Single-Ion Transfer Properties of Cations from Water Derived from Electrochemical Measurements[†]

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Gibbs energies, entropies (given as $T\Delta_tS°$ values), and enthalpies of transfer of cations from water into nonaqueous solvents are derived from electrochemical measurements. The Gibbs energies of transfer for the cations were based on the bis(biphenyl)chromium assumption. Values of $T\Delta_tS°$ were derived from the assumption of a negligible thermal diffusion potential. Enthalpies of transfer were calculated from the Gibbs energies and $T\Delta_tS°$ values. Comparison with data from the tetraphenylarsonium tetraphenylborate assumption is made. The applicability of transfer properties in understanding the physico-chemistry of chemical reactions in solution is suggested.

Introduction

Single-ion transfer properties are outside the realm of exact thermodynamics. Thermodynamic properties may only be obtained for neutral entities (e.g., complete salts or neutral molecules). However, considerable information about interactions of solvent molecules with cations and anions is available from single-ion transfer properties. Such data allow better understanding of chemical reactions in solution, as ionic species act quite differently depending on the solvent used.

Separating the transfer properties of a salt into individual contributions from the cation and anion requires suitable extrathermodynamic assumptions. It is in the nature of such assumptions that they cannot be proven in an exact thermodynamic sense. Support for single-ion transfer properties is provided when data obtained from different extrathermodynamic assumptions employing different experimental techniques agree within experimental error.

One set of such data is available from electrochemical measurements, albeit only for cations.[1−5] No reversible electrode reaction involving monatomic anions such as halide ions has been found in polarography. Electrochemical measurements are generally carried out by polarography or potentiometry and require electrode processes that are reversible on the time scale of the experiment for the calculation of single-ion transfer properties.

Among the transfer properties, Gibbs energies, entropies, and enthalpies of transfer have received considerable attention, and data based on at least two different assumptions for these transfer properties are available.

This paper focuses especially on entropies (given as $T\Delta_tS°$ values at 298 K) and enthalpies of transfer of cations from water as the reference solvent, although Gibbs energies of transfer are also discussed. Such data have been obtained on the basis of more than one extrathermodynamic assumption. Early measurements were based on the tetraphenylarsonium tetraphenylborate (TATB) assumption.[6] Gibbs energies of single ions based on the TATB assumption were generally obtained from solubility measurements, and the corresponding enthalpies were found from calorimetric studies. $T\Delta_tS°$ values at 298 K were then calculated from the difference between enthalpies and Gibbs energies of transfer.[6−9]

Gibbs energies of transfer from electrochemical measurements are generally derived from polarographic measurements and to a lesser degree from potentiometric studies. It is important to note that only redox systems in which the reduced form is either a metal (potentiometry) or an amalgam (polarography) may be included in this calculation. Gibbs energies of transfer from polarographic measurements are calculated from the following equation:

$$\Delta_tG° = nF[E_{1/2}(\mathrm{S}) - E_{1/2}(\mathrm{R})] \tag{1}$$

where $E_{1/2}(\mathrm{S})$ and $E_{1/2}(\mathrm{R})$ are the half-wave potentials of the species under study versus bis(biphenyl)chromium(I)/(0) as the reference redox system in the solvent (S) and reference solvent (R), respectively. The half-wave potentials of the species under study and the reference redox system in a given solvent were measured in the same solution to avoid contributions from liquid junction potentials. In eq 1, it is assumed that the polarographic half-wave potentials are a good approximation to the standard redox potentials. Possible reference redox systems and their applicability to the calculation of single-ion transfer properties have been discussed elsewhere.[4] The Gibbs energies of transfer for cations given in this paper are based on the bis(biphenyl)-chromium (BCr) assumption.[5]

Entropies of transfer from electrochemical measurements obtained in nonisothermal cells can be derived from the following relation:

$$\left(\frac{\partial \Delta G°}{\partial T}\right)_p = nF\left(\frac{\partial \Delta E°}{\partial T}\right)_p = -\Delta S° \tag{2}$$

However, the temperature dependence of the electrode potential, $(\partial\Delta E/\partial T)_p$, includes not only the variation of the Galvani potential, $(\partial\Delta E_\mathrm{G}/\partial T)_p$, but also the temperature dependence of the potential in the electrolyte bridge (Soret potential), $(\partial\Delta E_\mathrm{S})/\partial T)_p$, and that of the Thomson potential, $(\partial\Delta E_\mathrm{T}/\partial T)_p$, as given by eq 3:

$$\left(\frac{\partial \Delta E}{\partial T}\right)_p = \left(\frac{\partial \Delta E_\mathrm{G}}{\partial T}\right)_p + \left(\frac{\partial \Delta E_\mathrm{S}}{\partial T}\right)_p + \left(\frac{\partial \Delta E_\mathrm{T}}{\partial T}\right)_p \tag{3}$$

As discussed in detail in a previous publication, the changes in the Soret and Thomson potentials may be considered

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negligible in comparison with the changes in the Galvani potential.[10] This is the basis of the assumption of a negligible thermal diffusion potential (NTDP). Experimental apparatus and measuring techniques for both electrodes of the first kind (e.g., Ag|0.01 mol·dm^{-3} Ag$^+$) and polarographic studies have been published.[10,11]

For electrodes of the first kind (potentiometric measurements) the following equation holds:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -nF\left(\frac{\partial \Delta E}{\partial T}\right)_p = -\Delta S \tag{4}$$

In the case of polarographic experiments, it is assumed that the temperature dependence of the half-wave potentials represents the temperature dependence of the standard electrode potentials:

$$\left(\frac{\partial \Delta G^\circ}{\partial T}\right)_p = -nF\left(\frac{\partial \Delta E^\circ}{\partial T}\right)_p \approx -nF\left(\frac{\partial \Delta E_{1/2}}{\partial T}\right) = -\Delta S^\circ \tag{5}$$

For a redox system where the reduced form is a metal M (potentiometric measurements), eq 6 holds:

$$nF\left(\frac{\partial \Delta E^\circ}{\partial T}\right)_p = -[S^\circ(\mathrm{M}^{z+}) - S^\circ(\mathrm{M}^0)] \tag{6}$$

where $S^\circ(\mathrm{M}^{z+})$ refers to the entropy of the solvated ion. For polarographic measurements, the reduced form is the respective amalgam:

$$nF\left(\frac{\partial \Delta E_{1/2}}{\partial T}\right) \approx -\{S^\circ(\mathrm{M}^{z+}) - S^\circ[\mathrm{M(Hg)}]\} \tag{7}$$

When the difference is computed, the entropy of the reduced form $\{S^\circ(\mathrm{M}^0)$ or $S^\circ[\mathrm{M(Hg)}]\}$ cancels out, and the transfer entropy of an ion that moves from the reference solvent (R) to another solvent (S) is given by eq 8:

$$nF\left[\left(\frac{\partial \Delta E}{\partial T}\right)_{\mathrm{R}} - \left(\frac{\partial \Delta E}{\partial T}\right)_{\mathrm{S}}\right] = \Delta_t S^\circ \tag{8}$$

where E refers to E° for potentiometric measurements or $E_{1/2}$ for polarographic measurements.

Such electrochemical studies allow "direct" measurements of single-ion transfer entropies. Data at $T = 298$ K (25 °C) is generally given as the value of $T\Delta_t S^\circ$.

Multiplication of $\Delta_t S^\circ$ by 298 K followed by addition of the Gibbs energy of transfer yields the enthalpy of transfer at this temperature (eq 9):

$$\Delta_t H^\circ = \Delta_t G^\circ + T\Delta_t S^\circ \tag{9}$$

The TATB assumption, which in principle is a "reference electrolyte assumption", is based on the following relations:[6−9]

$$\Delta_t G^\circ(\mathrm{TA}^+) = \Delta_t G^\circ(\mathrm{TB}^-) = {}^1/_2\Delta_t G^\circ(\mathrm{TATB})$$
$$\Delta_t H^\circ(\mathrm{TA}^+) = \Delta_t H^\circ(\mathrm{TB}^-) = {}^1/_2\Delta_t H^\circ(\mathrm{TATB})$$
$$\Delta_t S^\circ(\mathrm{TA}^+) = \Delta_t S^\circ(\mathrm{TB}^-) = {}^1/_2\Delta_t S^\circ(\mathrm{TATB})$$

Water was chosen as reference solvent in this study. Although there are several arguments against using water as a reference

Table 1. Molar Gibbs Energies ($\Delta_t G^\circ$), $T\Delta_t S^\circ$ Values, and Enthalpies of Transfer ($\Delta_t H^\circ$) for Li$^+$ and Na$^+$ at 298 K with Water as the Reference Solvent

solvent	abbrev	$\Delta_t G^\circ(\mathrm{Li}^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(\mathrm{Li}^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(\mathrm{Li}^+)$ / kJ·mol^{-1}	$\Delta_t G^\circ(\mathrm{Na}^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(\mathrm{Na}^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(\mathrm{Na}^+)$ / kJ·mol^{-1}
water	W	0.0	0.0	0.0	0.0	0.0	0.0
methanol	MeOH	−4.3	−43.2	−47.5	4.3	−40.6	−36.2
ethanol	EtOH	1.5	−34.8	−33.3	8.7	−27.6	−18.9
trifluoroethanol	TFEtOH	–	–	–	–	–	–
1-propanol	PrOH	6.9	−27.9	−21.1	14.2	−20.7	−6.5
1-butanol	BuOH	9.6	−25.0	−15.4	17.0	−19.9	−2.9
1-hexanol	HxOH	8.9	−21.6	−12.7	16.0	−16.1	−0.1
1,2-ethanediol	ETDI	−1.3	−45.2	−46.4	1.4	−33.9	−32.6
acetone	AC	9.6	–	–	4.1	–	–
tetrahydrofuran	THF	6.3	–	–	1.4	–	–
butyrolactone	BL	15.4	–	–	9.3	–	–
propylene carbonate	PC	25.3	−38.0	−12.7	18.3	−42.6	−24.2
trimethylphosphate	TMP	−21.3	−45.7	−67.1	−10.0	−39.4	−49.4
formamide	FA	–	–	–	–	–	–
N-methylformamide	NMF	−15.5	–	–	−5.3	−29.6	−34.9
N,*N*-dimethylformamide	DMF	−11.9	−53.5	−65.4	−8.0	−43.2	−51.2
N,*N*-diethylformamide	DEF	−11.4	–	–	−6.4	–	–
N,*N*-dimethylacetamide	DMA	−18.3	–	–	−11.0	–	–
N,*N*-diethylacetamide	DEA	−25.6	–	–	−10.8	–	–
N-methyl-2-pyrrolidone	NMP	−19.0	−51.2	−70.2	−9.7	−42.0	−51.7
N,*N*,*N′*,*N′*-tetramethylurea	TMU	−25.1	–	–	−12.2	–	–
hexamethylphosphoric triamide	HMP	–	–	–	−24.9	−33.7	−58.6
tetramethylenesulfone	TMS	23.2	7.2	30.3	11.2	−11.2	0.0
dimethyl sulfoxide	DMSO	−34.7	–	–	−10.0	−35.7	−45.7
ethylenesulfite	ES	60.7	–	–	17.8	–	–
acetonitrile (ethanenitrile)	AN	28.9	−36.5	−7.6	14.3	−38.8	−24.6
propanenitrile	PRN	25.7	−43.2	−17.5	15.2	−42.9	−27.6
butanenitrile	BUN	–	–	–	16.3	–	–
isobutyronitrile	IBUN	27.9	–	–	16.8	–	–
benzonitrile	BN	34.6	−34.5	0.1	22.0	−33.9	−11.9
phenylacetonitrile	PAN	38.6	–	–	20.9	–	–
pyridine	PY	6.9	−63.9	−56.9	6.3	−51.8	−45.5
pyrrole	PL	71.5	−30.2	41.3	50.3	−30.2	20.1
aniline	ANI	44.4	−34.2	10.1	38.1	−36.6	1.5
2,2′-thiodiethanol	TDE	–	–	–	–	–	–
thiophenol	TP	–	–	–	–	–	–
tetrahydrothiophene	THT	–	–	–	–	–	–
N,*N*-dimethylthioformamide	DMTF	50.8	−30.6	20.3	34.7	–	–
N-methyl-2-thiopyrrolidone	NMTP	45.8	−28.8	17.1	31.7	−33.7	−1.9
hexamethylthiophosphoric triamide	HMTP	41.3	–	–	44.1	–	–

Table 2. Molar Gibbs Energies ($\Delta_t G^\circ$), $T\Delta_t S^\circ$ Values, and Enthalpies of Transfer ($\Delta_t H^\circ$) for K^+ and Rb^+ at 298 K with Water as the Reference Solvent

solvent	$\Delta_t G^\circ(K^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(K^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(K^+)$ / kJ·mol^{-1}	$\Delta_t G^\circ(Rb^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(Rb^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(Rb^+)$ / kJ·mol^{-1}
water	0.0	0.0	0.0	0.0	0.0	0.0
methanol	5.8	−40.0	−34.2	5.7	−38.0	−32.3
ethanol	9.4	−28.8	−19.4	8.5	−28.8	−20.3
1-propanol	15.7	−17.8	−2.1	15.9	–	–
1-butanol	18.9	–	–	19.8	−19.0	0.8
1,2-ethanediol	1.4	−33.4	−31.9	2.2	−17.3	−15.0
acetone	1.4	–	–	−0.4	–	–
tetrahydrofuran	9.1	–	–	8.5	–	–
butyrolactone	2.6	–	–	3.1	–	–
propylene carbonate	10.3	−42.6	−32.3	6.0	−40.6	−34.6
trimethylphosphate	−6.2	−44.0	−50.2	−3.8	−40.9	−44.6
N-methylformamide	−3.7	−32.5	−36.2	−4.1	−33.1	−37.2
N,*N*-dimethylformamide	−7.2	−46.6	−53.8	−6.4	−43.4	−49.8
N,*N*-diethylformamide	−4.8	–	–	−3.9	–	–
N,*N*-dimethylacetamide	−10.4	–	–	−5.5	–	–
N,*N*-diethylacetamide	−7.6	–	–	−4.9	–	–
N-methyl-2-pyrrolidone	−10.5	−47.5	−58.0	−7.0	−43.2	−50.2
N,*N*,*N*′,*N*′-tetramethylurea	−10.1	–	–	−6.7	–	–
hexamethylphosphoric triamide	−13.8	−43.2	−57.0	−9.1	−44.0	−53.1
tetramethylenesulfone	4.4	−24.2	−19.7	3.1	−26.8	−23.7
dimethyl sulfoxide	−8.3	−43.7	−52.0	−7.5	−40.0	−47.5
ethylenesulfite	12.6	–	–	–	–	–
acetonitrile (ethanenitrile)	7.0	−45.2	−38.1	6.6	−40.0	−33.4
propanenitrile	9.2	−40.9	−31.7	–	–	–
isobutyronitrile	19.9	–	–	17.6	–	–
benzonitrile	13.2	−37.4	−24.2	12.0	−33.9	−22.0
pyridine	6.3	−50.3	−44.1	5.8	−48.6	−42.8
pyrrole	51.7	–	–	51.6	−31.9	19.7
N,*N*-dimethylthioformamide	26.5	–	–	20.7	–	–
N-methyl-2-thiopyrrolidone	25.6	–	–	19.4	–	–

Table 3. Molar Gibbs Energies ($\Delta_t G^\circ$), $T\Delta_t S^\circ$ Values, and Enthalpies of Transfer ($\Delta_t H^\circ$) for Cs^+ and Ag^+ at 298 K with Water as the Reference Solvent

solvent	$\Delta_t G^\circ(Cs^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(Cs^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(Cs^+)$ / kJ·mol^{-1}	$\Delta_t G^\circ(Ag^+)$ / kJ·mol^{-1}	$T\Delta_t S^\circ(Ag^+)$ / kJ·mol^{-1}	$\Delta_t H^\circ(Ag^+)$ / kJ·mol^{-1}
water	0.0	0.0	0.0	0.0	0.0	0.0
methanol	6.9	−33.7	−26.7	2.1	−25.0	−22.9
ethanol	10.4	–	–	−0.2	−19.0	−19.2
trifluoroethanol	–	–	–	46.8	−14.1	32.7
1-propanol	14.1	−17.8	−3.8	2.6	−14.4	−11.8
1-butanol	20.0	−13.2	6.7	5.6	−12.7	−7.1
1-hexanol	–	–	–	6.9	−10.6	−3.8
1,2-ethanediol	5.2	−8.9	−3.7	−5.2	−19.0	−24.2
acetone	1.7	–	–	4.5	–	–
tetrahydrofuran	−0.9	–	–	2.8	–	–
butyrolactone	3.7	–	–	9.3	–	–
propylene carbonate	7.7	−41.4	−33.7	23.7	−27.6	−3.9
trimethylphosphate	−4.1	–	–	−8.6	−30.2	−38.8
formamide	–	–	–	−6.8	−23.0	−29.8
N-methylformamide	−0.6	−36.0	−36.5	−19.1	−30.8	−49.9
N,*N*-dimethylformamide	−4.5	−42.9	−47.4	−15.1	−34.8	−49.9
N,*N*-diethylformamide	−2.7	–	–	−12.1	–	–
N,*N*-dimethylacetamide	−5.4	–	–	−23.4	–	–
N,*N*-diethylacetamide	−5.2	–	–	−23.3	–	–
N-methyl-2-pyrrolidone	−5.4	−44.6	−50.0	−18.8	−31.9	−50.7
N,*N*,*N*′,*N*′-tetramethylurea	–	–	–	−22.4	–	–
hexamethylphosphoric triamide	−6.6	−47.2	−53.7	−36.4	−27.3	−63.7
tetramethylenesulfone	3.7	−32.5	−28.8	9.5	−17.0	−7.5
dimethyl sulfoxide	−7.0	−39.4	−46.5	−29.9	−28.5	−58.4
ethylenesulfite	–	–	–	20.6	−36.8	−16.2
acetonitrile (ethanenitrile)	7.8	−40.6	−32.7	−23.0	−34.8	−57.8
propanenitrile	–	–	–	−22.4	−36.8	−59.2
butanenitrile	–	–	–	−21.8	−34.8	−56.6
isobutyronitrile	16.2	–	–	−19.0	–	–
benzonitrile	11.6	−30.8	−19.2	−15.1	−17.0	−32.0
phenylacetonitrile	–	–	–	−12.7	−17.0	−29.7
pyridine	7.0	−48.3	−41.3	−63.4	−47.8	−111.1
pyrrole	51.2	−33.1	18.1	−28.6	−28.5	−57.0
aniline	–	−27.0	–	−36.1	−38.0	−74.1
2,2′-thiodiethanol	–	–	–	−55.7	–	–
thiophenol	–	–	–	−90.0	–	–
tetrahydrothiophene	–	–	–	−54.8	–	–
N,*N*-dimethylthioformamide	13.6	–	–	−97.2	−34.8	−132.0
N-methyl-2-thiopyrrolidone	14.4	–	–	−103.3	−37.1	−140.4
hexamethylthiophosphoric triamide	–	–	–	−79.4	−31.6	−111.0

Table 4. Molar Gibbs Energies ($\Delta_t G^\circ$), $T\Delta_t S^\circ$ Values, and Enthalpies of Transfer ($\Delta_t H^\circ$) for Tl^+ and Ba^{2+} at 298 K with Water as the Reference Solvent

solvent	$\Delta_t G^\circ(\mathrm{Tl}^+)$ / $\mathrm{kJ\cdot mol^{-1}}$	$T\Delta_t S^\circ(\mathrm{Tl}^+)$ / $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_t H^\circ(\mathrm{Tl}^+)$ / $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_t G^\circ(\mathrm{Ba}^{2+})$ / $\mathrm{kJ\cdot mol^{-1}}$	$T\Delta_t S^\circ(\mathrm{Ba}^{2+})$ / $\mathrm{kJ\cdot mol^{-1}}$	$\Delta_t H^\circ(\mathrm{Ba}^{2+})$ / $\mathrm{kJ\cdot mol^{-1}}$
water	0.0	0.0	0.0	0.0	0.0	0.0
methanol	1.3	−34.8	−33.6	3.7	−115.0	−111.3
ethanol	4.4	−20.1	−15.7	18.3	−76.9	−58.5
trifluoroethanol	33.0	−15.8	17.2	–	–	–
1-propanol	6.5	−16.4	−9.9	18.9	−54.5	−35.6
1-butanol	9.6	−12.1	−2.5	24.1	−38.1	−14.0
1-hexanol	6.6	−10.1	−3.5	11.4	–	–
1,2-ethanediol	−3.1	−24.5	−27.5	−12.9	−85.5	−98.4
acetone	3.1	–	–	5.6	–	–
tetrahydrofuran	2.9	–	–	0.4	–	–
butyrolactone	3.1	–	–	–	–	–
propylene carbonate	12.1	−38.8	−26.8	33.8	−105.3	−71.5
trimethylphosphate	−5.7	−34.5	−40.2	−42.3	−73.6	−115.9
formamide	1.1	−19.0	−17.9	–	–	–
N-methylformamide	−8.6	−32.2	−40.8	−45.2	−81.0	−126.2
N,*N*-dimethylformamide	−11.3	−42.0	−53.3	−39.6	−99.0	−138.5
N,*N*-diethylformamide	−10.2	–	–	–	–	–
N,*N*-dimethylacetamide	−11.5	–	–	–	–	–
N,*N*-diethylacetamide	−11.4	–	–	−48.2	–	–
N-methyl-2-pyrrolidone	−14.1	−41.7	−55.8	−55.2	−92.1	−147.3
N,*N*,*N*′,*N*′-tetramethylurea	−15.0	–	–	−41.9	–	–
hexamethylphosphoric triamide	−23.8	−37.7	−61.5	−73.5	−85.2	−158.7
tetramethylensulfone	3.1	−17.3	−14.2	18.1	2.9	21.0
dimethyl sulfoxide	−19.1	−38.3	−57.4	−49.4	−86.3	−135.7
ethylenesulfite	11.9	−39.4	−27.5	–	−90.9	–
acetonitrile (ethanenitrile)	9.8	−42.2	−32.4	42.6	−72.4	−29.7
propanenitrile	9.6	−42.3	−32.7	35.7	−92.8	−57.1
butanenitrile	10.7	–	–	31.5	–	–
isobutyronitrile	8.6	−32.9	−24.3	–	−60.6	–
benzonitrile	11.8	–	–	38.8	–	–
phenylacetonitrile	12.5	−17.3	−4.7	49.0	2.9	51.9
pyridine	−13.1	−50.3	−63.5	−6.2	−65.6	−71.8
pyrrole	7.9	−25.3	−17.4	87.4	−9.0	78.4
aniline	0.7	−37.4	−36.7	73.9	−29.2	44.7
2,2′-thiodiethanol	−2.6	–	–	–	–	–
thiophenol	−23.3	–	–	–	–	–
tetrahydrothiophene	−2.2	–	–	–	−21.3	–
N,*N*-dimethylthioformamide	−19.8	−31.6	−51.4	62.9	−49.5	13.4
N-methyl-2-thiopyrrolidone	−22.1	–	–	56.5	–	–
hexamethylthiophosphoric triamide	−6.5	−17.3	−23.7	–	2.9	–

solvent, enough data are now available to consider water as the reference solvent,[12] facilitating comparison of the "electrochemical" data with literature data derived from the TATB assumption. Arguments against using water as reference solvent include the poor solubility of TATB in this solvent, apparent interactions of water with the oxidized form of the ferrocene/ferrocenium couple, and the insolubility of bis(biphenyl)chromium(0) from the reference redox system bis(biphenyl)chromium(0)/bis(biphenyl)chromium(I) ion.

Results

The electrochemical data for the Gibbs energies of transfer based on the BCr assumption were taken from the literature[10−16] and calculated for water as the reference solvent using 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate as the supporting electrolyte. $T\Delta_t S^\circ$ values were derived from the temperature coefficients of the respective redox couples, again employing water as the reference solvent.[10−13] Enthalpies of transfer were obtained as the sum of the $\Delta_t G^\circ$ and the $T\Delta_t S^\circ$ values. The transfer properties of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, Tl^+, Ba^{2+}, Cu^{2+}, and Pb^{2+} are given in Tables 1 through 5.

Figure 1 shows the correlation between the $T\Delta_t S^\circ$ data for Ag^+ obtained from the two different assumptions employing different experimental techniques. Figure 2 presents the correlation between the enthalpies of transfer of Ag^+ from different assumptions. The $T\Delta_t S^\circ$ data as well as the enthalpies of transfer from the TATB assumption were taken from refs 6−9. The lines in Figures 1 and 2 have a slope of unity.

A linear correlation between the $T\Delta_t S^\circ$ values for Ag^+ based on the NTDP assumption and those based on the TATB assumption at 298 K for eight solvents yielded the following results:

$$\{[T\Delta_t S^\circ(\mathrm{Ag}^+)\ (\mathrm{NTDP})]/\mathrm{kJ\cdot mol^{-1}}\} = 3.31 + 1.00 \cdot \{[T\Delta_t S^\circ(\mathrm{Ag}^+)\ (\mathrm{TATB})]/\mathrm{kJ\cdot mol^{-1}}\}$$

with a correlation coefficient (r) of 0.861 and a standard deviation (sd) of 8.76.

Linear regression analysis for nine solvents for which data from both assumptions were available yielded the following results:

$$\{[\Delta_t H^\circ(\mathrm{Ag}^+)\ (\mathrm{TATB})]/\mathrm{kJ\cdot mol^{-1}}\} = 2.49 + 1.01 \cdot \{[\Delta_t H^\circ(\mathrm{Ag}^+)\ (\mathrm{BCr} + \mathrm{NTDP})]/\mathrm{kJ\cdot mol^{-1}}\}$$

with $r = 0.989$ and sd $= 7.32$. Both the correlation for $T\Delta_t S^\circ(\mathrm{Ag}^+)$ and that for the enthalpies of transfer of Ag^+ strongly indicate that the two assumptions lead to values that agree within experimental error.

Figures 3 through 5 show the transfer properties of Na^+ plotted versus the respective properties of Ag^+. The observations included in these plots will be considered in the Discussion.

Table 5. Molar Gibbs Energies ($\Delta_tG°$), $T\Delta_tS°$ Values, and Enthalpies of Transfer ($\Delta_tH°$) for Cu^{2+} and Pb^{2+} at 298 K with Water as the Reference Solvent

solvent	$\Delta_tG°(Cu^{2+})$ / $kJ\cdot mol^{-1}$	$T\Delta_tS°(Cu^{2+})$ / $kJ\cdot mol^{-1}$	$\Delta_tH°(Cu^{2+})$ / $kJ\cdot mol^{-1}$	$\Delta_tG°(Pb^{2+})$ / $kJ\cdot mol^{-1}$	$T\Delta_tS°(Pb^{2+})$ / $kJ\cdot mol^{-1}$	$\Delta_tH°(Pb^{2+})$ / $kJ\cdot mol^{-1}$
water	0.0	0.0	0.0	0.0	0.0	0.0
methanol	11.0	−100.5	−89.5	−0.4	−57.7	−58.1
ethanol	22.2	−60.0	−37.8	10.8	−35.7	−24.9
trifluoroethanol	139.7	−23.0	116.7	98.0	−40.3	57.8
1-propanol	24.7	−20.8	3.9	13.1	−27.7	−14.6
1-butanol	29.3	−8.1	21.2	28.9	−30.4	−1.4
1-hexanol	–	–	–	8.3	−16.3	−8.0
1,2-ethanediol	5.4	−42.9	−37.5	−10.8	−26.6	−37.4
acetone	69.1	–	–	46.1	–	–
tetrahydrofuran	−10.6	–	–	8.1	–	–
butyrolactone	49.4	–	–	–	–	–
propylene carbonate	72.9	–	–	42.8	−71.3	−28.5
trimethylphosphate	11.6	−17.3	−5.7	−23.9	–	–
formamide	−2.7	2.2	−0.5	−15.8	−16.9	−32.7
N-methylformamide	−28.8	−3.8	−32.6	−36.3	−55.2	−91.5
N,*N*-dimethylformamide	−32.0	−77.1	−109.1	−38.2	−74.8	−113.0
N,*N*-diethylformamide	−29.7	–	–	−40.3	–	–
N,*N*-dimethylacetamide	−28.4	–	–	−40.5	–	–
N,*N*-diethylacetamide	−26.2	–	–	−38.0	–	–
N-methyl-2-pyrrolidone	−18.9	−48.3	−67.2	−39.2	−69.6	−108.8
N,*N*,*N*′,*N*′-tetramethylurea	15.1	–	–	−48.0	–	–
hexamethylphosphoric triamide	−61.9	−22.4	−84.4	−60.0	−66.7	−126.8
tetramethylensulfone	69.9	29.3	99.2	33.2	16.7	49.9
dimethyl sulfoxide	−28.6	−53.5	−82.1	−56.0	−49.5	−105.4
ethylenesulfite	71.6	29.3	100.9	41.7	16.7	58.4
acetonitrile (ethanenitrile)	–	–	–	41.9	−66.7	−24.9
propanenitrile	–	–	–	38.6	−54.0	−15.4
butanenitrile	–	−46.9	–	41.9	–	–
isobutyronitrile	–	–	–	36.5	–	–
benzonitrile	–	–	–	45.5	−38.4	7.1
phenylacetonitrile	–	–	–	50.8	–	–
pyridine	–	–	–	−25.5	−79.4	−104.9
pyrrole	–	19.4	–	37.2	–	–
aniline	–	–	–	3.1	−48.7	−45.6
2,2′-thiodiethanol	−90.1	–	–	−5.0	–	–
thiophenol	–	–	–	−67.3	–	–
tetrahydrothiophene	–	–	–	−15.1	–	–
N,*N*-dimethylthioformamide	–	–	–	−35.9	−57.9	−93.8
N-methyl-2-thiopyrrolidone	–	–	–	−38.0	−46.6	−84.6
hexamethylthiophosphoric triamide	–	–	–	−6.2	−93.4	−99.6

A linear correlation between the $T\Delta_tS°$ values for Na^+ and those for Ag^+ based on the NTDP assumption was found:

$$\{[T\Delta_tS°(Na^+)\ (NTDP)]/kJ\cdot mol^{-1}\} = 7.74 + 0.939\cdot \{[T\Delta_tS°(Ag^+)\ (NTDP)]/kJ\cdot mol^{-1}\}$$

with $r = 0.861$ and sd $= 6.33$.

Discussion

The agreement between the data from electrochemical measurements based on the assumptions of a “solvent-independent reference redox system” and the assumption of a “negligible thermal diffusion potential” with values from the tetraphenylarsonium tetraphenyborate assumption may be considered acceptable. One must keep in mind that all techniques

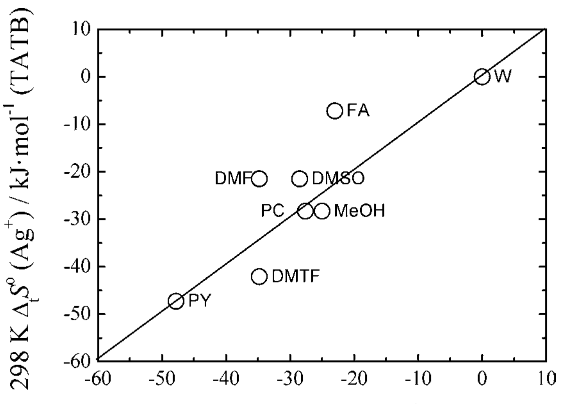

Figure 1. Molar $T\Delta_tS°$ values at 298 K for Ag^+ based on the TATB assumption [298 K $\Delta_tS°(Ag^+)$ (TATB)]$^{6-9}$ vs molar $T\Delta_tS°$ values based on the assumption of a negligible thermal diffusion potential [298 K $\Delta_tS°(Ag^+)$ (NTDP)]. The reference solvent was water.

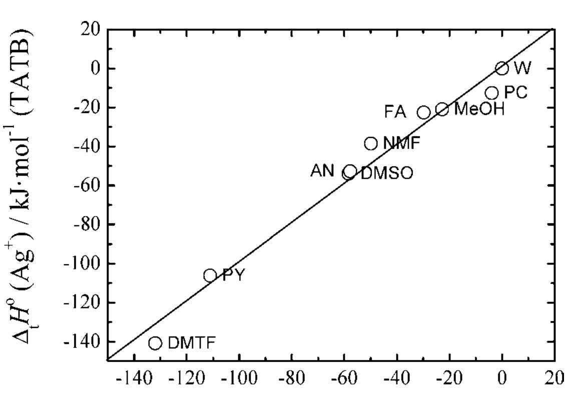

Figure 2. Molar enthalpies of transfer of Ag^+ based on the TATB assumption [$\Delta_tH°(Ag^+)$ (TATB)]$^{6-9}$ vs enthalpies of transfer of Ag^+ based on the BCr and NTDP assumptions [$\Delta_tH°(Ag^+)$ (BCr + NTDP)]. The reference solvent was water.

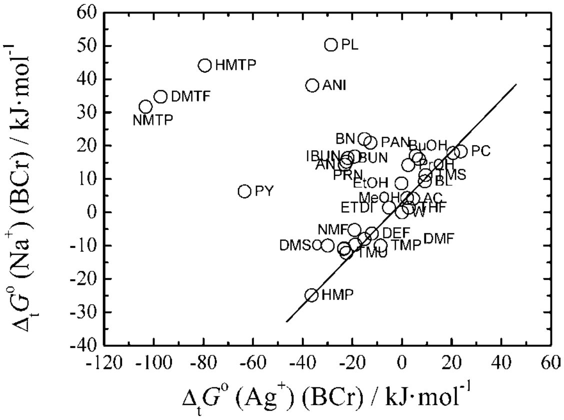

Figure 3. Molar Gibbs energies of transfer based on the BCr assumption for Na^+ and Ag^+ at 298 K. The reference solvent was water.

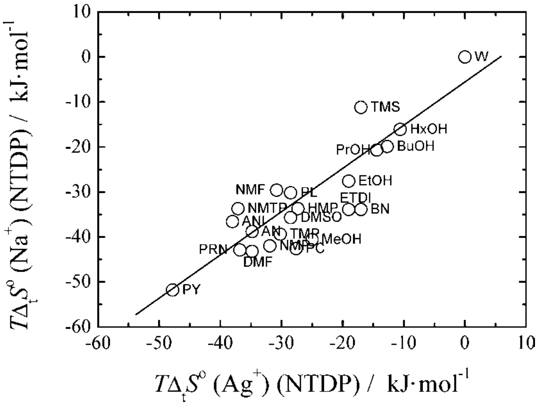

Figure 4. Molar $T\Delta_tS°$ values based on the NTDP assumption for Na^+ and Ag^+ at 298 K. The reference solvent was water.

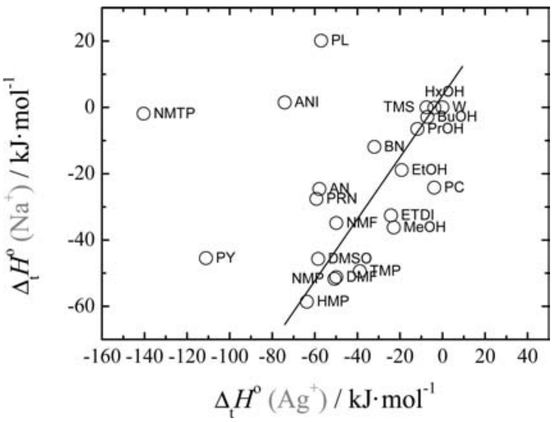

Figure 5. Molar $\Delta_tH°$ values based on the BCr and NTDP assumptions for Na^+ and Ag^+ at 298 K. The reference solvent was water.

include experimental errors. The TATB assumption has been subject to some criticism. Such views have been based on the different sizes of the TA^+ cation and TB^- anion and on the different interactions of the cation and anion of this reference substance with solvent molecules, especially water molecules.[17,18] While such calculations have their importance, one may well overemphasize the meaning of extrathermodynamic assumptions. Most of the "critical" views of extrathermodynamic assumptions are based on the Born model and consider the interactions between the surface of the reference substances and the solvent molecules basically from an electrostatic point of view. It may be better to compare data and evaluate the importance of single-ion transfer properties in connection with thermodynamic and kinetic properties of chemical reactions.

There is also a danger in collecting all of the literature data and publishing recommended values in the form of "weighted means". Such compilations would include both experimentally correct and incorrect data, which cannot be separated and would enter into the recommended values.[19,20]

Figures 3 through 5 show relations between the transfer properties of Na^+ and Ag^+. Figure 3 clearly shows that a correlation between the Gibbs energies of Na^+ and Ag^+ exists only for oxygen-donor solvents. The deviations for the other solvents have been discussed in several publications.[21,22] These deviations have been assigned to different interactions between the cations and the donor sites of the solvent molecules. Following such considerations, it was recommended that Gibbs energies of transfer of cations may be used to evaluate the meaning and limits of proposed solvent parameters.[21,22] Considerably less attention has been paid to the $T\Delta_tS°$ values of cations (and also of anions). $T\Delta_tS°$ values have been interpreted as being affected both by the loss of freedom of the solvent molecules as a result of coordination in the first solvation shell and by the influence of the coordinated species on the solvent structure. Figure 4 shows a linear dependence of the $T\Delta_tS°$ values of Na^+ on the $T\Delta_tS°$ values of Ag^+. A very similar dependence was observed for all of the monovalent cations.[1] It appears that the $T\Delta_tS°$ values are not affected by the nature of the interactions between the cations and solvent molecules.

While this view may not be shared by all researchers, the enthalpies of transfer sum up the interactions represented by the Gibbs energies of transfer (reflecting differences in the strength and nature of the chemical bonding between the cations and solvent molecules) and the $T\Delta_tS°$ values (reflecting the loss of translational freedom of the coordinated solvent molecules as well as structural changes in the solvation spheres).[1] The interesting information about ion−solvent interactions and their effect on the thermodynamics and kinetics of chemical reactions are in the Gibbs energies and $T\Delta_tS°$ values of transfer. These properties should be employed in elucidating the physicochemistry of reactions in solution.

Acknowledgment

This paper is dedicated to Professor Josef Barthel on the occasion of his 80th birthday.

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