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Free Energy Contribution Due to the Specific Solvation of Anions. A Comparison of "Pure" Acidity Solvent Scales[*]

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Four "pure" acidity solvent parameters (*i.e.* assumed to be free from non-specific solvation) proposed in the literature on quite different basis: E of Koppel and Palm [1], E^N of Krygowski *et al.* [2], α of Taft and Kamlet [3,4] and SA of Catalán and Díaz [5] gave the same contribution of the specific solvation of chloride ion to its standard molar free energy of transfer between a given solvent and water, as expected for "pure" scales.

Key words: solvent parameters, specific solvation, Lewis acidity

It was well recognized that the most popular empirical solvent scales are composite parameters, which include contributions from specific or chemical and non-specific, long-range solute/solvent interactions [1,6,7]. The former group includes solvent parameters describing the ability to solvate the negative and positive charges of a solute (including the charges of ions as well as local higher charge densities) and usually were considered as solvent acidity and basicity parameters, respectively. Only solvent acidity parameters (which are more similar to each other than basicity scales [2,7–9]) are considered in this work. They take into account electron-pair acceptor properties of solvents (Lewis acidity, which, however, should not be identified with the formation of a coordinative bond [10]) or solvent hydrogen-bond donor abilities.

A great number of correlations of a wide variety of physicochemical properties (kinetic, thermodynamic, spectroscopic, *etc.*) against solvent parameters can be found in the literature, however, usually only a relative change in a given property caused by the solvation was analyzed. On the other hand, the classical models of ion solvation, proposed by Born, Kirkwood, Onsager and others (*cf.* discussions and references *e.g.* in [1,6]) and assuming the solvent as a dielectric continuum, characterized only by macroscopic properties, offered the possibility to calculate the values of energy changes related to the solvation. They were widely used to calculate solvent effects on the individual ion properties, and also for simplified calculations of the solvent reorganization energy in kinetics of electron transfer processes, based on the Marcus theory [11]; there is an increasing interest [12,13] in applications of that ap-

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[*] Dedicated to Prof. Günter Häfelinger on his 65th birthday.

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proach to kinetics of a number of organic reactions. In an attempt to improve the Marcus model, an additional non-continuum correction term was proposed [14], however, that term was obtained from the correlation of redox potentials for the cationic redox couples of interest on the solvent donor number DN [15] with the assumption that the specific solvation term is absent for DN = 0. But the procedure proposed [14] is inappropriate, because the obtained result depends on the solvent scale used, as DN is the composite parameter, *i.e.* it includes unknown contribution from the non-specific solvation. On the other hand, "pure" solvent acidities basically should be free of any such contributions, however, they were introduced assuming different reference states for different scales, *i.e.*, different sets of solvents with the null acidity. As a consequence reliable correlations between two "pure" scales were observed only for solvents with relatively higher acidities [5], a poor correlation between E and α was reported [16], and linear correlations between pair of any such parameters have not the null intercept as expected; the last conclusion is evident from reported plots of SA against E and α [5]. Thus, it is hard to find in the literature the evident proof that the "pure" acidity scales are indeed completely free from non-specific solute/solvent interactions.

In order to find such an evidence, the solvent effect on the standard molar free energy of transfer of Cl^- ion from a given solvent to water, ΔG^0_{tr}, was analyzed below. ΔG^0_{tr} values are equal to the difference in standard chemical potential of ions of interest in water and in a given solvent and they represent the difference in the work of hydration of given ions and their desolvation; thus, for anions they depend strongly on the solvent acidity.

RESULTS AND DISCUSSION

Let us consider first the combine solvent parameters, which include contributions from non-specific solvation. The ΔG^0_{tr} values, based on the tetraphenylarsonium tetraphenylborate assumption (*i.e.*, ΔG^0_{tr} values of this electrolyte were equally divided between the cation and anion in each solvent) were extracted from the Marcus compilation [17]; only nitrobenzene, deviating strongly from all the correlation lines given below and 1,1-dichloroethane, for which some parameters are unknown, were omitted, but the addition of nitrobenzene does not change substantially the intercept. ΔG^0_{tr} values correlate well with the solvent acidity scales X: Dimroth and Reichardt's $E_T(30)$ and the normalized E_T^N [6], AN of Gutmann and Mayer [15] or Kosower's Z [18] as given by:

$$\Delta G^0_{tr} = 2.7(\pm0.3)E_T(30) - 167(\pm15), \quad n = 16, \quad r = 0.980, \quad \delta = 3.4 \tag{1}$$

$$\Delta G^0_{tr} = 89(\pm10)E_T^N - 83(\pm6), \quad n = 16, \quad r = 0.980, \quad \delta = 3.4 \tag{2}$$

$$\Delta G^0_{tr} = 1.3(\pm0.2)AN - 70(\pm4), \quad n = 16, \quad r = 0.979, \quad \delta = 3.5 \tag{3}$$

$$\Delta G^0_{tr} = 2.0(\pm0.2)Z - 183(\pm18), \quad n = 14, \quad r = 0.982, \quad \delta = 3.4 \tag{4}$$

where n is the number of solvents (the most deviating point for sulfolane was omitted in the last equation and Z value is unknown for NMPy), r the correlation coefficient, δ the mean quadratic deviation of ΔG^0_{tr} from the correlation line and 95% errors of the regression coefficients are given in parentheses. From the above presented equations it is evident that **the intercept** for the correlation with each solvent parameter X **is substantially different** and, thus, the assumption that the specific solvation effect vanishes at X = 0 gives different values of (ΔG^0_{tr} – Intercept) in a given solvent for each scale; the difference in the variability of ΔG^0_{tr}, caused by the specific solvation, estimated in that way using Z and AN scales is as large as 113 kJ mol^{-1}!

On the other hand, the use of "pure" acidity scales (α of Taft and Kamlet [3,4], E of Koppel and Palm [1], E^N of Krygowski *et al.* [2] and SA of Catalán and Díaz [5]) gives comparable results, with the intercept differing statistically in an insignificant way. This is shown by:

$$\Delta G^0_{tr} = 38(\pm 8)\alpha - 48(\pm 4), \qquad n = 23, \quad r = 0.914, \quad \delta = 7.7 \tag{5}$$

$$\Delta G^0_{tr} = 2.7(\pm 0.5)\mathrm{E} - 53(\pm 5), \qquad n = 23, \quad r = 0.924, \quad \delta = 7.2 \tag{6}$$

$$\Delta G^0_{tr} = 92(\pm 17)\mathrm{E}^{\mathrm{N}} - 51(\pm 5), \qquad n = 22, \quad r = 0.929, \quad \delta = 7.1 \tag{7}$$

$$\Delta G^0_{tr} = 59(\pm 13)\mathrm{SA} - 48(\pm 4), \qquad n = 18, \quad r = 0.924, \quad \delta = 5.6 \tag{8}$$

The ΔG^0_{tr} values, used for the above correlations, were extracted from the extended compilation of Marcus, Kamlet and Taft [19] and they are collected in Table 1 with all known values of "pure" solvent scales. It is evident that the mean value of the intercept in (5)–(8), equals to 50±5, does not differ more than one unit of error at the 0.95 significance level for any of the individual relationships. It should also be noted that the addition of the second explanatory parameter (the index of solvent dipolarity/polarizability π^* [19], the polarization $(\varepsilon - 1)/(2\varepsilon + 1)$, the function of refractive index $(n^2 - 1)/(n^2 + 2)$ or the normalized volume) was statistically rejected for each above equation with the probability higher than 90%, as estimated using [20] the Snedecor test F_{imp}. A different correlation than (5) was obtained by Marcus *et al.* [19] for the same ΔG^0_{tr} values. They applied the difference of a given solvent parameter in each solvent and in water and used a correlation with three solvent parameters: $\Delta\alpha$, $\Delta\pi^*$ and normalized volume 0.01 Δv. However, the careful statistical analysis of their data, using F_{imp} test [20], indicates that the addition of $\Delta\pi^*$ and 0.01 Δv is statistically unimportant at the 0.90 level of significance.

The same intercept of (5)–(8), which is independent of the solvent scale used, would not be expected before, because each scale was introduced on a different basis. First of all, the different set of reference solvents with no specific solvation ability towards negative charge at solutes was assumed (or obtained from statistical approach in the case of E^N) for each scale. For example, it is evident from Table 1 that dipolar aprotic solvents (as DMF, DMA, DMSO, HMPT) have $\alpha = 0$ but small positive (or negative for HMPT) values in other acidity scales. Moreover, two different approaches were used for the evaluation of contributions from the non-specific solvation: (i) the solvatochromic comparison method using two homomorph solutes (of which one can strongly interact with a solvent acidity center and the other has negligibly small interactions, as for SA scale) or calculating average values from experiments with more solutes (α scale), or (ii) subtracting the non-specific contribution (described by physical solvent parameters) from the empirical composite parameter $E_T(30)$ [1] (or E_T^N [2]) using statistical methods, as described by [1,2]:

$$E = E_T(30) - 25.57 - 14.39(\varepsilon - 1)/(\varepsilon + 2) - 9.08(n^2 - 1)/(n^2 + 2) \tag{9}$$

$$E^N = E_T^N + 0.212 - 1.186(\varepsilon - 1)/(2\varepsilon + 1) + 0.050(n^2 - 1)/(n^2 + 2) \tag{10}$$

(in (10) the error in the sign of 0.212 coefficient in the original paper [2] is corrected). Note, that the main differences in both above equations are the opposite signs of the regression coefficients at the polarizability function. In our opinion the positive sign of the coefficient at the polarization in equations describing $E_T(30)$ or E_T^N means a stronger solvation of the ground state of the Reichardt's betaine with the increase of the electric permittivity ε and the negative sign of the coefficient at the polarizability function of n^2 in the second equation means a stronger solvation of the excited state, because the ground state is not influenced by the electronic polarization. In the light of that explanation it is interesting to add that Koppel and Palm [1], using greater number of solvents, found also a negative contribution from polarizability (*cf.*, Eqn. II.1.2 in their Table 5.2).

Table 1. Standard molar free energy of transfer of the chloride ion from a given solvent to water [19] and "pure" solvent acidity parameters.

Solvent[a]	$-\Delta G^0_{tr}$ kJ mol^{-1}	E [1]	E^N [2]	α [4]	SA [5]
Water	0	21.8	0.641	1.17	–
MeOH	13.2	14.94	0.419	0.93	0.605
EtOH	20.2	11.57	0.212	0.83	0.400
1-PrOH	26	10.58	0.219	0.78	0.367
1-BuOH	29	10.30	0.282	0.79	0.341
TFE	–10	19.65	0.559	1.51	–
EG	9	12.87	0.446	0.83	0.717
Me_2CO	57	2.13	0.026	0.08	0.0
PC	39.8	4.97	0.136	0.0	0.106
NH_3	43	3.90	–	0.0	–
FA	13.7	14.59	0.440	0.71	0.549
DMF	48.3	2.60	0.060	0.0	0.031
DMA	54.9	2.13	0.057	0.0	0.028
NMPy	51	0.99	0.015	0.0	0.024
MeCN	42.1	5.21	0.114	0.19	0.044
$MeNO_2$	37.7	5.15	0.136	0.22	0.078
$PhNO_2$	35	0.3	–0.016	0.0	0.056
Py	34	0.0	0.024	0.0	0.033

Table 1 (continuation)

DMSO	40.3	3.7	0.096	0.0	0.072
TMS	47	2.39	0.063	0.0	0.052
HMPT	58	–0.2	–0.023	0.0	–
1,1-DClE	58	0.77	–0.013	0.10	–
1,2-DClE	52	2.99	0.041	0.0	0.030

[a]Solvent abbreviations: TFE = 2,2,2-trifluoroethanol, EG = ethylene glycol, Me_2CO = acetone, PC = propylene carbonate, FA = formamide, NMPy = N-methylpyrrolidinone, $PhNO_2$ = nitrobenzene, Py = pyridine, TMS = tetramethylene sulfone, HMPT = hexamethylphosphoric triamide, 1,1-DClE = 1,1-dichloroethane, 1,2-DClE = 1,2-dichloroethane.

Taking into account poor correlations between "pure" acidity solvent scales, as discussed before, it is very encouraging that contributions to the free energy of transfer of Cl^- ions from a given solvent to water, estimated from different "pure" acidity scales by (5)–(8), are the same with the accuracy of 4–5 kJ mol^{-1} (which is 7–9% of the highest ΔG^0_{tr} value). That result supports the view, that using one of the "pure" acidity scales under consideration, it is possible to obtain a contribution of the specific solvation of anions completely free from effects of the non-specific solvation.

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