Transfer Gibbs Free Energies of Divalent Anions from Water to Organic and Mixed Aqueous-Organic Solvents

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Dedicated to Professor Hitoshi Ohtaki on the occasion of his 60th birthday

The standard molar Gibbs free energies of transfer of divalent anions, in particular sulfate, from water into methanol, ethanol, ethylene glycol, dioxane, tetrahydrofuran, acetone, N-methylformamide, N,N-dimethylformamide, pyridine, acetonitrile, and dimethylsulfoxide and mixtures of some of them with water or some other solvent have been obtained from the literature. The tetraphenylarsonium tetraphenylborate extrathermodynamic assumption has been used as far as possible in order to obtain the single ion values. The generally unfavorable transfers from water (or protic solvents) into polar aprotic ones are interpreted in terms of the properties of the anions and of the solvents, dominated by the hydrogen-bonding acidity of water.

Key words: Divalent anions; Ion properties; Sulfate; Solvent properties; Transfer Gibbs energy.

Introduction

The energetics of the transfer of ions from a reference solvent into another solvent or solvent mixture has been reported extensively [1–8]. This pertains to Gibbs free energies (mainly from solubility and emf data), enthalpies (mainly from calorimetric data), entropies (mainly from temperature dependence of emf data), heat capacities (mainly from temperature dependence of calorimetric data), and volumes (from density data) of transfer. Interpretation of these data in terms of the properties of the ions and the solvents has shed a considerable amount of light on the interactions involved, i.e., the solvation properties of the ions in the various solvents. It has been necessary to use an extrathermodynamic assumption in order to separate the experimentally obtainable data into the contributions of the individual ions. One of the least objectionable assumptions is that the thermodynamic quantity of a suitable reference electrolyte can be split evenly between its constituent ions. The reference electrolyte commonly used for this purpose is tetraphenylarsonium (or tetraphenylphosphonium) tetraphenylborate (TATB or TPTB) [9]. The additivity of the individual ionic contributions to the standard molar thermodynamic quantity (i.e., pertaining to infinite dilution, where ion-ion interactions are absent) is invoked in order to calculate the individual ionic values, starting from salts involving the cation or the anion of TATB. Extensive tables of these transfer quantities, mainly for water as the reference solvent, have thus been published [1–5].

An examination of the ions for which the above applies shows that they comprise many univalent cations and anions (both monoatomic and polyatomic) as well as some divalent cations, but not divalent anions. A thorough literature search has revealed rather few data for such anions (mainly the sulfate anion), the transfer being from water into organic solvents or aqueous solvent mixtures. There is a good reason for the paucity of such data: the Gibbs free energies of transfer of divalent anions from water to practically all neat organic solvents are highly positive, i.e., very unfavorable. Hence, a small contamination of such solvents with water would cause an appreciable error, since it would reduce the measured Gibbs free energy of transfer. Furthermore, cation association with the divalent anion in solvents with a moderate relative permittivity takes place even at rather low concentrations, so that it is difficult to obtain truly standard Gibbs free energies by extrapolation to infinite dilution. These difficulties may be alleviated in aqueous-organic solvent mixtures, but the reliability of the extrapolation of such data to the neat organic solvent requires demonstration. The interpretation of the information regarding the mixed

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solvents in terms of the properties of the solvents is more difficult, due to the selective solvation of the divalent anion by the aqueous component.

For all these reasons it must be admitted that the presented data are necessarily approximate and their evaluation is tentative. Still, in view of the total lack of a compilation of such data on a common basis, it is deemed to be of interest for comparative purposes. The solvation of divalent anions in neat or aqueous organic solvents, and generalizations and predictions made on the basis of the present analysis of the data, do provide valuable information concerning the reactivity of such anions. They may possibly lead to a better selection of solvents that suit a particular application.

The Data

Transfer into Neat Solvents

The solubility of silver sulfate in water is only moderate, 0.0269 mol per kg water at 25 °C [10–13]. It is generally smaller in aqueous-organic solvent mixtures (except in water-rich aqueous pyridine and acetonitrile) and much smaller in neat organic solvents. These solubilities have been measured by several authors [14–22]. The activity coefficient of silver sulfate in water has been measured, so that its solubility product and standard Gibbs free energy of solution in water are well established:

$$K_{\mathrm{sp}} = 4m^3\gamma_{\pm}^3 = 10^{-4.719\pm0.008}, \tag{1}$$

$$\Delta_{\mathrm{soln}} G^0 = -RT\ln K_{\mathrm{sp}} = 26.95\pm0.04\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

at 25 °C. At 30 °C the corresponding values are $10^{-4.630}$ and 26.87 kJ mol^{-1} [13]. In organic solvents, due to the smaller solubility, it is assumed that in spite of the lower relative permittivity ε of the solvent the salt is still completely dissociated. The activity coefficient is given by

$$\ln\gamma_{\pm\mathrm{S}} = -2A\mu^{1/2}/(1+B\mu^{1/2}), \tag{3}$$

where $A = 1.8248\times10^6\,(\varepsilon_{\mathrm{S}}T)^{-3/2}$ and $B = 1.5\,(\varrho_{\mathrm{S}}/\varrho_{\mathrm{W}})^{1/2}(\varepsilon_{\mathrm{W}}/\varepsilon_{\mathrm{S}})^{1/2}$, μ being the (molal) ionic strength, ϱ the density and subscripts w and s denoting water and the solvent [23]. The standard molar Gibbs free energy of transfer for the silver sulfate salt is then

$$\Delta_{\mathrm{tr}} G^0 = -RT\ln(4m_{\mathrm{S}}^3\gamma_{\pm\mathrm{S}}^3) - \Delta_{\mathrm{soln}} G_{\mathrm{W}}^0. \tag{4}$$

The resulting quantities are shown in Table 1, transformed from the molality scale, on which the data have been reported, to the molarity scale (see below for rationale), by the addition of $3RT\ln(\varrho_{\mathrm{W}}/\varrho_{\mathrm{S}})$. Unfortunately, there are serious discrepancies in the solubilities reported for a given solvent by different authors, and even by the same author in different publications. Subtraction of twice the $\Delta_{\mathrm{tr}} G^0$ of silver ions on the TATB assumption [3] from $\Delta_{\mathrm{tr}} G^0$ of silver sulfate yields the $\Delta_{\mathrm{tr}} G^0$ of sulfate anions, also shown in Table 1.

Some further solubility data pertain to sodium and potassium sulfates [24, 25]. The aqueous solubility ($s_{\mathrm{W}} = 1.957$ m for Na_2SO_4 and 0.692 m for K_2SO_4) and activity coefficients ($\gamma_{\pm\mathrm{W}} = 0.1558$ for Na_2SO_4 and 0.2237 for K_2SO_4) [24] lead to the following standard molar Gibbs energies of solution at 25 °C:

$$\begin{aligned}\Delta_{\mathrm{soln}} G^0 &= -RT\ln(4m^3\gamma_{\pm}^3)\\ &= 5.40\ \mathrm{kJ\ mol^{-1}}\,(Na_2SO_4) \qquad (5\mathrm{a})\\ &= 10.44\ \mathrm{kJ\ mol^{-1}}\,(K_2SO_4). \qquad (5\mathrm{b})\end{aligned}$$

The logarithms of the solubility ratios in water and aqueous-organic mixtures of volume fractions ϕ_{S} have been presented as linear functions of ϕ_{S} [25]:

$$\log(s_{\mathrm{W}}/s_{\mathrm{S}}) = -a\cdot\phi_{\mathrm{S}}. \tag{6}$$

The Gibbs free energies of transfer to the neat solvents ($\phi_{\mathrm{S}} = 1$) are therefore

$$\Delta_{\mathrm{tr}} G^0 = 3RT\,[\ln(10)\,a + \ln\gamma_{\pm\mathrm{S}} - \ln\gamma_{\pm\mathrm{W}}] \tag{7}$$

on the assumption that a remains constant up to the neat solvent (the data extend up to $\phi_{\mathrm{S}} = 0.8$). The reported standard deviations range from 0.18 to 0.38, corresponding to uncertainties in $\Delta_{\mathrm{tr}} G^0$ of 3.0 to 6.5 kJ mol^{-1}. The results, converted to the molarity scale as above, are shown in Table 2. Subtraction of twice the $\Delta_{\mathrm{tr}} G^0$ of sodium and potassium ions on the TATB assumption [3] from $\Delta_{\mathrm{tr}} G^0$ of sodium and potassium sulfate yields the $\Delta_{\mathrm{tr}} G^0$ of sulfate anions, also shown in Table 2. The solubility of sodium (and lithium) sulfate in 1,2-dimethoxyethane at various temperatures has recently been reported [26], and the resulting transfer data at 25 °C are shown in Table 2.

There are only a few other data on the energetics of the transfer of sulfate or other divalent anions from water to neat organic solvents. The standard mercury/mercury(I) sulfate electrode potential in methanol has been measured at 20, 25, 30, and 35 °C with respect to

Solvent	Temp. °C	Solub.	$\Delta_{soln} G^0$ salt	$\Delta_{tr} G^0$ salt	$\Delta_{tr} G^0$ anion	Ref.
Water	25	269	27.0			
	30	287	26.9			
Methanol	25		75.7	48.7	36	[19]
	30	0.337	75.0	48.1	34	[20]
Ethanol	30	0.450	73.3	46.4	37	[20]
1,2-ethanediol	30	19.2	47.2	20.2	53	[18]
Dioxane	30	0.115	102.9	76.0		[21]
Dimethylsulfoxide	25		72.3	45.3	115	[15]
	25		65.5	38.5	108	[16]
	30	4.84	55.6	28.7	98	[21]
Pyridine	30	710	63.6	36.7	149	[22]
Acetonitrile	25		48	21	66	[14]
	30	0.621	70.5	43.6	89	[20]
	30	1.81	62.8	35.9	81	[21]
	30	2.45	60.7	33.8	79	[18]
N-methylformamide	25	16.85	44.4	17.4	47	[17]
N,N-dimethylformamide	25	0.76	67.9	40.9	83	[19]

Table 1. The solubility, in 10^{-4} mol (kg solvent)$^{-1}$, and Gibbs free energies of solution of silver sulfate in, and transfer from water to various solvents, and the Gibbs free energy of transfer of the sulfate anion (on the TATB assumption, with values for silver ions from [3], and the mol dm^{-3} scale), in kJ mol^{-1}.

Solvent	Sodium sulfate			Potassium sulfate		
	$\Delta_{soln} G^0$ salt	$\Delta_{tr} G^0$ salt	$\Delta_{tr} G^0$ anion	$\Delta_{soln} G^0$ salt	$\Delta_{tr} G^0$ salt	$\Delta_{tr} G^0$ anion
Water	5.4			10.4		
Methanol	68.1	62.7	46	57.5	47.1	28
Tetrahydrofuran				86.8	76.4	54[a]
1,2-dimethoxyethane	85.4	80.0	61[a]			
Dioxane	123.2	117.8	65[a]	77.2	66.8	59
Acetone	90.2	84.8	77			
Acetonitrile	48.6	43.2	13			

[a] The cation value is estimated with eq. (8) and the data in Table 5.

Table 2. The Gibbs free energies of solution of sodium and potassium sulfates at 25 °C in various solvents and transfer from water, and the Gibbs free energy of transfer of the sulfate anion (on the TATB assumption and the mol dm^{-3} scale), in kJ mol^{-1}.

the hydrogen electrode in sulfuric acid [27]. The "real" Gibbs free energy of transfer of the sulfate anion from water to methanol at 25 °C was estimated from these data as -63.5 kJ mol^{-1} [28], but this value is, of course, not comparable with the data from the solubility measurements on the basis of the TATB assumption. It is also improbable that the transfer of sulfate anions from water to methanol be so favorable. The comparison of the standard potential in methanol, 0.539_2 V [27], with that in water, 0.613 V [29] at 25 °C yields for the transfer of sulfuric acid $\Delta_{tr} G^0 = 14.2$ kJ mol^{-1}. (A combination of the "real" Gibbs free energies for sulfate and hydrogen ions [28] produces 14.6 kJ mol^{-1} for this quantity.) With $\Delta_{tr} G^0(\mathrm{H}^+, \text{water} \rightarrow \text{methanol}) = 10.4$ kJ mol^{-1} [3], this yields $\Delta_{tr} G^0(\mathrm{SO}_4^{2-}, \text{water} \rightarrow \text{methanol}) = -6.6$ kJ mol^{-1}, still favorable and inconsistent with the unfavorable values from the solubility data (Tables 1 and 2). Potentiometry with a copper electrode in copper sulfate solutions in 1,2-ethanediol [30] and its aqueous mixtures at 30, 35 and 40 °C led to the value $\Delta_{tr} G^0(\mathrm{Cu}^{2+}\mathrm{SO}_4^{2-}, \text{water} \rightarrow \mathrm{HOC_2H_4OH}) = 31$ kJ mol^{-1} at 30 °C. Since $\Delta_{tr} G^0(\mathrm{Cu}^{2+}, \text{water} \rightarrow \mathrm{HOC_2H_4OH}) = 4$ kJ mol^{-1} on the TATB assumption (at 25 °C [3]), the resulting $\Delta_{tr} G^0$ of the sulfate anion is 27 kJ mol^{-1}.

Current scan polarography was applied to the interfaces between aqueous solutions and water-saturated solutions of 1,2-dichloroethane, nitrobenzene, and chloroform containing crystal violet tetraphenyl borate or tetraphenylarsonium dipicrylaminate [31]. The standard molar Gibbs free energies of transfer of several anions from water to the organic phases were obtained from these measurements, on the TATB basis. The values reported for divalent anions are: $\Delta_{tr} G^0/\text{kJ mol}^{-1} = 31$ for dichromate and 1,2-dichloroethane, > 43 for molybdate and tungstate and 1,2-dichloroethane, and > 34 for these two anions and nitrobenzene.

Ion	Solvent	Max. x_S	Extrapol. expression	$\Delta_{tr} G^0$	Ref.
CO_3^{2-}	1,2-ethanediol	1.000	$0.2+4.6\,x_S$	5	[46]
SO_4^{2-}	Methanol	0.400	$-.1+57.3\,x_S$	57	[40]
	Ethanol	0.207	$0.0+99.1\,x_S$	99	[43]
	1,2-ethanediol	0.225	$1.0+45.9\,x_S$	47	[46]
	Acetone	0.146	$0.1+193.8\,x_S$	194	[36]
	Dimethylsulfoxide	1.000	$-1.5+171.5\,x_S-58.0\,x_S^2$	112	[46]
$S_2O_3^{2-}$	Ethanol	0.207	$-.3+85.3\,x_S$	85	[43]
	Dimethylsulfoxide	0.400	$0.2+88.3\,x_S$	89	[44]
$S_2O_6^{2-}$	Methanol	0.400	$-.2+34.4\,x_S$	34	[40]
	Ethanol	0.207	$-.5+92.9\,x_S$	92	[46]
	Acetone	0.318	$1.0+119.9\,x_S$	120	[36, 37]
$S_2O_8^{2-}$	Methanol	0.279	$-.2+11.7\,x_S$	12	[40]
$Cr_2O_7^{2-}$	Acetone	0.657	$0.2+79.9\,x_S-30.8\,x_S^2$	49	[42]
$ReCl_6^{2-}$	Methanol	1.000	$-.4+15.4\,x_S+5.1\,x_S^2$	20	[46]
$PtCl_6^{2-}$	Methanol	1.000	$0.2+15.2\,x_S+5.8\,x_S^2$	21	[46]
	Ethanol	0.370	$0.2+72.6\,x_S-51.6\,x_S^2$	21	[43]

Table 3. The Gibbs free energies of transfer in kJ mol^{-1} of divalent anions from water into neat organic solvents (on the TPTB assumption and the mol dm^{-3} scale, extrapolated, where required, with linear or quadratic extrapolation expressions).

Transfer into Solvent Mixtures

The transfer energetics of salts of the sulfate anion, as well as those of chromate, dichromate, and several $S_2O_x^{2-}$ anions ($x=3$, 6, 8), between a solvent and its mixtures with another one has also been studied [15–22, 25, 32–46]. The source solvent was not in all cases water: in several it was methanol [16, 17, 19, 20], but the transfer from water to aqueous methanol has been studied up to only 60 volume% of methanol (in addition to the neat methanol mentioned above). It is, therefore, difficult to relate all the reported transfer data to transfer from water, as was done for the neat solvents, where transfers via a third solvent can always be invoked.

In some cases the $\Delta_{tr} G^0$ for transfer of divalent anions from water into mixed aqueous-organic solvents, based on solubility data and the TPTB assumption, have been reported with results that permit fitting to linear or quadratic expressions in the mole fraction of the organic solvent, x_S. These data have then been extrapolated to the neat organic solvent, with results shown in Table 3. In some cases the extrapolation beyond the maximal x_S for which data are available is rather far, but the linear fit to the data appears to justify this, in view of the goodness of fit ($r_{corr} > 0.98$). The results for sulfate anions and methanol, ethanol, and acetone solvents are at variance with those in Tables 1 and 2. Data for several more divalent anions and aqueous-organic solvent mixtures (CrO_4^{2-}, $S_2O_3^{2-}$, $PtCl_4^{2-}$, $ReBr_6^{2-}$, $IrCl_6^{2-}$, $Fe(CN)_5NO^{2-}$ in aqueous methanol [40, 41]; CrO_4^{2-}, SiF_6^{2-}, $PtCl_6^{2-}$, $ReCl_6^{2-}$, $IrCl_6^{2-}$, $C_2O_4^{2-}$ in aqueous ethanol, CrO_7^{2-} in aqueous 2-propanol [43], SO_4^{2-}, CrO_4^{2-} in aqueous 1,4-dioxane [34, 39], SO_4^{2-} and $S_2O_8^{2-}$ in aqueous acetonitrile [35], and CO_3^{2-}, SO_3^{2-}, HPO_4^{2-}, $S_2O_6^{2-}$, $S_2O_8^{2-}$, $S_4O_6^{2-}$, CrO_4^{2-}, $Cr_2O_7^{2-}$ in aqueous acetone [33, 36, 37] generally pertain to such dilute solution that such an extrapolation is meaningless or very uncertain due to non uniform change of the $\Delta_{tr} G^0$ values with the composition.

On the other hand, the results of Schneider, Kalidas, and coworkers for the solubility of silver sulfate in solvent mixtures (not necessarily aqueous) have been obtained over the entire composition range [15–22, 32]. They reported $\Delta_{tr} G^0$ values for the transfer of the salt from one of the solvents to its mixtures with another one (and to the neat other solvent) at 25 or 30 °C at mole fraction steps of 0.1. The data, recalculated to the mol dm^{-3} scale and kJ mol^{-1} units, are shown in Table 4a. These authors employed the Fic$^+$/Foc extrathermodynamic assumption [47] and previously reported $\Delta_{tr} G^0(Ag^+)$ data for the solvent mixtures in order to obtain the $\Delta_{tr} G^0$ of the sulfate anion. This assumption asserts that the potential of the ferricinium (Fic$^+$)/ferrocene (Foc) half cell is independent of the solvent, an assumption that has been criticized on the basis of the charge asymmetry of the species and their openness and insufficient size [48], and is not in much use in more recent years. It yields $\Delta_{tr} G^0(Ag^+)$ values 5–20 kJ mol^{-1} more negative, hence $\Delta_{tr} G^0(SO_4^{2-})$ values 10–40 kJ mol^{-1} more positive than the TATB assumption for the neat solvents, probably more or less prorated for the solvent mixtures. However, the $\Delta_{tr} G^0(Ag^+)$ values on the more acceptable TATB assumption are generally not avail-

Table 4. The Gibbs free energy of transfer from solvent A[a] to its mixtures with solvent B[a] in kJ mol^{-1} on the mol dm^{-3} scale.

x_B	A = H_2O B = DMSO	A = MeOH B = DMSO	A = MeOH B = NMF	A = MeOH B = DMF	A = MeOH B = MeCN	A = EtOH B = MeCN	A = H_2O B = Py	A = Diox B = MeCN	A = Diox B = DMSO	A = EG B = DMSO	A = EG B = MeCN
$t/°C$	25	25	25	25	30	30	30	30	30	30	30
a) Transfer of silver sulfate											
0.1	6.3	−2.3[b]	−4.9	−3.5	−16.2	−5.9	−20.6	−15.5	−23.9	0.1	−10.7
0.2	11.8	−6.0	−12.8	−6.2	−20.8	−8.1	−20.5	−22.9	−29.4	0.7	−14.6
0.3	16.6	−9.6	−16.6	−8.2	−23.1	−9.2	−18.5	−25.9	−33.5	1.0	−16.4
0.4	20.8[b]	−11.6	−20.5	−10.0	−23.7	−10.5	−16.0	−28.6	−36.8	2.0	−16.6
0.5	24.7	−14.1	−24.2	−11.7	−22.8	−8.9	−13.5	−30.3	−38.1	3.0	−16.1
0.6	29.1[b]	−14.8	−26.2	−13.0	−21.3	−8.2	−7.3	−30.7	−38.8	3.4	−14.9
0.7	32.8[b]	−14.5	−27.9	−12.6	−18.2	−7.6	−0.9	−33.2	−39.3	4.6	−12.6
0.8	35.8	−13.5	−29.2	−11.8	−14.4	−6.7	7.5	−34.3	−39.8	5.4	−9.1
0.9	39.3[b]	−13.2	−30.5	−10.5	−9.9	−5.2	13.8	−36.1	−41.2	7.5	−3.0
1.0	42.4	−12.6	−33.5	−9.4	−4.5	−2.7	27.1	−41.2	−46.8	8.3	16.7
b) Transfer of the sulfate anion, with the Fic^+/Foc assumption.											
0.1	11.4		0.2	5.5	9.7	15.6	46.2	14.6	13.3	0.3	6.1
0.2	32.7	18.1	−3.9	7.2	14.1	22.0	54.3	27.6	29.0	1.9	5.6
0.3	52.7	23.7	−5.6	8.8	16.2	25.8	64.3	34.5	36.1	4.8	6.6
0.4		29.9	−8.1	10.3	17.7	27.6	74.0	38.7	41.6	8.4	8.8
0.5	84.3	33.1	−10.3	11.8	21.6	31.3	81.7	43.4	47.7	13.3	11.2
0.6		37.3	−10.1	12.5	26.0	33.8	91.8	46.0	50.5	16.7	14.4
0.7		41.6	−10.6	14.2	31.0	36.3	101.6	48.4	53.2	21.7	18.1
0.8	116.1	45.6	−9.3	15.7	36.0	39.4	111.4	50.7	55.6	25.7	23.9
0.9		49.3	−8.3	17.3	42.7	43.9	119.0	53.2	56.8	32.4	31.3
1.0	131.3	51.6	−7.9	18.0	52.3	49.0	132.7	52.8	53.6	40.6	53.8

[a] DMSO = dimethylsulfoxide, MeOH = methanol, NMF = N-methylformamide, DMF = N,N-dimethylformamide, MeCN = acetonitrile, EtOH = ethanol, Py = pyridine, Diox = 1,4-dioxane, EG = 1,2-ethanediol. [b] Interpolated.

able for the solvent mixtures under discussion. Table 4b therefore shows the $\Delta_{tr}G^0(SO_4^{2-})$ values on the Fic^+/Foc assumption, in spite of its being inadequate.

Discussion

Examination of the data in Tables 1–4 for sulfate anions shows some discrepancies in the values reported for transfer into a given solvent from some reference solvent (not only water). Some of these result from revisions of the raw solubility data themselves by the authors, whereas others are due to incompatibilities between the extrathermodynamic assumptions employed. (The effect of the different temperatures, mainly 25 and 30 °C, appears to be minor.) The standard molar Gibbs free energies of transfer of sulfate (and other divalent anions) from water to any solvent, however, are positive for any set of data, as are these energies for transfers from a protic solvent (such as methanol or 1,2-ethanediol) into polar aprotic solvents. Transfer Gibbs free energies between two protic solvents (except water) and between two aprotic solvents, on the other hand can be positive or negative, depending on the particular solvents examined.

The standard molar transfer Gibbs free energies of ions from water into other solvents have been correlated with the properties of the ions and solvents [3] in a manner that should permit the estimation of the $\Delta_{tr}G^0$ of the ions if the specified properties are known, The expressions obtained were

$$\begin{aligned}\Delta_{tr}G^0\,(\text{cations}) = &-(3.26\,\Delta\pi_S^* + 3.72\,\Delta\beta_S)\,z_i^2/r_i \\ &+ 530\,\Delta\alpha_S\,v_i + 30.3\,\Delta\pi_S^*\,\sigma_i \\ &- 3.78\,\Delta\beta_S\,R_{Di}\,, \end{aligned} \tag{8}$$

$$\begin{aligned}\Delta_{tr}G^0\,(\text{anions}) = &\,(3.02\,\Delta\pi_S^* + 7.47\,\Delta\alpha_S \\ &- 0.0383\,\Delta V_S)\,z_i/r_i + 30.3\,\Delta\alpha_S\,\sigma_i \\ &- 2.8\,\Delta V_S\,v_i + 0.29\,\Delta\pi_S^*\,R_{Di}\,, \end{aligned} \tag{9}$$

for $\Delta_{tr}G^0$ in kJ mol^{-1} on the mol dm^{-3} scale and the TATB assumption, with the Δ and subscript s denoting differences between solvent properties (α is the hydrogen bond acidity, β the electron pair donicity (basicity), π^* the polarity/polarizability, and V the molar volume in cm^3 mol^{-1} [3]) and the correspond-

Table 5. The relevant properties of some ions and solvents.
a) Ions

Ion	z_i	r_i/nm	v_i/nm^3	σ_i	R_{Di}/ cm^3 mol^{-1}
Na^+	1	0.102	0.0044	−0.60	0.65
K^+	1	0.138	0.0110	−0.58	2.71
Ag^+	1	0.115	0.0064	0.70	5.10
CO_3^{2-}	−2	0.178	0.0562	−0.50	11.45
SO_4^{2-}	−2	0.230	0.0510	−0.38	13.79
$S_2O_3^{2-}$	−2	0.250	0.0655	0.5–1.0	23.2
$Cr_2O_7^{2-}$	−2	0.320	0.1373	0.0–0.5	43.2
$PtCl_6^{2-}$	−2	0.313	0.1284	0.5–1.0	52.2

b) Solvents (relative to water)

Solvent[a]	$\Delta\alpha_S$	$\Delta\beta_S$	$\Delta\pi_S^*$	ΔV_S
MeOH	−0.24	0.19	−0.49	22.6
EtOH	−0.34	0.28	−0.55	40.6
EG	−0.34	0.05	−0.17	37.8
DME	−1.17	−0.06	−0.56	86.4
THF	−1.17	0.08	−0.51	63.5
Diox	−1.17	−0.10	−0.54	67.6
Me_2CO	−1.09	−0.04	−0.38	55.9
NMF	−0.55	0.33	−0.19	41.0
DMF	−1.17	0.22	−0.21	59.3
MeCN	−0.98	−0.07	−0.34	34.8
Py	−1.17	0.17	−0.22	62.8
DMSO	−1.17	0.29	−0.09	53.2

[a] The abbreviations as in Table 4, with Me_2CO = acetone, DME = 1,2-dimethoxyethane, THF = tetrahydrofuran, Py = pyridine.

Table 6. Comparison of the calculated[a], (9), and experimental[b] standard molar Gibbs free energies of transfer[c] of divalent anions from solvent A to solvent B.[d]

Anion	Solvent A	Solvent B	Calculated	Experimental
SO_4^{2-}	Water	MeOH	34	36 (1), 34 (1), 30 (2), 28 (2), 57 (3)
	Water	EtOH	46	37 (1), 99 (3)
	Water	EG	37	53 (1), 47 (3), 27 (ref. 30)
	Water	DME	118	61 (2)
	Water	THF	113	54 (2)
	Water	Diox	114	66 (1), 59 (2), 65 (2), 133 (4)
	Water	Me_2CO	103	77 (2), 194 (3)
	Water	MeCN	89	89 (1), 81 (1), 79 (1), 13 (2)
	Water	NMF	54	47 (1)
	Water	DMF	105	83 (1)
	Water	Py	106	149 (1), 133 (4)
	Water	DMSO	102	115 (1), 108 (1), 98 (1), 112 (3), 131 (4)
	MeOH	MeCN	55	53 (4)
	MeOH	NMF	20	−8 (4)
	MeOH	DMF	71	18 (4)
	MeOH	DMSO	68	52 (4)
	EtOH	MeCN	43	49 (4)
	Diox	MeCN	−25	53 (4)
	Diox	DMSO	−12	53 (4)
	EG	MeCN	52	54 (4)
	EG	DMSO	65	41 (4)
CO_3^{2-}	Water	EG	53	5 (3)
$S_2O_3^{2-}$	Water	EtOH	27–25	85 (3)
$Cr_2O_7^{2-}$	Water	Me_2CO	45–29	49 (3)
$PtCl_6^{2-}$	Water	MeOH	7–4	21 (3)
	Water	EtOH	9–4	21 (3)

[a] When a range is shown, the values pertain from the lower to the higher values of the softness parameter, σ. [b] The Table number in parenthesis after the experimental datum. [c] Mol dm^{-3} scale, kJ/mol, TATB assumption, except of data from Table 4. [d] The abbreviations of the solvents as in Tables 4 and 5.

ing ones of water, and subscript i denoting ion properties (z = charge, r = radius in nm, σ = softness, $v = (4\pi/3)r^3$, and R_D = molar refractivity in cm^3 mol^{-1} [3]). The ion properties of interest in the present context are given in Table 5a [3, 49], as far as they are known. For some of the anions in Table 3 estimated ranges of the softness values, σ_i, are shown, and for some others the ion properties are not known. The solvent properties relevant here are given in Table 5b [49, 50]. The quantities for silver, sodium and potassium are used with (8) to give the $\Delta_{tr}G^0$ of these cations into tetrahydrofuran, 1,4-dioxane and 1,2-dimethoxyethane for use in Tables 1 and 2 to give the value for the sulfate anion from that of the salt. The $\Delta_{tr}G^0$ of the anions estimated from (9) are shown in Table 6, together with the experimental values from Tables 1 to 4.

It is seen that the majority of the consistent values of $\Delta_{tr}G^0$ of sulfate anions in Table 1 are in agreement with the values calculated with (9). An important exception is the value for transfer into 1,4-dioxane, where the experimental solubility [21] could be too high (contamination with traces of water) and/or the assumption of complete dissociation of $Ag_2^+SO_4^{2-}$, hence the use of (3) and (4) to obtain the $\Delta_{tr}G^0$, is incorrect. This is, of course, also reflected in the discrepancy noted for the transfer from 1,4-dioxane into acetonitrile and into dimethylsulfoxide. The discrepancies noted with regard to the items from Table 2 can be readily ascribed to the fallacy of the assumption that the linear function of the volume fraction, (6), holds up to the neat solvent in the cases of the aprotic solvents. This could also explain some of the discrepancies with regard to the items in Table 3, although some are based on data extending up to the neat solvent, where only the transfer of carbonate does not agree with the calculated value (due to the flat rather than spherical shape, hence a non-representative radius?). The experimental data from Table 4, remembering that they are based on the $\mathrm{Fic}^+/\mathrm{Foc}$ rather than the TATB assumption, are in most cases in fair agreement with the calculated values, at least within the discrepancies between the extrathermodynamic assumptions noted above, the notable disagreement being the transfer from methanol to N,N-dimethylformamide (in addition to the transfers from 1,4-dioxane noted above), which cannot be readily explained. On the whole, however, it is seen that (9) provides a reliable means for the estimation of the $\Delta_{tr}G^0$ of sulfate anions between solvents, within, say, ±10 kJ/mol, and with a wider margin of uncertainty also for the $\Delta_{tr}G^0$ of other divalent anions, provided the necessary ion properties (Table 5a) are known.

On this basis, the transfer energetics of divalent ions from water into neat organic solvents can be related to the properties of the ions and the solvents. For a given ion (say, sulfate), the dominant terms in (9) are the ones in the negative $\Delta\alpha_S$ of the solvents, multiplied by the negative z_i and σ_i for hard anions, unless the ion is very large and soft. These terms make the transfer highly unfavorable. Each of the pairs of terms in $\Delta\pi_S^*$ and ΔV act in opposing manner, and they oppose each other too ($\Delta\pi_S^*$ is generally negative and ΔV is positive), hence have a smaller effect. For a given solvent, the larger the anion and the softer it is (hence also the larger its R_{Di}), the less positive $\Delta_{tr}G^0$ becomes, but still the transfer from water is unfavorable, since the dominant first term on the right hand of (9) remains positive, due to the negative z and $\Delta\alpha_S$ and $\Delta\pi_S^*$.

The transfer of salts of divalent anions into solvent mixtures is often characterized by heteroselective solvation, as pointed out by Schneider and coworkers [14–19]. This term signifies, in the present case, that the divalent anion is selectively solvated by water (or a protic solvent) whereas the cation may be selectively solvated by a dipolar aprotic solvent of high electron pair donicity (high β_S). The outcome of these opposing tendencies can be a favorable transfer into the mixed aqueous-organic solvent, as is the case for silver sulfate with water-rich aqueous acetonitrile and pyridine. As the organic solvent content in these mixtures increases, however, the unfavorable effect of the sulfate anion on the transfer dominates over the favorable effect of the silver cations. Therefore, the solubility of the salt in the mixtures exhibits a maximum. With most other solvents examined so far, $\Delta_{tr}G^0$ varies monotonously with the composition of the mixture, though not necessarily linearly. In fact, theoretical arguments [23, 49] point to the necessary non-linear dependence of $\Delta_{tr}G^0$ on the mole fraction (also volume fraction) of the organic component, due to selective solvation even for an individual ion. Only if the magnitude of $\Delta_{tr}G^0$ into the neat organic component is very large does the selective solvation by the water dominate over any other effects, and the dependence of $\Delta_{tr}G^0$ on the composition appears to be linear or nearly so.

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