Linearities in Gibbs Energies of Transfer of Alkali Metal Cations between Two Solvents and a New Aspect of Resolvation Related to Gas Phase Data

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A reported set of data on Gibbs energies of transfer of alkali metal cations between pure solvents $\Delta_t G°$(i) was analyzed in terms of linearities $\Delta_t G° = a_S + b_S\ \Delta G^0_{hydr}$(i). Propylene carbonate was chosen as a reference solvent. After reasonable correction of a numerical value of $\Delta G^0_{solv}(Rb^+)$ in propylene carbonate and adding data from other literature source for the transfers between propylene carbonate and nitromethane, good straight line correlations with $r = 0.98-0.99$ were obtained for 15 solvents. Straight lines mostly intersect near the region of $\Delta_t G°(i) = 0$ and $\Delta G^0_{hydr}(i) = -200$ kJ/mol and b_S coefficients correlate roughly with donor numbers of solvents. Gibbs energies of formation of small clusters in gas phase in water and acetonitrile show the same linear pattern as transfer values when plotted against ΔG^0_{hydr}(i) values. The pronounced tendency of the first two to three clusters to form a "future" 1:4 ion/solvent solvate of a saturation type is apparent. New scale of softness, proposed in the paper, is compared with previously proposed scale.

Introduction

The relative strength of solvation of ions in various solvents is an important topic. The distribution or transfer of ions between two solvents is encountered in areas such as solvent extraction, studies of ion selective electrodes, electrochemical studies of interface of two immiscible liquids (ITIES), and others. Appropriate models described in the literature treat the phenomenon of solvation from different points of view. For clarity, the respective models are in the following text marked in italic.

A simple Born model, simply relating the solvation energy of an ion in a solvent to the radius of ion and relative dielectric permittivity of the solvent, is known to be invalid, at least for simple inorganic ions. The *electrostatic model* was improved at an early stage, e.g., by Strehlow[1] into a variant in which the "effective ion radius" was used. The equation was written for transfer of cations from water into a solvent S as:

$$\Delta_t G°\ (i) = N_A z_i^{\,2} e^2 (8\pi\epsilon_0)^{-1} \{[1 - 1/\epsilon(H_2O)]/[(r_i + \delta(H_2O)] - [(1 - 1/\epsilon(S)]/[(r_i + \delta(S)]\} \quad (1)$$

where z_i is charge of ion, N_A and e have the usual meanings, ϵ_0, $\epsilon(S)$ are relative dielectric permittivities of vacuum and solvents, and $\delta(H_2O)$ and $\delta(S)$ are the correction empirical parameters $[(\delta(H_2O) \neq \delta(S)]$.

In further treatments, the original Born equation was changed to an equation that takes account of both "corrected radius" and of supposed dielectric saturation around the ion.[2] It was, for example, supposed that a dielectric constant at electrostricted layer of a thickness $r' = r_S + r_i$ (where r_S is a radius of solvent molecule and r_i is radius of an ion) was $\epsilon_{elstr} = 2$ and beyond the first electrostricted layer the macroscopical ϵ applied. In this model, sometimes called as "single layer model" SL,[3] the question arises as to what is the dielectric constant profile at the vicinity of ion.[4] Several attempts to solve the question are reviewed in a paper.[5] The Born equation ought to be split into three terms containing the values of ϵ_0, ϵ_{ir}, and ϵ_S corresponding, respectively, to electronic, atomic, and orientational polarization.[5] However, no such variant of the Born equation was practically applicable to the transfer of simple inorganic ions.[5] The problem with using "modified" or "corrected" Born equations is that the used "corrections" (much larger value of "corrected" radius of ion than crystallographic radius with obscure physical meaning, all applicable models) are essential and far beyond the "modification".[6] By assigning $\epsilon_{elstr} = 2$ (SL model) the resulting equation would suppose the predominance of the short range interactions at the electrostricted zone, however, the Born equation applies originally to long-range interactions.[6] On the other hand, Krishtalik et al. recently found that original Born equation well reproduced the experimental results for voluminous ions with a sufficiently dense envelop of inert functional groups not enabling access to the electronic shell of the central metal ion.[7] Thus, the failure of the Born equation may be restricted to small inorganic ions.

In *chemical treatments*,[8,9] the transfer of an ion from one solvent A to solvent B is considered as a complex forming reaction between ion i and solvent B. Implicit to the model is a neglect of any possible electrostatic interactions. For example, the transfer of silver cation from a reference solvent acetylacetone (AA) to any solvent S was proposed to be given simply by:

$$\Delta_t G^0_{AA\rightarrow S}\ (Ag^+) = -\ RT \ln \beta_n(S) \quad (2)$$

where $\beta_n(S)$ is overall complex forming constant.[9] Good agreement of the experimental data for transfer of Ag^+ into six different solvents with eq 2 was reported by the authors of the latter paper, despite differing values of n ($n = 1-4$ for individual solvents). $\Delta_t G^0_{AA\rightarrow S}\ (Ag^+)$ values well correlated with donor numbers of the solvents. But even the $-RT \ln \beta_1(S)$ values well

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correlated with donor numbers.[9] It seems puzzling that the behavior of 1:1 complexes reflected the total transfer energy; this point will be identified in this paper as an important feature of the systems under question.

Empirically, for large assembly of ions and solvents, *mutual linearities* of the transfers of two ions, e.g.,

$$\Delta_t G^0_{R\to S(N)}(K^+) = a + b\,\Delta_t G^0_{R\to S(N)}(\mathrm{Na}^+) \qquad (3)$$

where R is a reference solvent and S(1), S(2), S(3),..S(N) are various others solvents, were found by Gritzner.[10] These linearities generally applied in the two independent categories: (i) hard cations as Li^+, Na^+ and (ii) soft cations such as Ag^+ and Tl^+. The relative solvation of cations increased generally with the donor number of the solvent as a linear function. These finding would largely simplify any possible model of resolvation of ions.

In similar studies, the *linearities of* $\Delta_t G^0$ *on respective hydration energies (LGET)* were observed. For selected univalent inorganic ions, the relation was proposed for transfer from water to solvent S:[11]

$$\Delta_t G^0_{W\to S}\,(\mathrm{i}) = a_S + b_S\,\Delta G^0_{\mathrm{hydr}}(\mathrm{i})\ \text{or,}$$

$$\Delta G^0_{\mathrm{solv}}(\mathrm{i}) = \Delta_t G^0_{W\to S}\,(\mathrm{i}) + \Delta G^0_{\mathrm{hydr}}(\mathrm{i}) = a_S + (b_S + 1)\,\Delta G^0_{\mathrm{hydr}}(\mathrm{i}) \quad (4)$$

Later, for large assemblies of data for both univalent and bivalent ions, Notoya and Matsuda[12] have found:[12]

$$\Delta G^0_{\mathrm{solv}}(\mathrm{i})/z_\mathrm{i} - \Delta G^0_{\mathrm{solv}}(\mathrm{j})/z_\mathrm{j} = \beta_\mathrm{S}\,[\Delta G^0_{\mathrm{hydr}}(\mathrm{i})/z_\mathrm{i} - \Delta G^0_{\mathrm{hydr}}(\mathrm{j})/z_\mathrm{j}]\ \text{or}$$

$${}^{\mathrm{i}}\Delta^{\mathrm{j}}{}_{t}G^0_{W\to S}/z_\mathrm{i} = -\,(1-\beta_S)\,{}^{\mathrm{i}}\Delta^{\mathrm{j}}G_{\mathrm{hydr}}/z_\mathrm{i} \qquad (5)$$

where z_i is a charge of an ion i and ${}^{\mathrm{i}}\Delta^{\mathrm{j}}$ is a difference of values for the ions i and j. The correlation was surprisingly good if the data were plotted as two lines for "hard" and "soft" cations and reported correlation coefficients r^2 were in most cases higher than 0.999.[12a] However, for singled out group of alkali metal cations the scatter between reported and predicted values is uncertain or not negligible. This may be partly caused by author's using some older literature data as a source of experimental values.

More recently, Solomon referred to LGET as to commonly known mechanism "observed in many systems"[13] what is reminiscent to an older view of Gordon.[14]

Contrary to previous models, in which the $\Delta_t G°$ were correlated on relatively simple basis, Marcus proposed a sophisticated model based on *stepwise multivariate linear regression analysis* of collected data from the literature and using the properties of solvents and ions deemed as important for the resolvation process.[15] From obtained correlations, an attempt was made to rationalize which interactions are responsible for a behavior of a particular ion in a particular solvent.

Statistical equation for transfer of small univalent and divalent cations was found to be:[15i]

$$\Delta_t G^0 = P_i\Delta\pi^* + A_i\Delta\alpha + B_i\Delta\beta \qquad (6)$$

where Δ designates a difference between the properties of the target and reference solvent, π^* is the solvent polarity/polarisibility, and α and β are hydrogen-bond donor (HBD) acidity and hydrogen-bond acceptor (HBA) basicity of the solvent according to the Kamlet–Taft approach, respectively. The coefficients P, A, and B were reported to depend on the properties of the ions as[15i] $P = -3.62z^2/r + 30.3\delta$, $A = 225\,r^3$, and $B = -3.72z^2/r - 3.78R_D$; z, r, δ, and R_D are respectively the charge, radius, softness, and refractivity of the ion.

The absence of terms containing dielectric constant or dipole moment in eq 6 was explained by dielectric saturation in the vicinity of small ions and by relative unimportance of electrostatical interactions in transfer of primarily solvated ion compared to other terms of eq 6.[15g,i] Hence, the invalidity of Born equation was postulated according to the analysis. More involved explanation of $\Delta_t G°$ as appears in eq 6, compared to simple picture for previously discussed models, could imply that one reason of the different explanations may also lie in different input data[15a,b,f,g] that were analyzed.

For extraction and ion selective electrodes studies, the *selectivity* of transfer of alkali metal cations (e.g., $\Delta_t G^0_{W\to S}(\mathrm{Cs}^+) - \Delta_t G^0_{W\to S}(\mathrm{M}^+)$ values) between the mutually saturated immiscible solvents is of primary importance. We shall report on selectivity in water − several immiscible organic solvents in a future paper.[16] Recently, parameters leading to selectivity of extraction in a series of alkali metal cations were analyzed with the help of statistical approach and based on an equation similar to eq 6.[3] It was found that the selectivity for cesium largely arises from weak solvent HBA ability and increases as β decreases in agreement with older proposal that selectivity for cesium increases with decreasing Gutmann donor number.[3,11] A smaller effect of the same kind, i.e., an increase of selectivity with decreasing α was discerned, whereas solvent polarity/polarizability π^* seemed to contribute only little to selectivity.[3]

Collecting and analyzing the data on the transfers of cations between pure solvents is a necessary prerequisite step for any other studies of selectivity in mutually saturated solvents.

Consequently, in this article we shall (i) analyze the existing data of $\Delta_t G°$ and shall choose a particular set of preferred entry data, (ii) identify the main parameters responsible for the transfer, and (iii) discuss a new aspect of the solvation of alkali metal cations that emerges from this paper.

Input data

Reported $\Delta_t G^0$(i) Values, *A* and *B* sets. At present, two large sets of reference data of $\Delta_t G°$(i) for number of solvents and ions were published, but the sets are not mutually consistent. First set, denoted here as ***A*** set, is that of Marcus.[15g] His ionic values were compiled from original data of various authors as appeared in the literature (mainly papers[15a,b] with several corrections in further publications). The most reliable values from the variety of data were chosen based on the criterion of additivity of cationic and anionic values of a particular original set. Tetraphenylarsonium tetraphenylborate (TATB) extrathermodynamic assumption was preferred as a means of splitting the overall electrolyte values into ionic contributions. The reported values were given for transfers from water to other solvents.[15f,g] Not necessarily all of the original data were included into analysis, and we refer in this work to a few additional original measurements.

A second set is that published by Gritzner, set ***B***.[10i] Set ***B*** is based on the data of the $E_{1/2}$ of reduction of alkali metals in various solvents and data were obtained mostly by one experimental technique and in one laboratory. Bis (biphenyl) chromium (I)/(0) couple assumption was used as an extrathermodynamic assumption. The reported values were given for transfers from acetonitrile to other solvents.[10i]

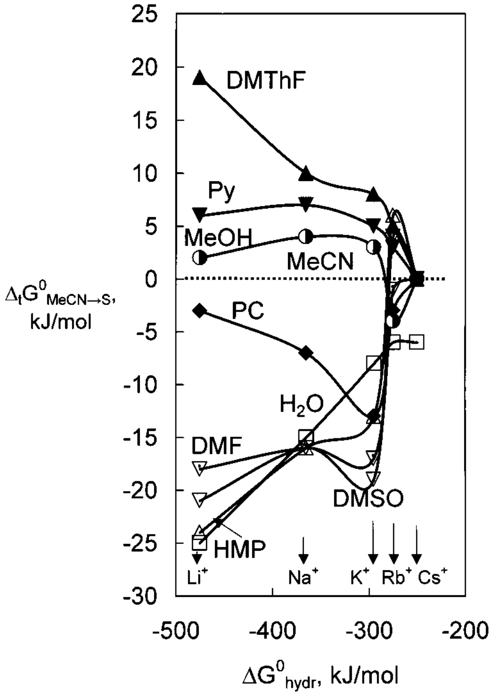

Figure 1. Gibbs energies of transfer of alkali metal cations from acetonitrile to a solvent recalculated from the data.[15g] See legend to Table 1 for abbreviations of solvents (ref 35).

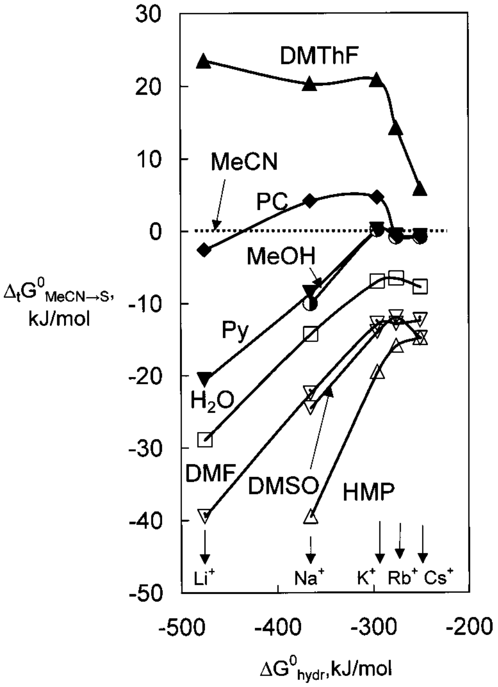

Figure 2. Gibbs energies of transfer of alkali metal cations from acetonitrile to a solvent according to the paper.[10i] See legend to Table 1 for abbreviations of solvents (ref 35).

The overlapping data for alkali metal cation transfers, existing in both sets, were recalculated from the set ***A*** in a manner to have one common solvent − acetonitrile − according to simple relation for three solvents S_1, S_2, and S_3 where X is any thermodynamic quantity:

$$X(S_1 \text{ to } S_2) = X(S_1 \text{ to } S_3) + X(S_3 \text{ to } S_2) \qquad (7)$$

Comparison of Figure 1 (set ***A***) and Figure 2 (set ***B***) reveals that data considerably differ. Let us notice, for example, that the overall span of $\Delta_t G^0_{\text{MeCN} \rightarrow \text{S}}(\text{i})$ values is from 20 to −25 kJ/mol in set ***A***, but larger, 25 to −45 kJ/mol, according to set ***B***. We can see also that pyridine and methanol are poorer solvents for alkali metal cations than acetonitrile according to the set ***A***, in contrast to what can be seen at set ***B***.

An evaluation of which set is more reliable would need cumbersome detailed search and checking of the original data, still without ensuring any convincing result, because such a task has been already undertaken by each author of sets ***A*** and ***B***.

At such situation, the sets can be checked as a whole looking at their characteristic features. Qualitatively, some preference was given to the set ***B*** because of the following indirect evidence:

- Values from the set ***B*** display more regular behavior in view of similarities of individual solvents as seen from Figures 1 and 2,
- Experimentally, we have found for many transfers between water and solvent S (mutually saturated solvents, extraction systems) the sequence of transfer or $\Delta G^0_{\text{W} \rightarrow \text{S}}$ is $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$. This is so for S = nitrobenzene, nitromethane, nitroethane, and nitropropane.[17] The same sequence was obtained for S = propylene carbonate, 1,2 − dichloroethane, mixtures of nitrobenzene with CCl_4, dioctylsebacate and others.[16] For highly basic tributylphoshate, the sequence was reversed.[16] In no case a local extreme of $\Delta_t G^0_{\text{W} \rightarrow \text{S}}(\text{i})$ values in the series was found. However, in set ***A*** the reported values $\Delta G^0_{\text{W} \rightarrow \text{S}}$ in several instances display the extreme.

Choice of the Reference Solvent. Although any solvent can be chosen as a standard, in our work, propylene carbonate was chosen. This is a solvent of high polarity; it is essentially not hydrogen bonded and is non toxic and was previously proposed as a reference solvent.[18] The original reference solvents used at publication of sets ***A*** and ***B***, i.e., water and acetonitrile, were not used because not all of the interactions can be easily discerned upon their choice.

Water is a highly structured solvent, and it was supposed that the transfer of alkali metal cations from water to other not structured solvents might be expressed by combination of electrostatical and nonelectrostatical parts:

$$\Delta_t G^0_{\text{w} \rightarrow \text{S}}(\text{i})_{\text{total}} = \Delta_t G^0_{\text{W} \rightarrow \text{S}}(\text{i})_{\text{el}} + \Delta_t G^0_{\text{W} \rightarrow \text{S}}(\text{i})_{\text{nonel}} \qquad (8)$$

in which the non electrostatical part $\Delta_t G^0_{\text{W} \rightarrow \text{S}}(\text{i})_{\text{nonel}}$ due to the structure of water could be perhaps equaled to $\Delta_t G°$ of inert gas of the same radius as is the ion.[11,18] To get rid of this possible interaction some other non structured reference solvent than water is of better use. Acetonitrile is a typical soft donor solvent and, hence, is not particularly suited as a reference solvent.

Used $\Delta_t G°(\text{i})$ values, *B′* set. Although as a basis for further analysis, the ***B*** set was used, still minor correction is necessary, leading to slightly modified ***B′*** set.

The dependences of $\Delta_t G^0_{\text{PC} \rightarrow \text{S}}(\text{i})$ values from ***B*** set generally give good overall straight line correlations according to eq 4 with exception of Rb^+ which is a regular outlier. This is apparent from Figure 3 where the values of $\Delta_t G^0_{\text{PC} \rightarrow \text{S}}(\text{i})$ for alkali metal cations are shown for transfers from propylene carbonate to water and alcoholic solvents. The same pattern is valid for the transfers from propylene carbonate to amide solvents, mean deviation of $\Delta_t G^0_{\text{PC} \rightarrow \text{S}}(\text{Rb}^+)$ as compared to other alkali metal cations is 2.6 kJ/mol (or the originally reported value of $E_{1/2}(\text{Rb}^+)$ in propylene carbonate in ***B*** set is more negative by 0.027 V than expected).

With regard to previous discussion on the absence of extreme in number of systems consisting of mutually saturated phases, we deliberately subtracted for all Rb^+ transfers in ***B*** set (from

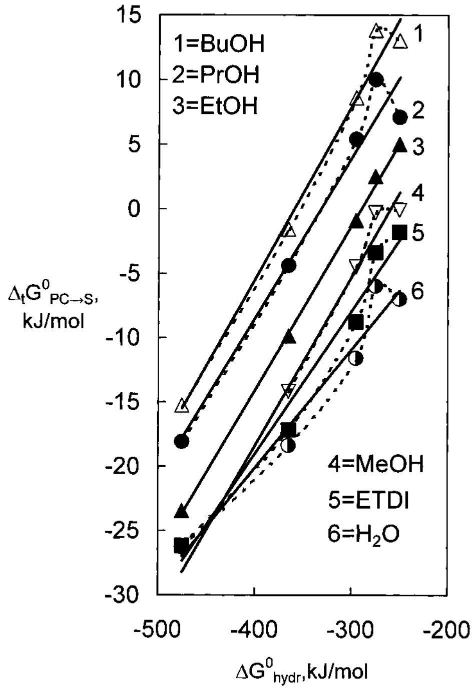

Figure 3. Data for transfers from propylene carbonate into water and alcohols according to the set of data.[10i] Analogous picture applies for transfer to amide solvents, the results suggest desirable correction of $\Delta G^0_{\mathrm{solv}}$ of Rb^+ ion in propylene carbonate.

propylene carbonate to any solvent) 2.6 kJ/mol, thus having ***B′*** set. This corresponds to correction of one value from 92 entries of the original ***B*** set.

The choice is supported by original data on transfers between pure solvents in which no irregularities of Rb^+ transfer were detected:

- In a study of $E_{1/2}$ values of reduction of alkali metal cations by L′Her,[19] the regular behavior of Rb^+ was reported for transfer from water to propylene carbonate. The data plotted as $\Delta_t G^0_{W \to PC}(i)$ on $\Delta G^0_{\mathrm{hydr}}(i)$ according to eq 4 fell on a straight line for K^+, Rb^+, and Cs^+ with $a_S = -34.452$, $b_S = -0.1036$, and $r = 0.9942$[20]
- Similarly, for the reported data of transfer of alkali metal iodides from water to PC by Cox,[21,22] the straight line applies with $a_S = -4.1902$, $b_S = -0.0856$, and $r = 0.9808$
- The data from the ***A*** set,[15g] although not linear in above coordinates, lie again on a smooth curve $\Delta_t G^0_{W \to PC}(i) = -103.5 - 0.52\Delta G^0_{\mathrm{hydr}}(i) - 0.000\,530[\Delta G^0_{\mathrm{hydr}}(i)x]^2$, $r = 0.9963$.

It may be noted that irrespective of whether the original ***B*** or corrected ***B′*** set is used, the conclusions of this work do not change, only the overall fit to straight lines would be worse for the original set of values.

The values $\Delta_t G^0_{PC \to NM}(i)$ for the transfer from propylene carbonate to nitromethane, obtained by non electrochemical methods, were added to analysis. The additional data can be considered as particularly reliable because data were measured by two different techniques yet with exact agreement. The original $\Delta_t G^0_{W \to NM}(i)$ values were obtained from the following:

- extraction data and appropriate corrections for mutual solubilities of solvents (relative $\Delta_t G^0_{W \to NM}(i)$ values without extrathermodynamical assumption).[18,23] The data read in terms of eq 4 as $\Delta_t G^0_{W \to NM}(i) = -a - 0.22449\Delta G^0_{\mathrm{hydr}}(i)$, $r = -0.999\,48$[18,23,20,22]
- solubility measurements and based on TATB assumption, the following straight line holds for transfer: $\Delta_t G^0_{W \to NM}(i) = -51.16 - 0.226\,49\Delta G^0_{\mathrm{hydr}}(i)$, $r = -0.999\,88$.[24,22]

For the sake of completeness, the data on transfers based on the older set of $E_{1/2}$ potentials[10e] are given in Appendix, but data were not used in the analysis.

Full set of data of ***B′*** set are given at legend to Table 1 together with abbreviations of the solvents (ref 35).

Standard Gibbs Energies of Hydration and Donor Numbers. Values of $\Delta G^0_{\mathrm{hydr}}$ of alkali metal cations which were used in this work, are in the order Li^+, Na^+, K^+, Rb^+, Cs^+ as follows; −475, −365, −295, −275, −250 in kJ/mol.[15g] For Ag^+ and Tl^+ −440 and −310 kJ/mol were used, respectively, from the same source.[15g]

For alkali metal cations, other reported sets of data give sometimes more negative absolute values than used here, e.g., for Li^+, −481,[15c] −517,[18] or −529.4[25] kJ/mol. Still, any other choice of $\Delta G^0_{\mathrm{hydr}}$ would not disparage the results of the present paper. It is because data for alkali metal cations from three other sets correlate excellently as straight lines ($r = 1.0000$) with the data used here, and relative positions of $\Delta G^0_{\mathrm{hydr}}$ are of primary importance for us.

Because of the reliability of the current reported $\Delta G^0_{\mathrm{hydr}}$ values and large amount of tabulated entries for various ions,[15g] these values were used as a basic parameter here. Furthermore, the $\Delta G^0_{\mathrm{hydr}}$ values are considered in a more broad sense as a general parameter expressing the strength of hydration and solvation of a given ion and are denoted as $\Pi_i (\Pi_i \equiv \Delta G^0_{\mathrm{hydr}}(i))$.

Donor numbers, DNs,[26] (in kJ/mol here) are negative values of standard enthalpies of the reaction of donor solvent D with $SbCl_5$ in dilute solution in an inert solvent, 1,2-dichloroethane, and they became a rather popular measure of the solvating properties of solvents for cations. Whereas for the cases when the DNs are experimentally measurable, everything is clear, for other solvents such as water and alcohols various controversial attempts have been made to evaluate DNs from other evidence. High values of DNs of alcohols (e.g., 134 kJ/mol for ethanol)[15h] as compared to water (75 kJ/mol)[15h] were derived from spectroscopic parameters (ethanol would be on this scale more basic than e.g., dimethylsulfoxide).[15h] On the other side, Abraham recently claimed, from the analysis of solubilities of various solutes in alcohols, that solvent hydrogen basicity remains same for studied alcohols and is practically same as for water.[27]

The nonspectroscopic values of *a* coefficients (measure of the solvent hydrogen-bond basicity) of alcohols and water[27] seem well correlate with the older values of donor numbers given by Gritzner[10h,f] and can be normalized with them as follows. The latter values were plotted against the former,[28] and a straight line was obtained ($r^2 = 0.9953$). From the obtained line, thus normalized DNs of alcohols are reported in Table 1. These are looked on only as orientation content and were therefore put in brackets and not used for subsequent correlation of b_S with DN.

Results

Phenomenological Analysis of the Data. The results of analysis of data from set ***B′*** according to eq 4 are given in Table 1. From the table, it is apparent that the straight line dependence with correlation coefficient $r > 0.99$ applies to 15 from 19 reported solvents (for five solvents—DMThF, NMThP, MeCN, BN, PL—only data for K^+, Rb^+, and Cs^+ from the available full set of five cations were used, see below). The mean standard deviation from straight lines of ΔG^0_{tr} for data collected in Table 1 is less than ±0.7 kJ/mol, which corresponds to an acceptable 7mV error of electrochemical measurements. These findings

TABLE 1: Linear Dependences of $\Delta_t G^0_{PC \rightarrow S}(M^+)$ on $\Delta G^0_{Hydr}(M^+)$ for Alkali Metal Cations for the Set of Data B′

solvent	cations	a_S (kJ/mol)	b_S	r	SD (kJ/mol)	DN[c] (kJ/mol)
DMThF[a,b]	K^+, Rb^+, Cs^+	−46.76 ± 1.87	−0.2138 ± 0.0068	−0.999 49	0.217	
NMThP[a,b]	K^+, Rb^+, Cs^+	−41.32 ± 10.4	−0.1931 ± 0.0380	−0.981 14	1.213	
NM	Na^+, K^+, Rb^+, Cs^+	−32.45 ± 1.95	−0.1248 ± 0.006 52	−0.997 28	0.558	11.3
PC	Li^+, Na^+, K^+, Rb^+, Cs^+	0	0	1.000 00	0	63.2
BN[a]	K^+, Rb^+, Cs^+	20.68 ± 4.90	0.0611 ± 0.01789	0.959 77	0.570	49.8
Py	Li^+, Na^+, K^+, Rb^+, Cs^+	19.41 ± 3.13	0.0812 ± 0.009 17	0.981 44	1.663	138
W (H_2O)	Li^+, Na^+, K^+, Rb^+, Cs^+	14.64 ± 1.72	0.0874 ± 0.005 05	0.995 04	0.915	91.7;(89.4)
ETDI	Li^+, Na^+, K^+, Rb^+, Cs^+	23.33 ± 2.80	0.1064 ± 0.008 18	0.991 25	1.484	83.7
DMF	Li^+, Na^+, K^+, Rb^+, Cs^+	15.93 ± 1.86	0.1127 ± 0.005 43	0.996 53	0.985	111
MeCN[a,b]	K^+, Rb^+, Cs^+	30.77 ± 1.40	0.1197 ± 0.005 11	0.999 09	0.163	59.0
PrOH	Li^+, Na^+, K^+, Rb^+, Cs^+	39.24 ± 3.17	0.1197 ± 0.009 26	0.991 14	1.680	(92.3)
EtOH	Li^+, Na^+, K^+, Rb^+, Cs^+	35.10 ± 1.66	0.1234 ± 0.004 86	0.997 69	0.881	83.7;(83)
MeOH	Na^+, K^+, Rb^+, Cs^+	31.18 ± 2.26	0.1235 ± 0.007 55	0.996 29	0.646	79.5;(84.6)
DMSO	Na^+, K^+, Rb^+, Cs^+	19.05 ± 2.78	0.1296 ± 0.009 28	0.994 91	0.794	125
BuOH	Li^+, Na^+, K^+, Rb^+, Cs^+	46.23 ± 1.42	0.1297 ± 0.004 15	0.998 47	0.752	(86.5)
NMF	Na^+, K^+, Rb^+, Cs^+	26.18 ± 0.72	0.1347 ± 0.002 41	0.999 68	0.206	113
NMP	Na^+, K^+, Rb^+, Cs^+	22.31 ± 1.31	0.1389 ± 0.004 37	0.999 01	0.374	114
PL[a]	K^+, Rb^+, Cs^+	83.49 ± 8.01	0.144 ± 0.029 25	0.980 02	0.932	
TMP	Na^+, K^+, Rb^+, Cs^+	33.88 ± 2.45	0.1707 ± 0.008 17	0.997 72	0.700	96.2
HMP	Na^+, K^+, Rb^+, Cs^+	53.61 ± 5.05	0.265 ± 0.016 87	0.995 97	1.442	162

[a] Only the points for K^+, Rb^+, and Cs^+ lie on a straight line, and the data for Na^+ and Li^+ are omitted in the correlation. [b] See Figure 4 for details. [c] The donor numbers from ref 10h,f, orientative values from a correlation described in the text and note[28] are in brackets. See ref 35.

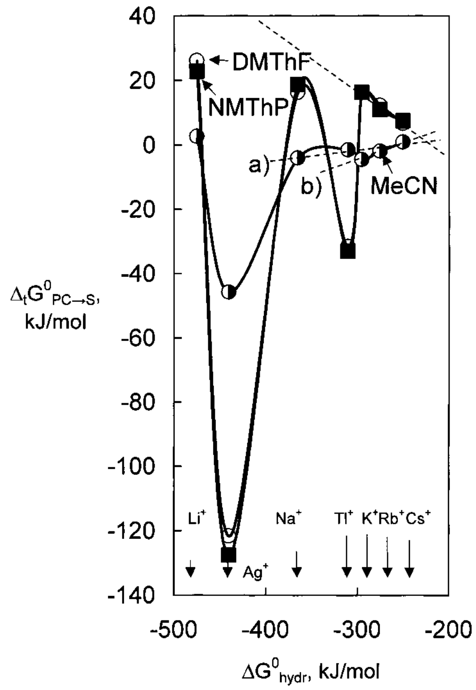

Figure 4. Transfer of alkali metal cations, Ag^+, and Tl^+ from PC (***B′*** set of data) into a few solvents not showing linearities in Table 1. Note that deviation from straight line connecting points for K^+, Rb^+, and Cs^+ and for DMThF and NMThP for Li^+ and Na^+ parallels behavior of Ag^+ and Tl^+. For MeCN the situation is less clear. Straight line can be plotted through Na^+, K^+, Rb^+, Cs^+, and Tl^+ (line *a* in the Fig.), or only for K^+, Rb^+, and Cs^+ (line b). In Table 1 the line *b* (see text) was used. In both cases, the point for Li^+ is an outlier.

enable us to consider eq 4 as significant in Gibbs energies of transfer of alkali metal cations between two solvents.

Data for three solvents with irregular behavior, i.e., DMThF, NMThP, and MeCN, are shown in Figure 4. The picture reveals that for the two former solvents, the points for three heaviest alkali metal cations lie on the straight line, whereas relative increase of solvation by these solvents is apparent for Na^+ and still more for Li^+ ions. This is reminiscent to a similar but larger increase for Tl^+ and Ag^+ ions and suggests that the deviations of Li^+ and Na^+ from the straight line may be more a regular feature than any possible error of measurement (if composite probability of straight line character of all set of data rather than individual points on particular straight line is taken into account).[29] Higher weight on the experimental data for K^+, Rb^+, and Cs^+ than on Li^+ and Na^+ should be assigned also from a reason that any experimental error possibly connected with not perfectly dry organic solvents would be lower for the former group. From this reason, only the former values were used in Table 1 for transfer from PC to MeCN (line b in Figure 4). However, as seen from the Figure 4, the data for PC → MeCN transfer are less regular than for two preceding solvents. Data for pyrolle were irregular in terms of eq 4.

All regression straight lines, for clarity without showing individual points and extrapolated to a region of mutual intersections, are shown in Figure 5. Lines display either negative or positive slopes, thus expressing the strength of solvation by a solvent relative to propylene carbonate according to eq 4. Propylene carbonate seems to be a solvent of only intermediate solvating ability because the straight lines in Figure 5 are arranged almost symmetrically in a "folding fan" manner around the *x*-axis at the figure.

Any possible model of solvation should presume that, for a hypothetical alkali metal cation with sufficiently large radius (or sufficiently positive ΔG^0_{hydr}), any interaction with solvent will ultimately disappear and indeed the lines mostly intersect at a value of ΔG^0_{hydr} −200 kJ/mol. Thus, more interesting than a_S parameter of eq 4 is a value $-a_S/b_S$, i.e., value of ΔG^0_{hydr} for $\Delta_t G° = 0$.

Classical correlation of the slopes b_S with donor numbers of solvents is given at Figure 6. Although the correlation is not perfect ($y = 0.0021x - 0.079$; $r = 0.8654$, not including the values of DN's put in brackets in Table 1), generally the donor number is highly responsible for the solvation. According to eq 4, the solvating abilities are given by ($b_S + 1$) values and range from 1.265 for HMP, the strongest donor solvent to 0.786 for DMThF being the weakest donor solvent. The change of total free energy of transfer from PC to any other solvent is less than 30% of the total solvation energy.

Although, for b_S values, the extrathermodynamic assumption is of no importance, it is not so for $-a_S/b_S$ values. Any deficiency of bis (biphenyl) chromium assumption for a concrete system PC−S may enter into play and the test is particularly severe. Fortunately, lines for most solvents intersect at relatively

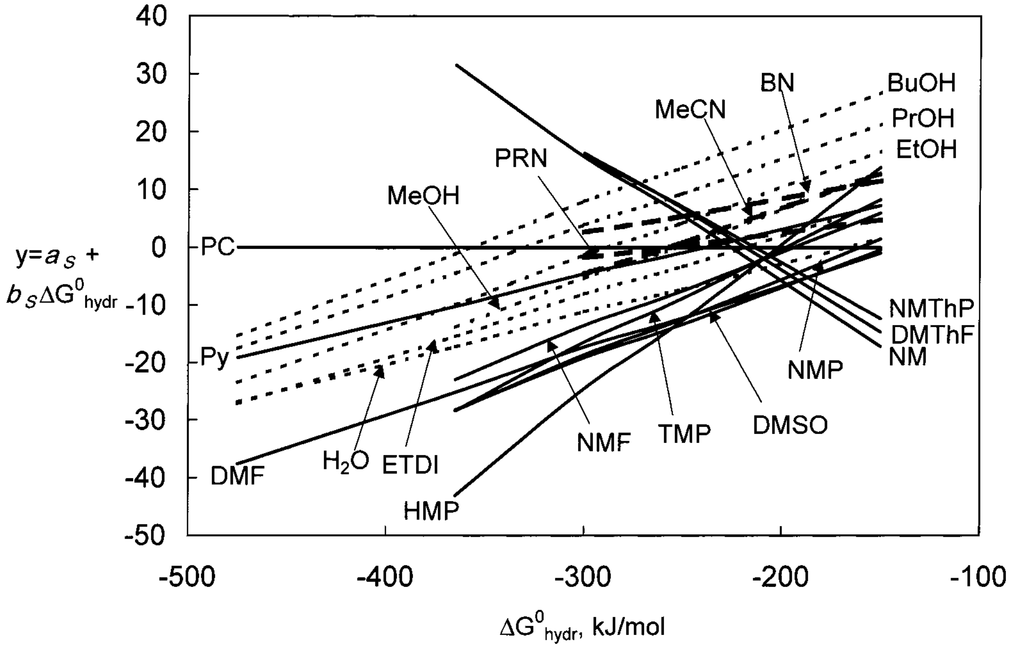

Figure 5. Analysis of a_S and b_S parameters. For clarity, only the straight lines, extrapolated to a region of intersection, are shown and individual points were omitted.

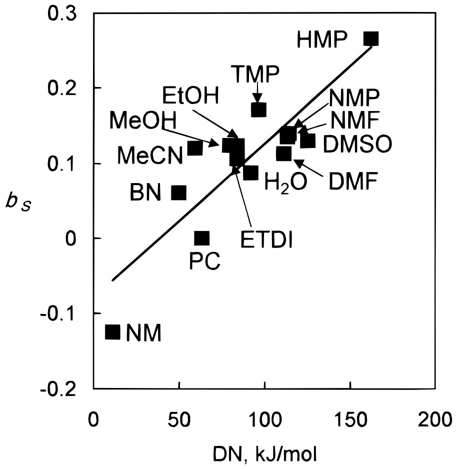

Figure 6. Dependence of parameter b_S of straight lines on donor numbers DN of the solvents. Data from Table 1.

small region of ΔG^0_{hydr} and $\Delta_t G° = 0$. Thus, the chosen bis (biphenyl) chromium assumption can be considered as a reasonable one. Not considering irregular behavior of nitrile solvents, already noted above, marked exception is observed for higher alcohols (EtOH, PrOH, and BuOH) with their abnormally negative $-a_S/b_S$ values. It is difficult to judge merely from the used data whether insufficiency of extrathermodynamic assumption or other factor is responsible for this irregularity.

One reason propylene carbonate was chosen as a reference solvent was a concern whether nonelectrostatical interaction term, causing expulsion of higher alkali metal cations from the structure of water according to eq 8, was not operating. Comparing the straight line for PC to water transfer with other transfers, however, seems to indicate that such an interaction is of less importance. This would be in accordance with statistical analysis of Marcus according to which the parameter related to structure of solvent applied only for large, nonalkali metal, cations.[15i] Previous proposals regarding the influence of $\Delta_t G°(\mathrm{i})_{\mathrm{nonel}}$ on magnitude of slopes for water to solvent transfers[11,18] do not seem to be fully supported here.

TABLE 2: Relative "Softness" Increment of Gibbs Energy of Transfer for $Ag^+$and Tl^+ and Softness Parameters from Present Paper, δ_s, Compared to Literature μ Parameter[15d,36]

	$\Delta_t G°\ (M^+)_s$ kJ/mol			
solvent	Ag^+	Tl^+	μ	δ_s
NMThP	−171.4	−51.7	1.35	1.71
DMTF	−169.0	−51.1	1.35	1.69
Py	−71.5	−20.6	0.64	0.72
BN	−34.0	−1.9	0.34	0.34
AN	−23.9	4.7	0.35	0.24
NMF	−9.7	−5.0	0.12	0.10
PrOH	−7.7	−7.7	0.16	0.08
1-BuOH	−7.3	−8.5	0.18	0.07
NMP	−5.8	−4.3	0.13	0.06
ETDI	−5.4	−5.4	−0.03	0.05
DMF	−4.7	−4.3	0.11	0.05
EtOH	−4.7	−4.4	0.08	0.05
H_2O	0	0	0	0.00
PC	0	0	−0.09	0.00
DMSO	0.9	−10.0	0.22	−0.01
MeOH	1.6	−3.7	0.02	−0.02
HMP	2.9	3.4	0.29	−0.03
TMP	8.7	1.3	−0.02	−0.09

Softness of Solvents. In the ***B*** set of transfer values, regularly also $\Delta_t G°$ s of two soft cations Ag^+ and Tl^+ are reported, from which we calculated by the method described above the respective values of ***B′*** set (data are given in legend to Table 2, ref 36). These values permit the construction of a scale of solvent softness according to HSAB concept, originating from linear dependences found for alkali metal cations.

From previous attempts to construct the scale of softness of the solvents, two particular examples exist: (i) the softness parameter *SP* defined as $SP = \Delta_t G^0_{BN \rightarrow S}(Ag^+)$ from benzonitrile to any other solvent[10f] and (ii) softness parameter μ based on the transfer of Ag^+ cation and corresponding sizes of ions.[15d] It was argued that the size of Ag^+ is intermediate of those of Na^+ and K^+ and the parametrized μ is, consequently:[15d]

$$\mu = \{(1/2)[\Delta_t G^0_{W\rightarrow S}(Na^+) + \Delta_t G^0_{W\rightarrow S}(K^+)] - \Delta_t G^0_{W\rightarrow S}(Ag^+)\}/(-100). \quad (9)$$

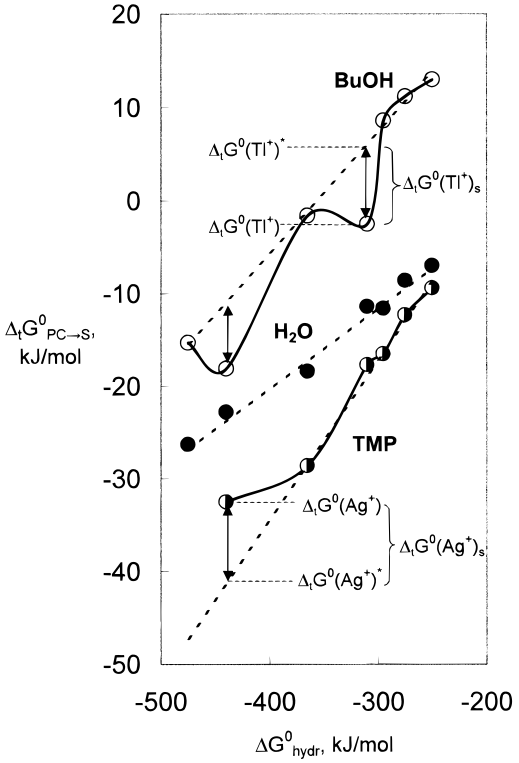

Figure 7. Transfers from PC into BuOH, H_2O and TMP. Meaning of the values $\Delta_t G^\circ$ (Ag^+), $\Delta_t G^\circ$ $(Ag^+)^*$, and $\Delta_t G^\circ$ $(Ag^+)_s$ is shown graphically. See text for details.

In this paper, we calculated a softness parameter δ_S as:

$$\delta_S = [\Delta_t G^0_{PC\rightarrow S}(Ag^+) - \Delta_t G^0_{PC\rightarrow S}(Ag^+)^*]/(-100) = \Delta_t G^\circ\ (Ag^+)_s/(-100) \quad (10)$$

where $\Delta_t G^0_{PC\rightarrow S}(Ag^+)^*$ is a Gibbs energy of transfer of a hypothetical ion having the same ΔG^0_{hydr} value as Ag^+ ion but with properties of the alkali metal cations group as extrapolated from the respective straight line $[\Delta_t G^0_{PC\rightarrow S}(Ag^+)^* = a_S - 440 b_S]$. Adopted procedure is best illustrated by Figure 7, where data for three chosen solvents were plotted. From the figure, it is apparent that the points for Ag^+ and Tl^+ for PC → H_2O transfer fall on the common line with values for alkali metal cations. Hence, both reference solvents appear to be of the same softness, and the parameters μ and δ_S ought to be mutually comparable. However, due to different reference points that were chosen for expressing the two parameters and different input data, their absolute values may differ especially for the cases when the softness of the solvent is low. Generally, good agreement of two sets is apparent from the Table 2. Alcohols are, as a rule, slightly harder solvents according to δ_S than from μ. Strong donor solvating solvents DMSO, HMP, and TMP are according to δ_S all three hard solvents, whereas according to μ, DMSO and HMP are to a certain degree soft solvent, both softer than alcohols.

From other properties connected with the softness of solvents the following additional information can be obtained:

- $\Delta_t G^\circ\ (Ag^+)_s$ values correlate quite well with $\Delta_t G^\circ\ (Tl^+)_s$ values. The dependence is given as $\Delta_t G^\circ\ (Tl^+)_s = 0.2765 \Delta_t G^\circ\ (Ag^+)_s - 2.2996$, and $r = 0.9486$, showing smaller HSAB effect for Tl^+ than for Ag^+ (~30%). Let us note that the straight line cross nearly at the beginning of coordinates thus supporting the consistency of results. If b_S and δ_S values are compared, the picture is as follows. For low δ_S values, around 0, b_S assume various values between 0 and 0.3, whereas for high δ_S values a decrease of b_S from some b_S 0.15 to −0.2 seems to be detected. This would mean a kind of competition between donor bond and soft bond, which starts to operate only when the softness of the solvent is sufficiently high.

New Aspect of Resolvation of Alkali Metal Cations

Outline of the Problem. When summarizing the results pertaining to $\Delta_t G^\circ$ values between two solvents and trying to explain them on the basis of one common model, a number of conceptual difficulties are encountered. The Born equation and, even more, any electrostatical terms containing dielectric constant or dipole moment of the solvent do not appear to be operative for $\Delta_t G^\circ$ magnitude.[15] Previously reported linearities in Gibbs energies of transfer would indicate that only one factor is of primary importance for $\Delta_t G^\circ$ for full one series of ions, viz. the 1:1 term of ion/solvent interaction.[12] This reflects in a b_s coefficient constant throughout the series of alkali metal cations and a particular solvent, as also reported here. A previous finding shows that the complexation constants of the type 1:1 of some ions with solvent donors follow the same trend as overall $\Delta_t G^\circ$ of them,[9] support such a point of view.

However, the latter view is in contradiction with available common information on the process of solvation, i.e., its picture of multi-interaction type in which the ion is surrounded and interacts with multitude of solvent molecules in a general fashion Ξ, where Ξ just differs for each ion, so that, generally, $\Xi\ (Li^+) \neq \Xi\ (Na^+) \neq \Xi\ (K^+)$, etc.

Gas-Phase Solvation Data as Clue to $\Delta_t G^0$ Values. To solve the riddle depicted in the previous paragraph, it is useful to look at the formation energies of small individual clusters. For that purpose, data on gas-phase solvations in water and acetonitrile by Kebarle et al.[30,31] (data referred to 1 atm. pressure and 298 °C) were used and from them a new, according to our knowledge not previously reported, information was extracted. The Gibbs energies of formation $-\Delta G^f(n, n+1)$ for individual clusters of Li^+, Na^+, K^+, Rb^+, Cs^+ (H_2O), and Na^+, K^+, Rb^+, Cs^+ (acetonitrile) were plotted against respective $\Pi_i \equiv \Delta G^0_{hydr}(i)$ in Figures 8 and 9, respectively.

From the two pictures, it is apparent that $-\Delta G^f(n, n+1)$s' for each individual cluster are straight line functions of $\Pi_i \equiv \Delta G^0_{hydr}(i)$, the behavior is exactly the same as for overall $\Delta_t G^\circ$'s reported in this paper.

The overall solvation Gibbs energy of an ion in a solvent S in terms of individual cluster formation energies can be viewed as a sum of all contributions:

$$\Delta G^{0,S}_{solv}(i) = \Delta G^{f,S}(0,1) + \Delta G^{f,S}(1,2) + \Delta G^{f,S}(2,3) + ... + \Delta G^{f,S}(n,n+1) = \Sigma \Delta G^{f,S} \quad (11)$$

and if any individual cluster energy for a series of alkali metal cations is a straight line function of Π_i, it can be written:

$$\Delta G^{0,S}_{solv}(i) = (a^S_{01} + b^S_{01}\Pi_i) + (a^S_{02} + b^S_{02}\Pi_i) + ... + n + p + q + ... \quad (12)$$

where in brackets are terms dependent linearly on Π_i and n, p, q are any non dependent terms. Alternatively, if all the independent terms are collected into one constant c_S and the sum of b is denoted as b^S:

$$\Delta G^{0,S}_{solv}(i) = (b^S_{01} + b^S_{12} + b^S_{23} + b^S_{34} + ...)\ \Pi_i + c_S = b^S\ \Pi_i + c_S \quad (14)$$

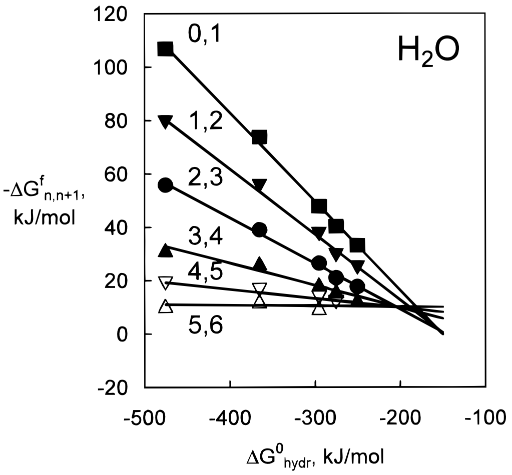

Figure 8. Dependences of consecutive Gibbs energies of formation of gas-phase clusters of ions with n molecules of water. The data after multiplying by 4.187 (to convert original data in kcal/mole to kJ/mol) were taken from the Table 1 of paper[30] (referred to 1 atm. and 298°K). The least-squares analysis of straight lines $\Delta G^f(n, n+1)$ vs ΔG^0_{hydr} reads (in the order: cluster number $(n, n+1)$, slope, intersect, correlation coefficient r, standard deviation SD, number of points) as follows: (0,1), 0.3325 ± 0.009 23, 50.10 ± 3.15, 0.9988, 1.673, 5; (1,2), 0.2451 ± 0.010 37, 36.25 ± 3.54, 0.9973, 1.879, 5; (2,3), 0.1715 ± 0.006 82, 25.02 ± 2.33, 0.9976, 1.237, 5; (3,4), 0.083 37 ± 0.011 08, 6.74 ± 3.79, 0.9745, 2.010, 5; (4,5), 0.033 89 ± 0.005 46, −3.10 ± 1.97, 0.9751, 0.853, 4; (5,6), 0.003 26 ± 0.013 57, −9.50 ± 5.23, 0.2335 (not straight line), 1.741, 3.

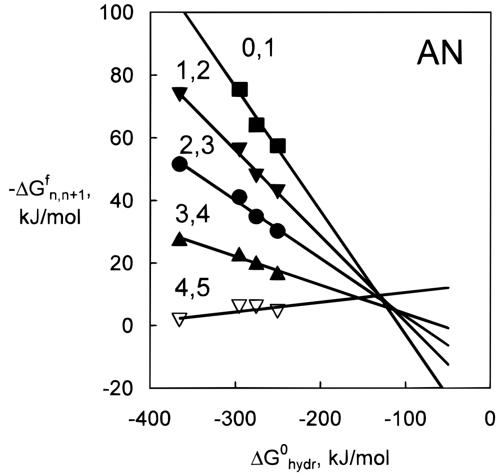

Figure 9. Dependences of consecutive Gibbs energies of formation of gas-phase clusters of ions with n molecules of acetonitrile. Data taken after recalculation to kJ/mol from the Table 1 of reference.[31] (referred to 1 atm and 298°K). The least-squares analysis of straight lines reads in order given at legend to Figure 8 as follows: (0,1), 0.3946 ± 0.084 33, 42.22 ± 23.10, 0.9779, 2.69, 3; (1,2), 0.2744 ± 0.017 36, 26.24 ± 5.20, 0.9960, 1.48, 4; (2,3), 0.1855 ± 0.017 97, 15.61 ± 5.38, 0.9907, 1.54, 4; (3,4), 0.091 78 ± 0.011 79, 5.34 ± 3.53, 0.9839, 1.01, 4; (4,5), −0.03093 ± 0.0196, −13.64 ± 5.87, −0.7446 (not straight line), 1.68, 4.

Writing eq 13 for two solvents S and R, the relation for Gibbs energy of transfer is arrived at:

$$\Delta_t G^0_{S\to R}(i) = \Delta G^{0,R}_{solv}(i) - \Delta G^{0,S}_{solv}(i) = (b^R - b^S)\,\Pi_i + (c_R - c_S) \quad (15)$$

or, the $\Delta_t G^0_{S\to R}(i)$ for the series of alkali metal cations is a linear function of their Π_i's values.

The causal explanation of the observed linearities in $\Delta_t G°$ thus seems to lie in the fact that the behavior of formed 1:1 cluster, which would explain the linearities on the first level of approximation, is in reality copied by the behavior of consecutive clusters. Thus, the enigmatic claims on the importance of 1:1 interaction for the transfer energetics[12] may be explained.

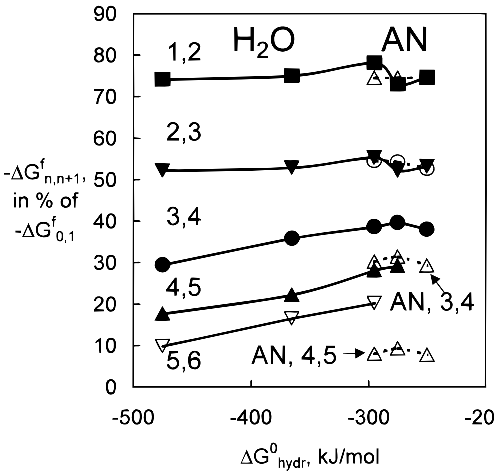

Figure 10. Relative Gibbs energies of formation of consecutive clusters referred to a cluster (0, 1) for water and acetonitrile (100%), from refs 30,31.

This point of view is corroborated by looking at the region where the straight lines cross at Figures 8 and 9. The existence of a common point at which all the Π_i dependent increments of $\Delta G^0_{solv}(i)$ level off, lies for water, and little worse for acetonitrile, at a region of Π_i near to −200 kJ/mol, i.e., roughly identical to the crossing region of the $\Delta_t G°$ straight lines for most solvents in Figure 5.

Although we have not found in the literature the relevant data for other solvents than water and acetonitrile, the general picture of linearities of individual cluster formation energies on Π_i is strengthened by the similar behavior of anions.[32]

The results shown at Figures 8 and 9 insinuate that in fact we deal with a new aspect of solvation and this must be explained.

Solvation of Alkali Metal Cations in Water and Acetonitrile. According to classical views, the energetics of solvation is treated as a mathematical solution of number of mutual interactions of ion and solvent. The results of this paper indicate a new aspect, namely that the intrinsic property of an alkali metal cation expressed here as Π_i is of decisive importance both for overall energies of solvation and for individual cluster energies. For the overall energies of solvation, this aspect can be perhaps viewed as if in the strong electrical field of ion the assembly of available solvating molecules would always accommodate the positions around the ion in some optimal manner in which the total energetical need of the ion is saturated. In this manner, the proportionalities among the overall ΔG^0_{solv} values can appear.

Even more intriguing is this question: Why is such behavior in a rudimentary form also copied by the individual clusters? To have more insight into the question, the analysis of the energetical levels of individual clusters taken from literature[30,31] is useful. In Figure 10, the -$\Delta G^f(0, 1)$ were equaled to 100% and the percentages of this value for consecutive clusters were plotted.

The energies -$\Delta G^f(1, 2)$ and -$\Delta G^f(2, 3)$ lie for all alkali metal cations and water and acetonitrile as solvents very near to the values 75% and 50% of -$\Delta G^f(0, 1)$ as seen from Figure 10. From another paper of Kebarle,[33] only data for K^+ ion could be used for additional solvents (data referred to pressure P extrapolated to 0 atm. and temperature 300°K,[33] in variance with results at[30,31]). The data read in % of $-\Delta G^f(0, 1)$ (solvent, (1, 2) and (2, 3) clusters, respectively): H_2O, 78.1, 55.3; MeCN, 68.4, 47.4; DMF, 65.2, 41.7; DMA, 68.7, 45.8; DMSO, 76, 44. The average values amount to 71.3% and 46.8% for second and third cluster as a mean for these five solvents.

Thus, for the behavior of the first two or three clusters (0, 1), (0, 2), and (0, 3), for all alkali metal cations and considered solvents, a kind of saturation interaction leading to the future solvate 1:4 seems to be expressed. This would correspond to consecutive competition of donor molecule for available sites (if one site is already occupied, the remaining energy for the second site is 75% of the total etc.) and is in accord with other data on first hydration or solvation shell of alkali metal cations.[34] Such an interaction must be overridden for higher clusters by additional interaction, mainly outside the first solvation shell.[34] This second interaction may be probably considered as essentially of nonsaturation type, i.e., of ion−dipole character, and partial increments may be according to Figures 8 and 9 for larger clusters constant and mostly independent of the size of alkali metal cation.

The reason for the first clusters copying the overall Gibbs energy of solvation remains unclear. Because the results on $-\Delta G^f$ and $\Delta_t G^0$ were obtained by different techniques and at independent laboratories, hardly any artifact comes into play. Mutual agreement supports the correctness of data of both $\boldsymbol{B'}$ set and reported gaseous cluster formation energies. The results are further strengthened by analogous behavior of univalent anions to be published in our next communication.[32] Nonetheless, the correlation can be hardly understood in the scope of the classical models of solvation. In fact, it implies some deeper causal interconnection of the partial and total values, not noticed until now.

Conclusions

In this paper, one of two existing literature sets of individual Gibbs energies of transfer $\Delta_t G°(i)$ of simple monatomic univalent cations was used for analysis of dependences of $\Delta_t G°(i)$ values on standard hydration energies of the ions. In agreement with several previous works, linearities were proved to be valid for alkali metal cations and for majority of solvents.

The linearities, according to the present paper, originate largely from the linearities of the formation of simple consecutive clusters of an ion with solvent and total $\Delta_t G°(i)$ magnitudes are thus reflected already in the behavior of the first 1:1 cluster.

Various preceding claims on the driving force of resolvation, such as unimportance of electrostatical terms and decisive role of 1:1 solvent/ion interactions, are conserved in the present empirical model. The general parameter of the strength of solvation $\Pi_i = \Delta G^0_{hydr}$ is used in the paper. Any Π_i dependent energetical increment disappears for most transfer systems for Π_i less negative than about −200 kJ/mol in accordance with behavior of the gas-phase clusters in water and acetonitrile. The first two to three clusters of any alkali metal cation display a tendency to form “future” 1:4 cluster of a saturation type. The simple behavior detected here may serve as a guide for future comparisons of resolvation energetics, but theoretical reasons for it remain to be clarified.

In agreement with number of previous studies, the donor number of the solvent, here expressed in form of a parameter b_S, is the main factor controlling the selectivity of transfer.

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Appendix

Additional Solvents, Data from a Previous Compilation of Polarographic Half-Wave Potentials Tabulated in Paper.[10e] For the sake of completeness, we have recalculated Gibbs energies of transfer for other additional solvents reported in older compilation of $E_{1/2}$ values of reduction of alkali metal cations referred to bis (biphenyl) chromium (I)/(0) couple.[10e]

The recalculated values were obtained by:

$$\Delta_t G^0_{PC \to S}(M^+) = 96.486\ [E_{1/2}(M^+, S) - E_{1/2}(M^+, PC)]\ (V, kJ/mol) \quad (16)$$

and instead of reported value of $E_{1/2}$ (Rb$^+$, PC) = −1.23 V,[10e] a corrected value, −1.203 V, was used, see the main text for justification. For the solvents given in the main text, the values $\Delta_t G^0$ recalculated from the older[10e] and newer paper[10i] sometimes slightly differ and newer data were given preference in the main text.

The respective data $\Delta_t G^0_{PC \to S}(M^+)$ in kJ/mol then read as (abbreviation of the solvent, solvent, $\Delta_t G^0_{PC \to S}(M^+)$ for Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, n/a means the value did not exist): **A**, acetone: −14.5, −15.1, −8.9, −9.0, −4.8; **BuL**, butyrolactone: −8.7, −9.8, −6.9, −5.5, −2.9; **DEA**, diethylacetamide: −49.7, −29.9, −17.9, −13.5, −11.8; **DEF**, diethylformamide: −35.5, −25.5, −15.1, −12.4, −9.3; **DMA**, dimethylacetamide: −42.5, −30.1, −20.7, −14.1, −12.0; ***^{i}*BuN**, isobutyronitrile (2-methylpropanenitrile): 3.8, −2.3, 9.6, 9.0, 9.6; **THF**, tetrahydrofuran: −17.8, −17.7, −1.3, −0.1, −7.4; **TMS**, tetramethylene sulfone (tetrahydrothiophene-1,1-dioxide), at 30 °C: −1.0, −7.9, −5.9, −5.5, −2.9; **TMU**, tetramethylurea: −49.2, −31.2, −20.5, −15.2, n/a.

For four solvents well pronounced straight line dependences of $\Delta_t G^0_{PC \to S}(M^+)$ on ΔG^0_{hydr} were found. The respective parameters are as follows (solvent: a, and b, parameters, r: correlation coefficient, SD: standard deviation, n: number of points): **DEA**: 32.94, 0.1732, $r = 0.9981$, SD = 1.1304, $n = 5$; **DEF**: 19.72, 0.1183, $r = 0.9940$, SD = 1.365, $n = 5$; **DMA**: 21.73, 0.1374, $r = 0.9907$, SD = 1.974, $n = 5$; **TMU**: 29.45, 0.1659, $r = 0.9985$, SD = 0.9993, $n = 4$.

References and Notes

(1) Strehlow, H. W. *The Chemistry of Non-Aqueous Solvents*; Academic press: New York, 1966.

(2) Abraham, M. H.; Liszi, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 1604; Abraham, M. H.; Liszi, J. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 2858.

(3) Moyer, B. A.; Sun, Y. In *Ion Exchange and Solvent Extraction*; Marcel Dekker: New York, 1997; Vol. 13, p 295.

(4) Markin, V. S.; Volkov, A. G. *Electrochim. Acta* **1989**, *34*, 93.

(5) Krishtalik, L. I.; Alpatova, N. M.; Ovsyannikova, E. V. *Electrochim. Acta* **1991**, *36*, 435.

(6) Osakai, T.; Ebina, K. Ion Solvation and Resolvation. In *Liquid Interfaces in Chemical, Biological, and Pharmaceutical Applications*; Volkov, A. G., Ed.; Marcel Dekker: New York, 2000.

(7) Krishtalik, L. I.; Alpatova, N. M.; Ovsyannikova, E. V. *Russ. J. Electrochem. (English translation)* **1995**, *31*, 802.

(8) Cox, B. G.; Parker, A. J.; Waghorne, W. E. *J. Phys. Chem.* **1974**, *78*, 1731.

(9) Sakamoto, I.; Okazaki, S.; Sogabe, K.; Sato, K.; Hashimoto, S.; Munechika, M. *J. Electroanal. Chem.* **1990**, *286*, 181.

(10) (a) Gritzner, G. *J. Chem. Soc. Far. Trans. 1* **1986**, *82*, 1955. (b) Gritzner, G.; *J. Phys. Chem.* **1986**, *90*, 5478. (c) Gritzner, G. *J. Chem. Soc.*

Far. Trans. 1 **1988**, *84*, 1047. (d) Gritzner, G. *Pure Appl. Chem.* **1988**, *60*, 1743. (e) Gritzner, G. *Pure Appl. Chem.* **1990**, *62*, 1839. (f) Gritzner, G. *Rev. Inorg. Chem.* **1991**, *11*, 81. (g) Gritzner, G. *J. Chem. Soc. Far. Trans.* **1992**, *88*, 3013. (h) Gritzner, G.; Hörzenberger, F. *J. Chem. Soc., Faraday Trans*. **1992**, *88*, 3013. (i) Gritzner, G. *Electrochim. Acta* **1998**, *44*, 73.

(11) Rais, J. *Collect. Czech. Chem. Comm*. **1971**, *36*, 3080.

(12) (a) Notoya, R.; Matsuda, A. *J. Phys. Chem.* **1985**, *89*, 3922, (b) Matsuda, A.; Notoya, R. *6th USSR-Japanese Seminar on Electrochemistry*, Moscow 1986, Proceedings, p 32. (c) Notoya, R.; Matsuda, A. *Elektrokhimia* (Russian) **1991**, *27*, 341. (d) Notoya, R. In *Trends in Phys. Chem.*; Menon, J., Ed.; Vilayil Gardens: India, 1994; Vol. 4, p 219.

(13) Solomon, T. *J. Electroanal. Chem.***1991**, *313*, 29.

(14) Gordon, J. E. *The Organic Chemistry of Electrolyte Solutions*; John Wiley: New York, 1975; p 227.

(15) (a) Marcus, Y. *Rev. Anal. Chem.* **1980**, *5*, 53. (b) Marcus, Y. *Pure Appl. Chem.* **1983**, *55*, 997. (c) Marcus Y. *Ion Solvation*; Wiley-Interscience: New York, 1985. (d) Marcus, Y. *J. Phys. Chem*. **1987**, *91*, 4422. (e) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem.* **1988**, *92*, 3613. (f) Marcus, Y. Ion Solvation In *Liquid−Liquid Interfaces, Theory and Methods*; Volkov, A. G., Deamer, D. W., Eds.; CRC Press: New York, 1996. (g) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997. (h) Marcus, Y. *Properties of Solvents*; Wiley: Chichester, 1998. (i) Marcus, Y., *Electrochim. Acta* **1998**, *44*, 91.

(16) Rais, J.; Okada, T.; Alexova, J. *unpublished results.*

(17) Selucky, P.; Rais, J.; Krtil, J. *International Solvent Extraction Conference*, The Hague, 1971; paper 616.

(18) Friedman, H. L.; Krishnan, C. V., *Water. A Comprehensive Treatise*; Plenum Press: New York, 1973; Vol. 3.

(19) L′Her, M.; Morin-Bozec, D.; Courtout-Coupez, J. *J. Electroanal. Chem*. **1974**, *55*, 133.

(20) We put higher weight on these results because the authors of the paper reported data $\Delta_t G°$ (i) for various compositions of the solvents and data for pure solvents can be in this way checked or extrapolated.

(21) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* **1981**, *103*, 1384.

(22) Data not included to analysis in papers.[15a,b]

(23) Haugen, G. R.; Friedman, H. L. *J. Phys. Chem*. **1968**, *72*, 4549.

(24) Danil de Namor, A. F.; Ghousseini, L. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2843.

(25) Tissandier, M. W.; Coven, K. A.; Feng, W. Y.; Gundlach, E.; Cohen, M. H.; Earhart, A. D., Coe, J. V.; Tuttle, T. R., Jr. *J. Phys. Chem*. A **1998**, *102*, 7787.

(26) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

(27) Abraham, M. H.; Le Joelle; Acree, W. E., Jr. *Collect. Czech. Chem. Commun.* **1999**, *64*, 1748. *a* parameter (“measure of the solvent hydrogen-bond basicity”) enters linear multiparameter dependence of gas−liquid partition coefficient of various solutes in a term $a\Sigma\alpha^{H}_{2}$, where $\Sigma\alpha^{H}_{2}$ is the “overall or summation hydrogen-bond basicity”, see original reference.

(28) Five points of comparison are (*a*; DN in kJ/mol): H_2O (3.904; 91.7), MeOH (3.701; 79.5), EtOH (3.635; 83.7), DMF (4.756; 111) and $CHCl_3$ (0.138; 0) (DN = 0 is supposed tentatively for $CHCl_3$ because the solvent should be similar to 1,2-dichlorethane, but the exact position of this far-distant point is not crucial).

(29) Specific interaction of some “hard” cations with “soft” multidentate donor ligands containing sulphur or nitrogen donor atoms is now well documented from the studies of ion selective electrodes and from the development of separation methods in nuclear technology. For example, Li^+ cations binds to several polydentate nitrogen ligands (Okada, T.; Sugihara, H.; Hiratani K. *Anal. Chim. Acta* **1986**, *186*, 307, Sugihara, H.; Okada, T.; Hiratani, K, *Anal. Sci*. **1993**, *9*, 593), trivalent Am^{3+} is complexed by phenanthroline (Rais, J.; Tachimori, S. *Sep. Sci. Technol*. **1994**, *29*, 1347) or aromatic dithiophosphinic acids (Modolo, G.; Odoj, R. *J. Radioanal. Nucl. Chem.* **1998**, *228*, 83). It seems probable that such a kind of interaction can occur with molecules containing only one N or S atom, because of the magnitude of effect much larger than expected experimental error, but independent supporting evidence is needed. Respective values of $\Delta_t G°\,(M^+)_s$ from the present analysis are for Li^+ and Na^+ ions −27.7 and −10.6 kJ/mol for NMThP, and −28.7 and −15.1 kJ/mol for DMTF.

(30) Dzidic, I.; Kebarle, P. *J. Phys. Chem*. **1970**, *74*, 1466.

(31) Davidson, W. R.; Kebarle, P. *J. Am. Chem. Soc*. **1976**, *98*, 6125.

(32) Rais, J.; Okada, T, *unpublished results.*

(33) Sunner, J.; Kebarle, P. *J. Am. Chem. Soc*. **1984**, *106*, 6135.

(34) From recent study of Na^+ and K^+ gas-phase clusters in mixtures of water and benzene, the relative importance of 1:4 cluster as a main constituent of the first solvation shell seems to be apparent. The authors (Cabarcos, O. M.; Weinheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110*, 8429) have discovered a structure $Na^+(H_2O)_4(C_6H_6)_8$ with water molecules present in a first hydration shell and benzene in the second one. For the $K^+(C_6H_6)_3(H_2O)_2$ cluster it was reported that one water molecule was forced to the second solvation shell, thus having three benzene and one water molecules in the first solvation shell and for the cluster Na^+-$(H_2O)_2(C_6H_6)_3$ one benzene molecule was forced into the second solvating shell thus leaving again 1:4 solvate in the first shell, composed, this time, from two benzene and two water molecules (3D diagrams 6 and 4, respectively, in the original paper).

(35) Data in Table 1 pertain to the relation $\Delta_t G^0{}_{PC \to S}(M^+) = a_S + b_S \Delta G^0{}_{hydr}(M^+)$ in kJ/mol, molar scale, 25 °C. See text for the source of input data, set ***B′***. The data are arranged in increasing order of solvation power of solvent (b_S coefficient). The donor numbers in kJ/mol are from refs 10h and f. The values in brackets were normalized according to the text. The following abbreviations are used for the solvents: **BN** = benzonitrile, **BuOH** = 1-butanol, **DMF** = *N*,*N*-dimethylformamide, **DMThF** = *N*,*N*-dimethylthioformamide, **DMSO** = dimethyl sulfoxide, **ETDI** = 1,2-ethanediol, **EtOH** = ethanol, **HMP** = hexamethylphoshoric triamide, **MeCN** = acetonitrile, **MeOH** = methanol, **NM** = nitromethane**,** **NMF** = *N*-methylformamide, **NMP** = *N*-methyl-2-pyrrolidone, **NMThP** = *N*-methyl-2-thiopyrrolidone, **PC** = propylene carbonate, **PL** = pyrrole, **PRN** = propanenitrile, **PrOH** = 1-propanol, **Py** = pyridine, **TMP** = trimethyl phosphate, **W(H_2O)** = water. The following values of $\Delta G^0{}_{hydr}$ (kJ/mol) were used: Li^+, −475; Na^+, −365; K^+, −295; Rb^+, −275; Cs^+, −250.[15g] The data of ***B′*** set are as follows (abbreviation of the solvent, $\Delta G^0{}_{tr}(M^+)_{PC \to S}$ for Li^+, Na^+, K^+, Rb^+, Cs^+, n/a = not available): **BN**: 9.6, 3.4, 2.9, 3.4, 5.6; **BuOH**: −15.3, −1.6, 8.6, 11.2, 13; **DMF**: −36.9, −26.6, −17.5, −14.9, −11.6; **DMThF**: 26.1, 16.2, 16.2, 12.2, 6.6; **DMSO**: n/a, −28.6, −18.6, −16.1, −14.1; **ETDI**: −26.2, −17.2, −8.8, −6, −1.8; **EtOH**: −23.5, −9.9, −0.9, −0.1, 5; **HMP**: n/a, −43.6, −24.1, −17.9, −14; **MeCN**: 2.6, −4.1, −4.6, −2, 0.8; **MeOH**: n/a, −14.2, −4.5, −2.9, −0.1; **NM**:[24] n/a, 13.2, 3.85, 2.45, −1.35; **NMF**: n/a, −22.9, −13.7, −11, −7.3; **NMP**: n/a, −28.3, −19.1, −15.6, −12.4; **NMThP**: 22.7, 18.6, 16.2, 10.8, 7.4; **PC**: 0, 0, 0, 0,0; **PL**: 46.5, 31.7, 41.4, 43.1, 47.8; **PRN**: 0.7, −3.3, −1.1, n/a, n/a (data were not linearly correlated, not given in the table); **PrOH**: −18.1, −4.4, 5.4, 7.4, 7.1; **Py**: −18, −12.7, −4.5, −2.7, 0; **TMP**: n/a, −28.6, −16.5, −12.3, −9.4; **W(H_2O)**: −26.3, −18.4, −11.6, −8.6, −7.

(36) The following $\Delta G^0{}_{hydr}$ were used: −440 (Ag^+) and −310 (Tl^+) kJ/mol.[15g] The data for $\Delta G^0{}_{tr}(M^+)$ for Ag^+ and Tl^+ are from the set ***B′*** and read as (abbreviation of the solvent, $\Delta_t G^0{}_{PC \to S}(M^+)$ for Ag^+, Tl^+): **BN**: −40.2, −0.2; **BuOH**: −18.1, −2.5; **DMF**: −38.4, −23.3; **DMThF**: −121.7, −31.6; **DMSO**: −37.1, −31.1; **ETDI**: −28.9, −15.1; **EtOH**: −23.9, −7.6; **HMP**: −60.1, −35.7; **MeCN**: −45.8, −1.6; **MeOH**: −21.6, −10.8; **NMF**: −42.8, −20.6; **NMP**: −44.6, −25.1; **NMThP**: −127.7, −33.2; **PC**: 0, 0; **PrOH**: −21.1, −5.6; **Py**: −87.9, −26.4; **TMP**: − 32.5, −17.7; **W(H_2O)**: −22.8, −11.4.