assumptions. (i) The assumption that the Gibbs energies of transfer of a salt with a large symmetrical cation and anion can be equally divided into the contribution of the cation and the anion. The salt most often used as a reference electrolyte is tetraphenylarsonium tetraphenylborate [3–7]. (ii) The assumption that the electrode potential of a redox couple consisting of a large organometallic cation and its neutral analog does not depend on the nature of the solvent, such as the bis(biphenyl)chromium assumption [8–14] or the ferrocene assumption [15–18]. (iii) The assumption that the liquid junction potential between two organic solvents can be suppressed by suitable salt bridges in organic solvents (e.g. 0.1 mol dm^{-3} solutions of tetraethylammonium picrate [19–21]) in either one of the respective solvents.

Application of the tetraphenylarsonium tetraphenylborate assumption to solubility data of 1:1 electrolytes lead to a large number of Gibbs energies of transfer for monovalent cations and anions. Electrochemical measurements yielded additional data for monovalent cations. Summaries of such Gibbs energies of transfer can be found in the literature [1, 2]. Gibbs energies of transfer of divalent cations however are scarce. Data for Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} derived from polarographic studies and based on the bis(biphenyl)chromium assumption were recently reported, together with previously published Gibbs energies of transfer for these four cations obtained from other assumptions [14].

Data for Gibbs energies of transfer for Ba^{2+}, a typical hard [22] or class (*a*) [23] cation and data for Hg^{2+}, a typical soft or class (*b*) cation, will be given for 21 solvents. Amongst the solvents studied are both hard and soft donor solvents.

Any differences in interaction between the hard Ba^{2+} ion and the soft Hg^{2+} ion should become apparent from the measured Gibbs energies of transfer. Such data allow exploration of the applicability of the principle of hard and soft acids and bases (HSAB principle) and its precursor, the division of cations into class (*a*) and class (*b*) acceptors, to solution chemistry. Both concepts were originally of a very qualitative nature and proposals to put these models on a quantitative basis were very vague. The HSAB principle merely states in general terms the preference of soft acids (soft acceptors) to interact with soft bases (soft donors). Gibbs energies of transfer report-

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ed in this study together with another recent set of data for Ag^+, Tl^+, Cu^+, Zn^{2+}, Cd^{2+} and Pb^{2+}, however, allow a quantitative description of hard–hard and soft–soft interactions between cations and solvents. These data will also be employed to screen the more prominent solvent parameters with respect to their capability to distinguish between hard–hard and soft–soft interactions and their ability to predict Gibbs energies for solvents where such data are not yet available.

Experimental

Compounds

$Hg(CF_3SO_3)_2$ is quite sensitive to hydrolysis and thus required special care in its preparation. An excess of HgO (Merck p.A., F.R.G.) was slowly added in small portions into a 50 vol.% aqueous solution of trifluoromethanesulfonic acid (purum, Fluka A.G., Switzerland). Towards the end of the reaction the mixture was heated to boiling. Upon cooling to room temperature, both unreacted HgO and $Hg(CF_3SO_3)_2$ were filtered off. The filter cake was dried at 60 °C and 1 mbar. The solids were then dissolved in boiling acetonitrile and undissolved HgO was separated by a hot filtration. The filtrate was heated under reduced pressure at 35 °C until a white residue, found to be approximately $Hg(CF_3SO_3)_2 \cdot 2.5CH_3CN$, was obtained. *Anal.* Calc. (found): Hg, 33.35 (33.1); S, 10.66 (10.5); C, 13.98 (13.9); H, 1.26 (1.36); N, 5.82 (6.0)%. Pure $Hg(CF_3SO_3)_2$ was obtained by prolonged heating of the acetonitrile solvate at 60 °C and 1 mbar: Hg, 42.79 (43.0); S, 12.86, (12.7)%. Anhydrous $Ba(ClO_4)_2$ [24] was prepared as previously reported.

Analysis

The Hg^{2+} content was analyzed by both complexometric titration and, together with the sulfur determination, by X-ray fluorescence. A modification of a published procedure [25] was employed for the complexometric titration of Hg^{2+}. A known amount of the sample was dissolved in 50 cm^3 of 10% nitric acid. The pH of this solution was then carefully adjusted to 5 with 0.1 mol dm^{-3} NaOH solution. Upon adding 25 cm^3 of titriplex (0.1 mol dm^{-3}) and 1 ml of a 25% NH_3 solution, uncomplexed titriplex was backtitrated with a 0.1 mol dm^{-3} solution of $ZnSO_4$. The analysis by X-ray fluorescence was carried out as follows. A known amount of $Hg(CF_3SO_3)_2$ was dissolved in 50 ml of 10% nitric acid for the X-ray fluorescence measurements. Standards made from $HgSO_4$ were also dissolved in 10% nitric acid. The solutions were filled into liquid sample holders. The X-ray fluorescence was carried out on a Rigaku Geigerflex 3064 M spectrometer under a He atmosphere employing a Rh cathode (35 kV 15 mA). The mercury determination was made with a LiF-(200) crystal (*d*: 4.028 Å) at a 2θ value of 35.91°, measuring time 20 s; sulfur was analyzed with a PET(002) crystal (*d*: 8.742 Å) at a 2θ value of 75.85, measuring time 100 s.

Electrochemical Measurements

The polarographic and cyclovoltammetric studies of the reduction of Ba^{2+} in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate as supporting electrolytes were carried out following published techniques [26]. The potentials for the Hg/0.01 mol dm^{-3} $Hg(CF_3SO_3)_2$ electrodes *versus* the reference redox system bis(biphenyl)chromium(I)/(0) [27] were measured in a published electrochemical cell [26] employing a three electrode arrangement. A Hg/0.01 mol dm^{-3} $Hg(CF_3SO_3)_2$ electrode in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in the respective solvent served as the reference electrode. The half-wave potential for the reduction of bis(biphenyl)chromium(I) tetraphenylborate *versus* the Hg/Hg^{2+} ion electrode was recorded in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in the same solvent. 0.01 mol dm^{-3} solutions of $Hg(CF_3SO_3)_2$ in hard solvents were made by dissolving a weighted amount of $Hg(CF_3SO_3)_2$ in the supporting electrolyte in a 10 cm^3 volumetric flask. A few cm^3 of this solution were sufficient to fill the reference electrode. Another 5 cm^3 of this solution were analyzed for the Hg^{2+} content by the complexometric titration described above, using 0.01 mol dm^{-3} solutions of titriplex and of $ZnSO_4$. For cases where the actual Hg^{2+} content deviated slightly from 0.01 mol dm^{-3}, the measured potentials were corrected employing the Nernst equation. The acetonitrile solvate was added to the typically soft donor solvents tetrahydrothiophene, hexamethylthiophosphoric triamide, *N*-methyl-2-thiopyrrolidinone and *N,N*-dimethylthioformamide, since unsolvated $Hg(CF_3SO_3)_2$ reacted with these solvents leading to black, unidentifiable products. Similar effects were previously observed for the reaction of $Hg(ClO_4)_2$ with *N*-methyl-2-thiopyrrolidinone [28]. All measurements were carried out at 25 °C except those in hexamethylthiophosphoric triamide (30 °C).

Results

Electrochemical data

The polarographic half-wave potential for the reduction of Ba^{2+} as well as the respective differences in one-quarter and three-quarter-wave potentials are given in Table 1. Data for the solvents ethanol, propylene carbonate, *N,N*-dimethylformamide, acetonitrile, butanenitrile and pyridine were collected in this study. Limiting currents for the reduction waves of Ba^{2+} were diffusion-controlled. The Kalousek

TABLE 1. Half-wave Potentials (V) and Differences in $E_{1/4} - E_{3/4}$ (mV) for the Polarographic Reduction of Ba^{2+}, Potentials of the Hg/0.01 mol dm^{-3} $Hg(CF_3SO_3)_2$ Electrodes (E*Hg) in 0.1 mol dm^{-3} Solutions of Tetrabutylammonium Perchlorate (V) and Molar Gibbs Energies of Transfer (ΔG_t°) for Ag^+, Ba^{2+} and Hg^{2+} (kJ mol^{-1}) from Acetonitrile at 25 °C

Solvents	$E_{1/2}Ba^{2+}$	$E_{1/4} - E_{3/4}$	E*Hg	ΔG_t°		
				Ag^+	Ba^{2+}	Hg^{2+}
Alcohols						
1 Methanol	−1.06[29]	31		29.5	−34.2	
2 Ethanol	−0.991	42	1.349	23.6	−20.8	2.5
Ketones						
3 Acetone	−1.075[24]	33		27.5	−37.1	
Ethers						
4 Tetrahydrofuran	−1.102[30]	41	1.367	25.8	−42.3	0.6
Esters						
5 Propylene carbonate	−0.941	42	1.606	46.7	−11.2	52.1
Amides, Lactams						
6 *N*-Methylformamide	−1.330[27]			8.7	−86.3	
7 *N,N*-Dimethylformamide	−1.305	35	1.144	7.9	−81.4	−37.1
8 *N,N*-Dimethylacetamide	−1.340[31]			−0.5	−88.2	
9 *N,N*-Diethylacetamide	−1.354[32]	54		−0.3	−90.9	
10 *N*-Methyl-2-pyrrolidinone	−1.390[33]	40	1.118	0.2	−97.9	−42.1
11 *N,N,N,N*-Tetramethylurea	−1.321[34]	46		0.6	−84.5	
Nitro compounds						
12 Nitromethane			1.686	52.2		67.5
13 Nitrobenzene			1.601	49.8		51.1
Nitriles						
14 Acetonitrile	−0.883	28	1.336	0	0	0
15 Propanenitrile			1.423	−0.4		16.8
16 Butanenitrile	−0.941	48	1.427	2.8	−11.2	17.6
17 Benzonitrile	−0.88[35]		1.448	7.9	0.6	21.6
18 Phenylacetonitrile	−0.83[36]		1.469	10.2	6.4	25.7
Heterocyclic compounds						
19 Pyridine	−1.036	33	0.783	−40.4	−29.5	−106.7
Sulfur compounds						
20 2,2′-Thiodiethanol			0.979	−32.7		−68.9
21 Tetrahydrothiophene			0.784	−40.3		−113.9
22 *N,N*-Dimethylthioformamide			0.501	−74.2	−36.5	−161.2
23 *N*-Methyl-2-thiopyrrolidinone			0.452	−81.9		−170.6
24 Hexamethylthiophosphoric triamide[a]			0.699			−122.8
25 Ethylensulfite			1.595	43.5		50
26 Dimethyl sulfoxide	−1.360[37]		1.022	−6.9	−92.1	−60.6
27 Tetramethylene sulfone[a]	−1.010[29]	29		30.8	−24.5	
Phosphorous compounds						
28 Trimethyl phosphate	−1.33		1.292	14.4	−86.3	−8.5
29 Hexamethylphosphoric triamide	−1.485[38]	82	0.929	−13.4	−116.2	−78.6

[a] 30 °C.

polarograms yielded unseparated anodic–cathodic waves in all cases. Half-wave potentials for the reduction of Ba^{2+} in the other solvents were taken from the literature [24, 27, 29–38]. Half-wave potentials for the reduction of Ba^{2+} in acetonitrile [39–41], *N,N*-dimethylformamide and dimethylsulfoxide [41–43], propylene carbonate [44] and ethanol [29] were previously published. These measurements, however, were carried out in two electrode arrangements *versus* an aqueous saturated calomel electrode. Such data include liquid junction potentials and had to be remeasured *versus* bis(biphenyl)chromium(I)/(0) as an internal standard. $Ba(ClO_4)_2$ was found practically insoluble in propanenitrile, tetrahydrothiophene, hexamethylthiophosphoric triamide and *N*-methyl-2-thiopyrrolidinone. The potentials of the Hg/0.01 mol dm^{-3} Hg^{2+} ion electrodes in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate are listed in Table 1.

Gibbs Energies of Transfer

The data for the Hg/0.01 mol dm^{-3} Hg^{2+} ion electrodes and the half-wave potentials of Ba^{2+} were used to calculate Gibbs energies of transfer for these two ions. The calculations are based on the assumption that the electrode potential of the reference redox system bis(biphenyl)chromium(I)/(0) is independent of the nature of the solvents. Acetonitrile was chosen as a reference solvent, in which the Gibbs energies of all ions were assumed to be zero. The Gibbs energies of transfer for Ba^{2+} and Hg^{2+} together with those of Ag^+ are also summarized in Table 1.

Discussion

The HSAB principle so far has been mainly used to describe the stabilities of complexes formed between hard and soft acids, respectively, with hard and soft bases. The differences in the respective bonds between donors and acceptors in compounds consisting of soft acids and soft bases and hard–hard complexes were subject to various theoretical explanations. It was claimed that the bonding in hard–hard complexes is predominantly ionic or electrostatic, whereas soft–soft complexes are held together by covalent bonding [22]. Other models describing soft–soft interactions consider the ability of π bonds through donation of d electrons from the acceptor to the donor [45] or compare symmetry and energies of the highest occupied orbitals and lowest unoccupied orbitals of the base (donor) and the acid (acceptor) [46].

It is not intended to go into the theoretical aspects of the HSAB principle, which at present is still mainly a qualitative ordering scheme for a large number of experimental observations. Rather, the applications of this principle to solution chemistry are investigated. Thus, this paper provides a set of data for hard and soft cations in hard and soft solvents in order to gain information on what solvents can act as soft donors, on how such solvents interact with hard and soft cations and on how the strength of hard and soft donor properties of solvents can be put on a quantitative basis. Such an endeavour requires a pragmatic rule, which allows the selection of solvents that are capable of soft interactions. The selection rule applied throughout this paper considers solvents, in which the Cu^+ ion is considerably more stable than the Cu^{2+} ion, soft solvents [47]. Acetonitrile, propanenitrile, butanenitrile, benzonitrile, pyridine, tetrahydrothiophene, hexamethylthiophosphoric triamide, *N,N*-dimethylthioformamide and *N*-methyl-2-thiopyrrolidinone are soft solvents among those studied.

It should also be noted that soft donor properties of the solvent molecules alone are not sufficient for soft–soft interactions. It is mandatory that the cation is also a soft or borderline acceptor. The results of this study will be discussed with these considerations in mind.

Gibbs Energies of Transfer

A plot of the Gibbs energies of transfer for the hard Ba^{2+} ion *versus* Gibbs energies of transfer for the soft Hg^{2+} ion reveals the grouping of the data according to hard and soft solvents (Fig. 1). The Gibbs energies of transfer for these two ions into solvents, which donate *via* the oxygen atom in the molecule form one line. Another line can be envisioned, which

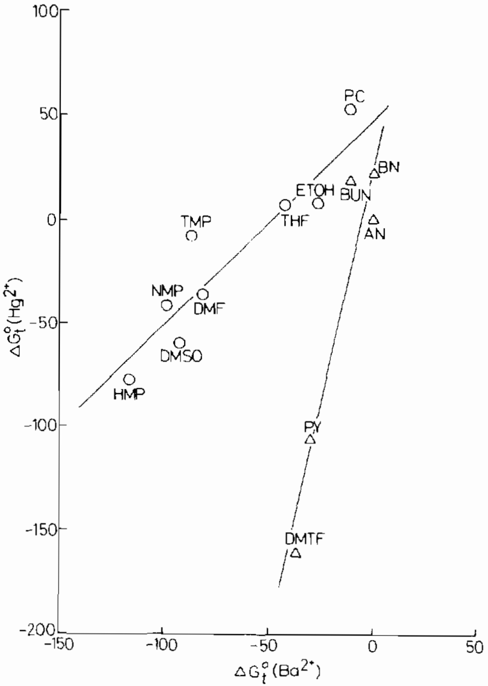

Fig 1. Gibbs energies of transfer of Hg^{2+} ($\Delta G_t^\circ(Hg^{2+})$) *vs.* Ba^{2+} ($\Delta G_t^\circ(Ba^{2+})$). Reference solvent acetonitrile.

correlates the Gibbs energies of transfer into the soft solvents acetonitrile, butanenitrile, benzonitrile, pyridine and *N,N*-dimethylthioformamide. Within each group there is a linear dependence of the data on each other. Similar observations were made when Gibbs energies of transfer for Tl^+, Zn^{2+}, Cd^{2+} and Pb^{2+} were correlated with the respective properties of Ag^+ [14, 47]. Following these studies the dependence of the Gibbs energies of transfer for Ba^{2+} and Hg^{2+} on the transfer data of Ag^+ was also investigated. The parameters for these linear regressions are summarized in Table 2. The lines for the Gibbs energies of transfer for Ba^{2+} *versus* Ag^+ covering hard and soft solvents are nearly parallel yet clearly distinguishable (Fig. 2). The linear correlation observed for the hard solvents studied with these three cations show that the interactions of hard solvents with cations are of the same nature. The degree of interactions as expressed by the slopes, however, depends on the cation and increases in the order Ag^+, Ba^{2+} and Hg^{2+}. Correlations between the Gibbs energies of transfer for the soft Hg^{2+} and Ag^+ do not come unexpected, but the correlation between Ba^{2+} and Ag^+ in soft solvents is somewhat surprising, since the interactions of the hard Ba^{2+} with these solvents is definitely different from the solvent interactions with Ag^+ and Hg^{2+}. It is not possible to fully explain these observations at this time. The mutual dependence of the Gibbs energies of transfer for Ag^+, Ba^{2+} and Hg^{2+} in hard solvents on one hand and in soft solvents on the other can be employed to predict transfer energies for these cations as soon as values for one of the cations become available.

Correlations with Solvent Parameters

The Gibbs energies of transfer for Ba^{2+} and Hg^{2+} obtained in this study allow in combination with the previously reported values for Ag^+, Tl^+, Zn^{2+}, Cd^{2+} and Pb^{2+} an evaluation of the ability of published solvent parameters to account for interactions of solvents with hard and soft cations. The solvent parameters presently used in the literature can be divided into those based on Lewis-type donor–acceptor interactions and those based on macroscopic

TABLE 2. Linear Correlations between Molar Gibbs Energies of Transfer from Acetonitrile for Ba^{2+}, Hg^{2+} and Ag^+ as well as Solvent Parameters ($Y = a_1 + a_2X$)[a]

Y	X	Solvents	*n*	Intercept a_1	Slope a_2	Standard error estimate	Correlation Coefficient
Ba^{2+}	Ag^+	1, 3–11, 26–29	14	−91.53	1.803	9.1	0.963
Ba^{2+}	Ag^+	14, 16–19, 22	6	−4.110	0.486	6.4	0.945
Ba^{2+}	*DN*	1–10, 14, 16–18, 26 28, 29	17	64.40	−5.218	14.5	0.941
Ba^{2+}	*B*	3, 4, 7, 8, 14, 17, 26, 29	8	72.65	−0.865	14.1	0.955
Ba^{2+}	β	1, 3–5, 7–11, 14, 17 19, 26, 29	14	62.53	−186.3	14.6	0.935
Hg^{2+}	Ba^{2+}	2, 4, 5, 7, 10, 26, 28, 29	8	62.91	1.155	16.2	0.942
Hg^{2+}	Ba^{2+}	14, 16, 17, 19, 22	5	25.15	4.627	31.4	0.945
Hg^{2+}	Ag^+	2, 4, 5, 7, 10, 12, 13, 25, 26, 28, 29	11	−46.88	2.125	5.1	0.995
Hg^{2+}	Ag^+	14–17, 19–24	10	3.995	2.283	11.8	0.989
Hg^{2+}	*DN*	2, 4, 5, 7, 10, 12, 13, 14–17, 19, 25, 26, 28, 29	16	90.06	−4.731	19.9	0.924
Hg^{2+}	*B*	4, 7, 12, 13, 14, 15, 17, 19, 26, 29	10	102.7	−0.8476	15.6	0.966
Hg^{2+}	β	4, 5, 7, 10, 13–15, 17	10	89.18	−168.9	22.1	0.889
Hg^{2+}	*SP*	14–17, 19–23	10	78.15	−2.274	12.1	0.989
Hg^{2+}	D_s	2, 4, 5, 7, 10, 12–17, 19, 20–24, 26, 28, 29	20	83.29	−4.434	17.0	0.972
Hg^{2+}	μP	2, 5, 7, 10, 12–14, 17, 19, 21–24, 26, 29	15	24.36	−154.5	44.2	0.851

[a] Solvent numbering is given in Table 1, *n*: number of solvents studied, *DN*: donor number [48, 49], *B*: *B* parameter [50], β: hydrogen bond acceptor properties [51, 52], *SP*: softness parameter of solvents [47], D_s: solvent donor scale towards soft acceptors [56, 57], μP: scale describing the softness of solvents [58].

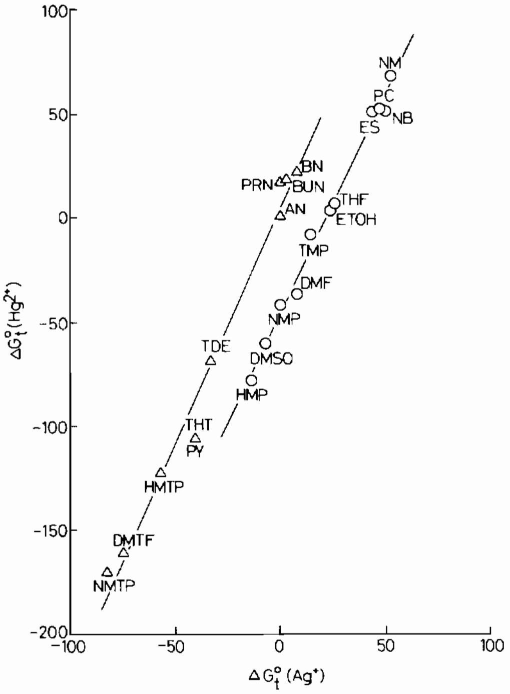

Fig. 2. Gibbs energies of transfer of Hg^{2+} ($\Delta G_t{}^\circ(Hg^{2+})$) *vs.* Ag^+ ($\Delta G_t{}^\circ(Ag^+)$). Reference solvent acetonitrile.

electrostatic properties of the solvents. The most frequently used solvent parameters, which reflect Lewis-type donor properties of solvents are the donor number [48, 49], the B parameter [50] and the β parameter [51, 52]. These three parameters were established at a time when data for soft solvents were quite scarce, thus no explicit distinction was made between hard and soft interactions. Since these three scales of solvent donor properties were almost exclusively derived from experimental data based on the interactions of model substances with hard, mainly oxygen donor solvents, they represent hard Lewis-type donor properties. They have been successfully applied to correlate physicochemical properties resulting from hard–hard interactions. Values for solvents capable of soft–soft interactions, such as the nitriles and pyridine were also included in these scales. Whenever data for Ag^+ or Cu^+ in nitriles and pyridines were included in studies, deviation from the relationships for typically hard solvents occurred. Special d^{10} interactions were claimed to explain these deviations [21, 53].

A limitation to hard donor solvents, excluding the thio-donor solvents and pyridine, yields a linear dependence of Gibbs energies of transfer for both Ba^{2+} and Hg^{2+} on either the donor number or the B parameter or the β parameter (Table 2). The nitriles, although weak soft donor solvents do not undergo strong soft–soft interactions with Hg^{2+} and thus the data for nitriles do not deviate too much in correlations of the Gibbs energies of transfer for these two ions with the donor number, β or B parameters. Treatment of soft–soft ion–solvent interactions however requires a different set of solvent parameters. In 1985 two such parameters, namely the D_s parameter derived from the differences between the symmetric Hg–Br stretching frequency of $HgBr_2$ in the gaseous state and in solution and a scale based on Gibbs energies of transfer of Ag^+ were proposed at the same time [54, 55]. The later scale was expanded and lead to the *SP* parameter [47].

These two parameters claim to represent soft donor properties, although in different ways. The D_s scale is limited to very soft acceptors [56, 57] and includes the interaction of such soft acceptors with both hard and soft donor solvents. The *SP* scale on the other hand takes notice of the observed grouping of hard–hard and soft–soft interactions. The application of the *SP* parameter is restricted to soft–soft interactions between cations and solvent molecules.

The correlations between the Gibbs energies of transfer of Hg^{2+} and the D_s parameter are quite good (Table 2). This shows that the solvent effects on the symmetrical stretching frequency of $HgBr_2$ and on the electrode potentials of the Hg/Hg(II) ion electrodes are of the same nature. But the D_s parameter is restricted to very soft acceptors and does not account for solvent effects on the Gibbs energies of transfer of Tl^+, Zn^{2+}, Cd^{2+} and Pb^{2+} in a consistent manner [14, 47].

The very good correlations found between the Gibbs energies of transfer not only for Hg^{2+} but also for Ag^+, Tl^+, Zn^{2+}, Cd^{2+} and Pb^{2+} and the *SP* parameter, on the other hand, in soft solvents [14, 47] support the concept of separate, independent parameters for hard and soft donor properties of solvents.

Recently the μ parameter for the softness of solvents was also published [58]. This parameter is a modification on using the Gibbs energies of transfer of Ag^+ to quantify soft donor properties of solvents. The values for the μ scale were obtained by subtracting the mean of the sum of the Gibbs energies of transfer for Na^+ and K^+ from the Gibbs energies of transfer for Ag^+. Correlations between the Gibbs energies of transfer for Hg^{2+} with the μ parameter are considerably worse than either with the D_s or the *SP* parameters (r: 0.851 s: 44.2). Multiple linear correlations employing both the μ and the β parameter do not improve the correlation (r: 0.838 s: 36.4).

Solvent parameters, which primarily account for the acceptor properties of solvents, such as the acceptor numbers [49, 59] or the E_T values [60, 61] did not correlate with either the Gibbs energies of transfer for Ba^{2+} or Hg^{2+}. Correlation coefficients were below 0.3. This observation does not come unexpected, since cations are acceptors themselves and interact with the donor sites and not with the acceptor sites of the solvents.

Correlations between the reciprocal of the dielectric constants or the dipole moments and the Gibbs energies of transfer for either Ba^{2+} or Hg^{2+} were not observed ($r < 0.3$).

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