Solvation of Ions. XII. Changes in the Standard Chemical Potential of Anions on Transfer from Protic to Dipolar Aprotic Solvents

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Abstract: Solvent activity coefficients of anions and of cations at 25° for transfer from methanol to water, formamide, dimethylformamide, dimethylacetamide, dimethyl sulfoxide, acetonitrile, and hexamethylphosphorotriamide are reported. They are based on an extrathermodynamic assumption about the solubility of tetraphenylarsonium tetraphenylboride.

The change in the standard chemical potential of a solute, i, unimolar solution, hypothetically ideal with respect to Henry's law, on transfer from a reference solvent (superscript 0) to another solvent (superscript S) at temperature T is given by

$$\bar{\mu}_i{}^S - \bar{\mu}_i{}^0 = RT \ln {}^0\gamma_i{}^S \qquad (1)$$

where ${}^0\gamma_i{}^S$ is a distribution coefficient[2] or solvent activity coefficient.[3]

The solubility product $K^S{}_S$ of a salt AB, in the solvent S, when expressed as a quotient of molar concentrations, is related to the solubility product $K^0{}_S$ in the reference solvent at the same temperature, through (2), provided that the solid AB is the same in both solvents and that the saturated solutions are not ion paired. We assume the former provision and try to avoid situations where ion association is significant.

$$K^0{}_S = K^S{}_S({}^0\gamma^S{}_{A^+})({}^0\gamma^S{}_{B^-}) \qquad (2)$$

Although $({}^0\gamma^S{}_{A^+})({}^0\gamma^S{}_{B^-})$ can be calculated from (2), it will forever be impossible to estimate with certainty the individual values of ${}^0\gamma^S{}_{A^+}$ and ${}^0\gamma^S{}_{B^-}$.[2,4] This fact has not prevented chemists from applying extrathermodynamic assumptions to solubility and electrochemical data in their efforts to understand the behavior of ions in different solvents.[4-16] This communication examines what is to us the most acceptable of these assumptions, in an effort to explain the spectacular and important changes in the chemistry of anions upon transfer from water and related solvents to dipolar aprotic solvents.[3,17-20]

Grunwald, Baughman, and Kohnstam[7] have argued in favor of the assumption that we are considering. They suggest that species such as tetraphenylmethane, tetraphenyltin, tetraphenylphosphonium cation, tetraphenylarsonium cation, and tetraphenylboride anion respond in the same way to solvent transfer; *i.e.*, ${}^0\gamma^S{}_{Ph_4P^+} = {}^0\gamma^S{}_{Ph_4As^+} = {}^0\gamma^S{}_{Ph_4B^-} = {}^0\gamma^S{}_{Ph_4C} = {}^0\gamma^S{}_{Ph_4Sn}$.

These very large[21] solutes are symmetrical species of much the same size and shape with a central atom "buried" under an insulating layer of phenyl groups. It is possible that the structure-making or structure-breaking effects of such solutes are the same for each solute no matter what the charge. The ions have a very low density of surface charge so that the electrostatic contribution to solvation is small, much as if the central charge were not there. Since the central atom is insulated from the solvent, there will be no donor-acceptor interactions between the central atom and the solvent which are specific to any of the solutes.

This extrathermodynamic assumption is based on reasoning similar to the assumption, popular with electrochemists, that the ferrocene-ferricinium redox potential is independent of solvent.[4,9,10]

Those solubility products necessary for the "tetraphenylarsonium tetraphenylboride" assumption are in Table I. Methanol is our arbitrary choice as reference solvent, but other solvents can be used as reference by subtracting log ${}^M\gamma^S{}_i$ for the appropriate solvent from the values in Table I for other solvents. The data have been manipulated[5] in Table II to estimate log ${}^M\gamma^S{}_{Ag^+}$ using eq 2 and assuming that log ${}^M\gamma^S{}_{Ph_4As^+}$ = log ${}^M\gamma^S{}_{BPh_4^-}$. It is apparent from Table I that log ${}^M\gamma_{Ph_4C}$ equals log ${}^M\gamma^S{}_{Ph_4Sn}$ but that it is only very approximately equal to 0.5 log $({}^M\gamma^S{}_{Ph_4As^+})({}^M\gamma^S{}_{Ph_4B^-})$. The agreement is better between DMF and acetonitrile as reference and other solvent, respectively. This, however, does not necessarily invalidate the assumption that log ${}^M\gamma^S{}_{Ph_4As^+}$ = log ${}^M\gamma^S{}_{Ph_4B^-}$, because there may be some electro-

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Table I. Formal Solubility Products (Molar Concentrations) of Electrolytes Expressed as Solvent Activity Coefficients at 25° with Methanol as Reference Solvent[g]

	$\mathrm{p}K_S$[a]	Log $({}^{M}\gamma^{S}_{A^+})({}^{M}\gamma^{S}_{B^-}) = \mathrm{p}K_S(\text{solvent}) - \mathrm{p}K_S(\text{MeOH})$							
Solute	MeOH	MeOH	H_2O	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT[b]
Ph_4AsBPh_4	8.5[c]	0.0	8.2	−0.2[c]	−4.8[c]	−5.1[c]	−5.2[c]	−3.3[c]	−5.4[c]
Ph_4C	3.7[d]	0.0	...	...	−1.6[d]	−1.4[d]	...	−0.5[d]	...
Ph_4Sn	3.6[d]	0.0	...	...	−1.6[d]	...	...	...	...
Ferrocene	1.2[e]	0.0	3.6[f]	...	...	...	...	−0.3[f]	...
Ph_4AsI[h]	(1.4)	0.0	3.7	+0.3	−0.3	...	...	+0.6	...
Ph_4AsSCN[h]	(1.2)	0.0	4.4	...	...	...	...	...	...
Ph_4AsPic[e]	3.6	0.0	5.2	...	...	...	...	−1.5	...
Ph_4AsClO_4[e]	4.7	0.0	3.5	...	...	...	...	...	...
$KBPh_4$	5.0[i]	0.0	2.5[i]	...	...	...	...	−2.3[c,h]	...
$KClO_4$[i]	4.5	0.0	−2.8	...	(−4.4)	...	(−5.3)	...	...
KPic[i]	4.2	0.0	−0.8	...	(−4.4)	...	...	+0.3	...
KCl[i]	2.5	0.0	−3.4	...	+2.9	...	...	+4.7	...
KI[i]	(0.2)	0.0	...	...	(−0.7)	...	...	(+1.8)	...
CsCl[i]	1.7	0.0	...	−2.2	3.2	...	...	5.1	...
CsI[i]	1.9	0.0	...	−2.1	−0.2	...	...	1.1	...
$CsBPh_4$	6.1[c,h]	0.0	2.6[c]	−2.5[c,h]	...	...	...	−3.0[c,h]	...
CsPic[i]	4.2	0.0	−0.1	...	(−3.7)	...	...	+0.2	...
$AgBPh_4$[i]	13.9[j]	0.0	...[j]	−3.6	−7.2	−8.0	−9.3	−6.7	−9.2
AgI[i]	18.3	0.0	−2.3	−3.8	−2.5	−3.6	−6.9	−4.1	...
AgPic[k]	2.9	0.0	−0.2	...	...	...	...	...	...
AgSCN[i]	13.9	0.0	−2.0	−4.0	−2.4	−3.4	−6.8	−3.9	−6.5
$FBPh_4$[c,m]	5.4	0.0	...	...	...	...	...	−1.6	...
NBu_4BPh_4[l]	5.2[l]	0.0	7.8[l]	...	...	...	...	−3.3[c,h]	...
$TABBPh_4$[n]	4.9[l]	0.0	8.8[l]	...	...	...	...	...	...

[a] Molecules are recorded as −log solubility in moles $l.^{-1}$; salts are recorded as solubility products, $-\log K_S$, in moles^2 $l.^{-2}$ calculated from formal concentration of saturated solutions. [b] Hexamethylphosphorotriamide. [c] Estimated spectrophotometrically as in ref 5, solutions saturated under nitrogen atmosphere. [d] Saturated solutions poured into water and estimated turbidometrically. [e] Estimated spectrophotometrically. [f] Reference 4. [g] Data in parentheses are subject to uncertainty; saturated solutions are at high ionic strength and ion association may interfere. [h] Saturated solution analyzed for anion by titration with silver nitrate. [i] Reference 20. [j] The potentiometric titration of sodium tetraphenylboride with silver nitrate in water and in methanol gave a variety of titration curves depending on the time allowed to equilibrate. The apparent $\mathrm{p}K_S$ of 12 ± 1 for $AgBPh_4$ in water[20] is too low by 4 units when compared with all other data in this table and has been disregarded. Solubility products of $AgBPh_4$ in dipolar aprotic solvents were reproducible and constant over long periods. [k] Reference 2. [l] Reference 5. [m] F^+ = ferricinium cation. [n] TAB = triisoamylbutylammonium cation.

Table II. Calculation of the Solvent Activity Coefficient for Silver Cation at 25°, Using the Tetraphenylarsonium Tetraphenylboride Assumption[d] with Methanol as Reference Solvent

	Log ${}^{M}\gamma_{i}^{S}$							
i	MeOH	H_2O	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT
$Ph_4As^+ = Ph_4B^-$[a]	0.0	+4.1	−0.1	−2.4	−2.5	−2.6	−1.6	−2.7
$Ph_4AsI - Ph_4As^+$[b] $= I^-$	0.0	−0.4	(+0.4)	+2.1	...	...	+2.2	...
$Ph_4AsSCN - Ph_4As^+ = SCN^-$	0.0	+0.3	...	...	...	...	...	...
$Ph_4AsPic - Ph_4As^+ = Pic^-$	0.0	+1.1	...	...	...	...	+0.1	...
$Ph_4AsClO_4 - Ph_4As^+ = ClO_4^-$	0.0	−0.6	...	...	...	...	...	...
$KBPh_4 - Ph_4B^- = K^+$	0.0	−1.6	...	...	...	...	−0.7	...
$CsBPh_4 - Ph_4B^- = Cs^+$	0.0	−1.5	−2.4	...	...	...	−1.4	...
$NBu_4BPh_4 - BPh_4^- = NBu_4^+$	0.0	+3.7	...	...	...	...	−1.6	...
$FBPh_4 - BPh_4^- = F^+$[e]	0.0	...	...	...	...	...	0.0	...
$AgPic - Pic^- = Ag^+$	0.0	−1.3	...	...	...	...	...	...
$AgI - I^- = Ag^+$	0.0	...	−4.2	−4.6	...	...	−6.3	...
$CsCl - Cs^+ = Cl^-$	0.0	...	+0.2	...	...	...	+6.5	...
$AgCl - Cl^- = Ag^+$	0.0	...	−3.9	...	...	...	−6.5	...
$\log ({}^{A}\gamma^{S}_{Ag^+})({}^{A}\gamma^{S}_{BPh_4^-}) - \log {}^{A}\gamma^{S}_{BPh_4^-} = \log {}^{A}\gamma^{S}_{Ag^+}$	...	...	+1.5[c]	+0.2[c]	−0.4[c]	−1.6[c]	0.0[c]	−1.5[c]
Log ${}^{M}\gamma^{S}_{Ag^+}$ (mean)	0.0	−1.3	−4.0	−5.4	−6.8	−8.0	−6.4	−7.9

[a] These values from 0.5 log $({}^{M}\gamma^{S}_{Ph_4As^+})({}^{M}\gamma^{S}_{BPh_4^-})$ (Table I). [b] *I.e.*, log $({}^{M}\gamma^{S}_{Ph_4As^+})({}^{M}\gamma^{S}_{I^-})$ (Table I) − log ${}^{M}\gamma^{S}_{Ph_4As^+}$ (this table). [c] Acetonitrile is the reference solvent in this row. [d] See ref 5 for similar calculations. [e] F^+ = ferricinium cation.

static contribution to solvation of these ions which is absent with the molecules.

In a later paper we will examine other extrathermodynamic assumptions[4,12] such as the "cesium" assumption,[9,11] the "triisoamylbutylammonium tetraphenylboride" assumption,[5] the "ferrocene–ferricinium" assumption,[9,10,12] the "tris(4,7-dimethyl-1,10-phenanthroline)iron(II)" assumption,[10] the Feakins and Watson extrapolation,[6] and the Izmailov[14] and Coetzee[22] assumptions. For the present, the consequences of accepting the tetraphenylarsonium tetraphenylboride assumption, as applied to formal molar concentrations of saturated solutions, are shown in Table III.

Table III gives the resulting values of log ${}^{M}\gamma^{S}_{B^-}$ for anions B^- in a solvent S relative to methanol as reference solvent at 25°. A positive value of log ${}^{M}\gamma^{S}_{i}$ means that i is less solvated in the solvent S than in methanol. The values are calculated from log $({}^{M}\gamma^{S}_{Ag^+})({}^{M}\gamma^{S}_{B^-})$[20] and from log ${}^{M}\gamma^{S}_{Ag^+}$ (Table II). Solvent activity coefficients for some cations are included. Cations are more sol-

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Table III. Solvent Activity Coefficients of Ions[a,g] at 25° with Methanol as Reference Solvent

	Log $^{M}\gamma_{i}^{S}$							
i	MeOH	H_2O	$HCONH_2$	DMF	DMAC	DMSO	CH_3CN	HMPT
Ag^{+} [b]	0.0	−1.3	−4.0	−5.4	−6.8	−8.0	−6.4	−7.9
OAc^{-} [c]	0.0	−2.4	...	+9.5	+10.4	+6.3	+7.9	...
Cl^{-} [c]	0.0	−2.0	+0.3	+6.8	+8.0	+5.3	+6.4	+6.7
Br^{-} [c]	0.0	−1.6	+0.2	+5.2	+6.1	+3.4	+4.3	+5.0
N_3^{-} [c]	0.0	−1.3	+0.5	+5.2	+6.4	+3.3	+4.8	+5.1
OTs^{-} [c]	0.0	−0.6	...	+3.5	...	...	...	...
I^{-} [c]	0.0	−1.0	+0.2	+2.9	+3.2	+1.1	+2.5	...
SCN^{-} [c]	0.0	−0.7	0.0	+3.0	+3.4	+1.2	+2.7	+1.3
Pic^{-}	0.0	+1.1[c]	...	(−0.4)[d]	...	...	+0.1[d]	...
ClO_4^{-}	0.0	−0.6[d]	...	(−0.4)[d]	...	(−0.3)[d]	...	...
BPh_4^{-} [e]	0.0	+4.1	−0.1	−2.4	−2.5	−2.6	−1.6	−2.7
$AgCl_2^{-}$ [c]	0.0	−2.4	...	+0.1	+0.4	−0.8	+1.0	−4.6
$AgBr_2^{-}$ [c]	0.0	−1.3	...	−0.9	−0.8	−1.8	−0.9	−5.9
AgI_2^{-} [c]	0.0	+0.5	...	−2.4	−2.9	−3.3	...	...
I_3^{-} [c]	0.0	+2.7	+1.3	−1.7	−2.8	...	−0.3	...
Na^{+}	0.0	...	...	(−4.1)[f]	...	(−3.6)[f]	+1.3[f]	−4.2[f]
K^{+}	0.0	−1.8[f]	...	−3.8[f]	...	(−4.5)[f]	−1.7[f]	−2.7[f]
Cs^{+}	0.0	−1.4[f]	−2.4[b]	−3.3[f]	...	...	−1.4[b]	...
NBu_4^{+}	0.0	+3.7[b]	...	...	...	...	−1.6[b]	...
NEt_4^{+}	0.0	...	...	−1.6[f]	...	...	...	...
Ph_4As^{+}	0.0	+4.1[e]	−0.1[e]	−2.4[e]	−2.5[e]	−2.6[e]	−1.6[e]	−2.7[e]

[a] Assuming that the tetraphenylarsonium tetraphenylboride assumption is valid. [b] From Table II. [c] Calculated from log $(^{M}\gamma^{S}_{Ag^{+}})\cdot(^{M}\gamma^{S}_{B^{-}})$ (ref 20) − log $^{M}\gamma^{S}_{Ag^{+}}$ (Table II). [d] Calculated from log $(^{M}\gamma^{S}_{K^{+}})(^{M}\gamma^{S}_{B^{-}})$ (Table I) − log $^{M}\gamma^{S}_{K^{+}}$ (Table II). [e] From 0.5 log $(^{M}\gamma^{S}_{Ph_4As^{+}})(^{M}\gamma^{S}_{BPh_4^{-}})$ (Table I). [f] Calculated from log $(^{M}\gamma^{S}_{A^{+}})(^{M}\gamma^{S}_{B^{-}})$ in ref 20 and log $^{M}\gamma^{S}_{B^{-}}$ in this table. [g] Values in parentheses are uncertain; ion association has not been allowed for in the calculation of any values in this table.

vated by DMF, DMSO, and HMPT than by water. Acetonitrile is as good a solvent for alkali metal cations as water and is a better solvent for large cations and silver.

The solvent activity coefficients for anions agree with our qualitative observation[17,23] that small densely charged anions are more strongly solvated by protic solvents than by dipolar aprotic solvents, whereas large polarizable anions are more solvated by dipolar aprotic than by protic solvents. Most anions are more solvated by water than by methanol, but very large and polarizable anions like BPh_4^- and I_3^- are considerably more solvated by methanol than by water, just as most organic molecules are more solvated by methanol than by water.

If our application of the tetraphenylarsonium tetraphenylboride assumption is valid, then the effect of solvent structure and mutual polarizability interactions (dispersion forces[24]), as well as hydrogen bonding to small anions,[17] must be considered if we are to explain the significant changes in the chemistry of anions, on transfer from water and methanol to dipolar aprotic solvents.

The numbers in Table III could account for a change of up to 10^{17} in a rate[3] or equilibrium[19,20] constant, on transfer from water to DMF. There are occasional anomalies such as when the numbers are used to predict solubilities of some tetraphenylborides in hydroxylic solvents. However, Table III does help us to interpret solvent effects on rate, on acid–base equilibria, on redox potentials, on instability constants, and on solubilities.[3,17,18] The role of dipolar aprotic solvents in a number of organic reaction mechanisms[17,18] is also now better understood.

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