

Determination of the Transfer Thermodynamic Functions for the Zinc(II), Cadmium(II), Mercury(II) and Mercury(I) Ions from Water to Methanol, Dimethyl Sulfoxide, Acetonitrile, Pyridine and *N,N*-Dimethylthioformamide and of Standard Electrode Potentials of the $M^{2+}/M(s)$ Couples in these Solvents

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The transfer thermodynamic functions for the zinc, cadmium, mercury(II) and mercury(I) ions from water to methanol, dimethyl sulfoxide, acetonitrile, pyridine and *N,N*-dimethylthioformamide are reported. The $\Delta_t G^\ominus$ values are calculated from potentiometrically determined standard electrode potentials in the different solvents with a silver reference electrode, and the $\Delta_t H^\ominus$ values are obtained from calorimetrically determined enthalpies of solution of the anhydrous metal trifluoromethylsulfonates. The entropies of transfer, $\Delta_t S^\ominus$, are calculated from the experimentally obtained $\Delta_t G^\ominus$ and $\Delta_t H^\ominus$ values; all of the measurements were performed at 25 °C. The extrathermodynamic tetraphenylarsonium tetraphenylborate (TATB) assumption has been applied in order to calculate the contributions from the single ions. The studied ions are more strongly solvated in *N,N*-dimethylthioformamide, pyridine and dimethyl sulfoxide than in water, while they are more weakly solvated in methanol and acetonitrile. The entropies of transfer are negative for all the systems under study except for the cadmium ion to *N,N*-dimethylthioformamide.

Most previous transfer thermodynamic studies have been performed on monovalent ions from water to mainly oxygen donor solvents such as alcohols, acetone, acetonitrile, dimethyl sulfoxide and *N,N*-dimethylformamide and to acetonitrile, while very few refer to di- and tri-valent ions or to soft donor solvents.^{1,2} Transfer thermodynamic studies to typical soft donor solvents, *e.g.* pyridine, tetrahydrothiophene and *N,N*-dimethylthioformamide have only been reported by Gritzner³ and this laboratory. Gritzner used the bis(biphenyl)chromium(0)/(I) (BCr) extrathermodynamic assumption, which states that the bis(biphenyl)chromium(0) and (I) species are equally solvated pairwise in every solvent.³ As the BCr assumption is only applicable to electrochemical measurements their direct studies are limited to determination of Gibbs energies and entropies of transfer. Gritzner and co-workers have reported Gibbs energies of transfer for mono- and di-valent cations from acetonitrile to typical soft donor solvents such as pyridine, tetrahydrothiophene, *N,N*-dimethylthioformamide, *N*-methylthiopyrrolidone(2) and hexamethylthiophosphonic triamide.^{3–13} This laboratory has previously reported the complete transfer thermodynamics for 11 monovalent cations, 12 monovalent and two divalent anions from water to methanol, dimethyl sulfoxide, acetonitrile, pyridine, tetrahydrothiophene and *N,N*-dimethylthioformamide using the TATB assumption.^{14–18}

The transfer thermodynamics of some divalent ions are studied. The same solvents as in the previous investigations (see, *e.g.* the previous paper) are studied except tetrahydrothiophene. It has been excluded because the solubility and the degree of dissociation of salts containing a divalent ion are very low in this solvent owing to its low relative permittivity. The transfer thermodynamics of the divalent ions

zinc, cadmium, mercury(II) and mercury(I) from water to methanol, dimethyl sulfoxide, acetonitrile, pyridine and *N,N*-dimethylthioformamide are reported in this paper. Ahrlund and co-workers^{19,20} and Hedwig and Parker²¹ have previously reported transfer thermodynamics for the zinc, cadmium and mercury(II) ions from water to dimethyl sulfoxide using the TATB assumption. Libus *et al.*²² have reported heats of transfer for the zinc ion from water to acetonitrile and dimethyl sulfoxide using the TATB assumption. Gritzner *et al.* have determined the Gibbs energies and entropies of transfer from water to acetonitrile and dimethylformamide,¹² and Gibbs energies of transfer from acetonitrile to a large number of solvents for the zinc, cadmium and mercury(II) ions.^{8,10} Gritzner *et al.* have performed electrochemical measurements and they have applied the BCr extrathermodynamic assumption.

The Gibbs energies of transfer of an ion can be calculated from the difference in standard electrode potential of a couple, where the pure element is the red- or ox-form, in the solvent under study and the reference solvent; in the non-aqueous solvents the difference in electrode potential of the reference cell, in this study the silver electrode, between water and the other solvent, when all concentrations are extrapolated to one molar, must be added, see Calculation section. The reliability of the logarithmic medium ion activity coefficients obtained from solubility product measurements has been checked by potentiometric measurements.¹⁴

The Gibbs energies of transfer have been calculated from the standard electrode potentials of the couples $Zn^{2+}/Zn(s)$, $Cd^{2+}/Cd(s)$, $Hg_2^{2+}/Hg(l)$ and Hg_2^{2+}/Hg_2^{2+} in the solvents used in this study. The standard electrode potentials have been determined *vs.* the $Ag^+/Ag(s)$ electrode. This electrode was selected as it performs well in the solvents studied and the Gibbs energies of transfer of the silver ion have been determined from solubility product measurements in the studied solvents.^{14,15,23} The standard electrode potentials *vs.* the normal hydrogen electrode in water have been calculated from the $\Delta_t G^\ominus$ values for the silver ion and the experimentally determined standard electrode potentials *vs.* the silver

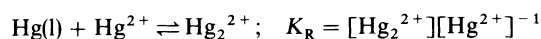
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electrode. The standard electrode potentials of the $\text{Hg}_2^{2+}/\text{Hg(l)}$ and $\text{Hg}_2^{2+}/\text{Hg}_2^{2+}$ couples in methanol and acetonitrile, of the $\text{Zn}^{2+}/\text{Zn(s)}$, $\text{Cd}^{2+}/\text{Cd(s)}$ and $\text{Hg}_2^{2+}/\text{Hg(l)}$ couples in methanol, acetonitrile and pyridine, and of the $\text{Zn}^{2+}/\text{Zn(s)}$, $\text{Cd}^{2+}/\text{Cd(s)}$ and $\text{Hg}_2^{2+}/\text{Hg(l)}$ couples in *N,N*-dimethylthioformamide have been determined in this study, while the remaining standard electrode potentials have been taken from the literature.²⁴⁻²⁶

Metallic mercury reduces the mercury(II) ion according to the following reaction:



The equilibrium of this reaction is dependent on the relative solvation of the mercury(I) and (II) ions. The solvation of the d^{10} acceptor, mercury(II), is increasingly favoured over mercury(I) with increasing softness of the solvent. This means that the reproporationation constant K_R will decrease with increasing softness of the solvent.

The enthalpies of transfer are calculated from the experimentally determined enthalpies of solution of the anhydrous metal trifluoromethylsulfonate salts. Trifluoromethylsulfonate salts have been used because they are easy to prepare in anhydrous form, they have high solubility in the most solvents and the trifluoromethylsulfonate ion very rarely forms complexes with the studied metal ions. However, anhydrous mercury(II) trifluoromethylsulfonate, nitrate and acetate decomposes when added to *N,N*-dimethylthioformamide and a black compound is formed; this compound is not metallic mercury. The reason for this reaction is not understood, and a similar reaction takes place in the strongly electron-pair donating solvent liquid ammonia also. A direct measurement of the enthalpy of transfer of the mercury(II) ion from water to *N,N*-dimethylthioformamide is therefore not possible. The only non-coordinating mercury(II) salt which does not decompose in *N,N*-dimethylthioformamide is the perchlorate, and it cannot be prepared in anhydrous form.

Calculations

The basis of the TATB assumption has been given elsewhere.¹⁵ The following relationships are only valid if the salt is completely dissociated.

The Gibbs energies of transfer are calculated from standard electrode potentials according to

$$\Delta_t G^\ominus = nF(E_{\text{solv}}^\ominus - E_w^\ominus)$$

where the E_w^\ominus and E_{solv}^\ominus are the standard electrode potentials of a couple in water and another solvent, respectively, vs. the normal hydrogen electrode in water. The calculation of E_{solv}^\ominus has been described elsewhere.¹⁵

The enthalpies of solution, $\Delta_{\text{sol}} H^\ominus$, of $\text{M}(\text{CF}_3\text{SO}_3)_2$ determined in water and another solvent are used to calculate the enthalpy of transfer for the compound $\text{M}(\text{CF}_3\text{SO}_3)_2$ from water (W) to this solvent (solv):

$$\begin{aligned} \Delta_t H^\ominus[\text{M}(\text{CF}_3\text{SO}_3)_2, \text{W} \rightarrow \text{solv}] \\ = \Delta_{\text{sol}} H^\ominus[\text{M}(\text{CF}_3\text{SO}_3)_2, \text{solv}] - \Delta_{\text{sol}} H^\ominus[\text{M}(\text{CF}_3\text{SO}_3)_2, \text{W}] \end{aligned}$$

The enthalpy of transfer of the individual cation is then calculated by subtracting the previously determined enthalpy of transfer of the trifluoromethylsulfonate ion^{14,15} from the enthalpy of transfer of the compound $\text{M}(\text{CF}_3\text{SO}_3)_2$ according to

$$\begin{aligned} \Delta_t H^\ominus(\text{M}^{2+}, \text{W} \rightarrow \text{solv}) = \Delta_t H^\ominus[\text{M}(\text{CF}_3\text{SO}_3)_2] \\ - 2\Delta_t H^\ominus(\text{CF}_3\text{SO}_3^-) \end{aligned}$$

The entropies of transfer, $\Delta_t S^\ominus$, are calculated according to

$$\Delta_t S^\ominus = (\Delta_t H^\ominus - \Delta_t G^\ominus)T^{-1}$$

The Gibbs energies, enthalpies and entropies of solvation are calculated by adding the Gibbs energies, enthalpies and entropies of transfer and hydration.

$$\Delta_{\text{sv}} X^\ominus = \Delta_{\text{hyd}} X^\ominus + \Delta_t X^\ominus$$

where X denotes G , H or S .

Determination of K_R

The reproporationation constant, K_R , of the mercury system in methanol was determined by analysis of the total mercury concentration after dissolution of mercury(I) trifluoromethylsulfonate and after adding metallic mercury to a mercury(II) trifluoromethylsulfonate methanol solution. The analysis of the total mercury concentration was made by EDTA titration²⁷ where mercury(I) is oxidised to mercury(II) by nitric acid before the titration. The procedure to calculate K_R from these analyses is given elsewhere.²⁰

The standard electrode potential of the couple $\text{Hg}_2^{2+}/\text{Hg(l)}$, E_{02}^\ominus , in all solvents except *N,N*-dimethylthioformamide, cannot be directly measured owing to the reproporationation reaction. It has instead been calculated from the standard electrode potentials of the $\text{Hg}_2^{2+}/\text{Hg(l)}$, E_{01}^\ominus and $\text{Hg}_2^{2+}/\text{Hg}_2^{2+}$, E_{12}^\ominus , couples according to

$$E_{02}^\ominus = (E_{01}^\ominus + E_{12}^\ominus)/2$$

The reproporationation constant K_R can be calculated from the standard electrode potentials according to

$$\ln K_R = (E_{12}^\ominus - E_{01}^\ominus)/(RT/F)$$

When the standard electrode potential E_{12}^\ominus is determined experimentally, it is important that the ratio $\text{Hg}_2^{2+}/\text{Hg}_2^{2+}$ is less than K_R during measurements as no reproporationation reaction is allowed to take place in such an experiment.

Experimental

Materials

Solvents

The solvents used were purified by standard distillation methods.²⁸ Methanol (Merck; analytical grade) was distilled over calcium hydride immediately before use. Acetonitrile (Fluka) and dimethyl sulfoxide (Merck) were purified as described elsewhere.^{24,26} Pyridine (Merck; analytical grade) was dried and stored over 3 Å molecular sieves and used without further purification.

N,N-Dimethylthioformamide was prepared by adding phosphorus pentasulfide to a benzene solution of *N,N*-dimethylformamide (Merck) as described by Gutmann *et al.*²⁹ The phosphorus pentoxide formed in the reaction was filtered off, the benzene was distilled off and the remaining *N,N*-dimethylthioformamide solution was distilled once more to remove unreacted *N,N*-dimethylformamide.

Preparation of Salts

The zinc, cadmium, mercury(II) and pyridinium trifluoromethylsulfonate salts were prepared according to methods described previously.^{21,26} The prepared salts were stored in a desiccator at 120 °C. Ammonium perchlorate (G. F. Smith) was dried over phosphorus pentoxide and stored at 120 °C.

Table 1 (a) Experimentally determined cell potentials, (in V), where the silver electrode has been used as reference cell, in methanol (M), acetonitrile (AN), dimethyl sulfoxide (DMSO), pyridine (Py) and *N,N*-dimethylthioformamide (DMTF) at 25 °C and in 0.1 mol dm⁻³ ionic medium. The given values have been extrapolated to 1 mol dm⁻³ concentrations of all species in the cell reaction ($a = 1$). (b) Standard electrode potentials based on the Gibbs energies of transfer of the silver ion, E°/V , of the silver, zinc, cadmium, mercury(I), mercury(II) and mercury(II)/mercury(I) couples in water (W), M, DMSO, Py, DMTF and liquid ammonia [NH₃(l)].

(a) cell	M	AN	DMSO	Py	DMTF		
Ag(s) Ag ⁺ Zn ²⁺ Zn(s)	-1.3859	-1.0437	-1.4613 ^a	-0.9586	-0.6972		
Ag(s) Ag ⁺ Cd ²⁺ Cd(s)	-1.0894	-0.7820	-1.1492 ^a	-0.6788	-0.7543		
Ag(s) Ag ⁺ Hg ₂ ²⁺ Hg(l)	+0.2152	+0.4514 ^b	+0.0072 ^a	(+0.2102) ^c			
Ag(s) Ag ⁺ Hg ₂ ²⁺ , Hg ²⁺ Pt	+0.3327	+0.6096 ^b	+0.0900 ^a	+0.1647 ^c			
Ag(s) Ag ⁺ Hg ₂ ²⁺ Hg(l)	(+0.2740)	(+0.5305) ^b	(+0.0486) ^a	(+0.1855) ^c	+0.1004		
(b) system	W	M	AN	DMSO	Py	DMTF	NH ₃ (l) ^e
Ag ⁺ Ag(s)	+0.7996	+0.876	+0.568	+0.445	+0.208	-0.244	-0.240 ^f
Zn ²⁺ Zn(s)	-0.7628	-0.510	-0.476	-1.016	-0.751	-0.941	-1.54 ^f
Cd ²⁺ Cd(s)	-0.4026	-0.213	-0.214	-0.704	-0.471	-0.998	-1.20 ^f
Hg ₂ ²⁺ Hg(l)	+0.7961	-1.091	+1.019	+0.452	+0.418		
Hg ₂ ²⁺ Hg ₂ ²⁺	+0.905	+1.209	+1.178	+0.535	+0.373		
Hg ₂ ²⁺ Hg(l)	+0.851	+1.150	+1.099	+0.494	+0.394	-0.143	-0.33 ^f
K_R	69	97	472	25	0.170		

Values within parentheses have been calculated from analysis of disproportionation or reproporation constants of the mercury system; for further details see Experimental section. ^a Ref. 20. ^b Ref. 26. ^c Ref. 25. ^d The standard electrode potential of the normal hydrogen electrode in liquid ammonia is -1.00 V vs. the normal hydrogen electrode in water, ref. 36–38. ^e Ref. 39.

Mercury(I) Trifluoromethylsulfonate. A slurry of 2–3 g of HgO (Merck) in 50–100 ml of de-ionized water was prepared. Deficient trifluoromethylsulfonic acid (Fluka) was added to the slurry. The solution was filtered to remove excess of HgO. A few drops of metallic Hg was added to the filtrate, and the slurry was stirred for 4–5 h. The temperature of the slurry was maintained at 30 °C during the reaction. The excess of metallic mercury was decanted off, the solvent was evaporated off from the remaining solution, and the obtained salt was dried at 120 °C. Elemental analysis of Hg₂(CF₃SO₃)₂ gave: Found: Hg, 57.5%; C, 3.60%, S, 9.2%; Calc.: Hg, 57.4%; C, 3.44%; S, 9.2%.

Bis(*N,N*-dimethylthioformamide)mercury(II)perchlorate. Mercury(II) perchlorate, trihydrate (G. F. Smith) or hexahydrate [prepared from HgO and perchloric acid (BDH Chemicals)],³⁰ 0.01 mol, was dissolved in 100 ml methanol (Merck). A few drops of concentrated perchloric acid had previously been added to the methanol in order to reduce the hydrolysis of mercury(II). It was sometimes necessary to decant the solution in order to remove a slight solid residue. The solution was cooled to about -75 °C in an ethanol-carbon dioxide bath. 0.02 mol *N,N*-dimethylthioformamide was dissolved in a small volume methanol, and the obtained solution was cooled to about -75 °C. The *N,N*-dimethylthioformamide solution was added to the mercury(II) solution and white crystals precipitated immediately. The obtained crystals were filtered off and stored in freezer or refrigerator, even though the crystals are stable at room temperature.

It was not possible to determine the mercury content in the sample with EDTA titration owing to the extreme stability of this compound.

If the ratio *N,N*-dimethylthioformamide : mercury(II) is greater than two a very viscous compound, tetrakis(*N,N*-dimethylthioformamide)mercury(II) perchlorate, is formed instead. This tetrasolvate is extremely soluble in *N,N*-dimethylthioformamide, and we have not been able to obtain crystals of this salt. *N,N*-Dimethylthioformamide solutions of mercury(II) perchlorate should preferably be stored in a freezer.

Amalgams

Zinc and cadmium amalgams containing about 2.5 wt.% Zn and 6 wt.% Cd were prepared and stored as described by

Persson.³¹ The dissolution took place at 60 °C. Small variations in the zinc and cadmium content are of no importance as a two-phase amalgam is formed in the ranges 2.18–45 wt.% Zn and 6–14 wt.% Cd, respectively, at 25 °C.³² The liquid amalgam phases with well-defined compositions were used in the potentiometric measurements. The amalgams were stored under a nitrogen atmosphere to prevent surface oxidation.

Calorimetric Measurements

The enthalpies of solution, $\Delta_{\text{sol}}H^\ominus$, were measured in an ampoule calorimeter described elsewhere.³³ Pure solvents without supporting electrolyte were used in the ampoule calorimetric experiments. A gold vessel containing 80 ml of solvent was used for the zinc and cadmium salts, while a glass vessel was used for the mercury salts to avoid formation of gold amalgam and gold(I) species. Two or three ampoules were smashed without changing the solvent. The salt concentration never exceeded 1.5 mmol dm⁻³. The enthalpies of solution were independent of concentration in the concentration range studied. The solubility of the salts used in the calorimetric studies was always at least 10 times larger than the concentration reached in the experiments. The ampoules were sealed off with an oxygen-propane flame and they were cooled during the sealing to avoid decomposition of the salt. At least six independent experiments in agreement were performed for each salt and solvent. The measurements were performed at 25 ± 0.002 °C.

Potentiometric Measurements

The apparatus and procedure used have been described previously.^{24–26} The potentiometric measurements were performed in a glove box in order to minimize the uptake of water. The glove box was dried with silica gel, 3 Å molecular sieves and phosphorous pentoxide. 0.1 mol dm⁻³ ammonium perchlorate was used as ionic medium in methanol, and 0.1 mol dm⁻³ pyridinium trifluoromethylsulfonate was used in acetonitrile, pyridine and *N,N*-dimethylthioformamide. The cation in the ionic medium must be somewhat acidic in the aprotic solvents, otherwise the surfaces of the amalgams are affected.²⁶

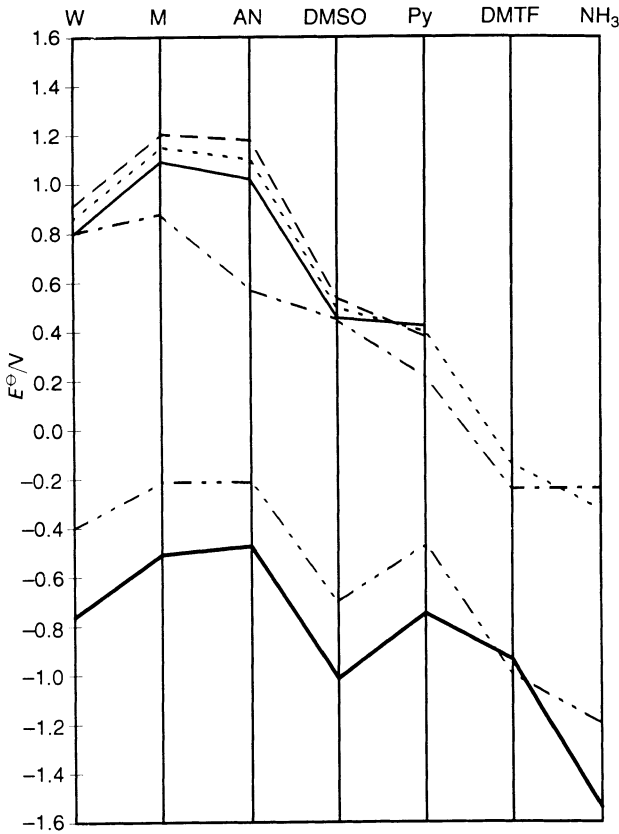


Fig. 1 Diagram of standard electrode potentials of the couples $\text{Zn}^{2+}/\text{Zn(s)}$ (—), $\text{Cd}^{2+}/\text{Cd(s)}$ (---), $\text{Hg}^{2+}/\text{Hg(l)}$ (....), $\text{Hg}_2^{2+}/\text{Hg(l)}$ (— · —) and $\text{Hg}_2^{2+}/\text{Hg}_2^{2+}$ (— · —) in water (W), methanol (M), acetonitrile (AN), dimethyl sulfoxide (DMSO), pyridine (Py), *N,N*-dimethylthioformamide (DMFT) and liquid ammonia (NH_3). The standard electrode potentials for the $\text{Ag}^+/\text{Ag(s)}$ couple (---) are given for comparison.

The emfs of the cells $\text{Ag(s)}|\text{Ag}^+(10.0 \text{ mmol dm}^{-3})||\text{M}^{2+}(1\text{--}30 \text{ mmol dm}^{-3})|\text{M(am)}$, $\text{M} = \text{Zn}$ or Cd and where M(am) is equal to Hg(l) for the mercury system, and $\text{Ag(s)}|\text{Ag}^+(10.0 \text{ mmol dm}^{-3})||\text{Hg}_2^{2+}(1\text{--}30 \text{ mmol dm}^{-3})|\text{Pt(s)}$ were determined; the ratio $[\text{Hg}_2^{2+}]/[\text{Hg}_2^{2+}]$ must be less than the value of K_R . The couples studied obeyed Nernst's law with slopes within 1 mV

of the theoretical one. The resistance of the cells was always less than 1 MΩ. The cells were kept at $25.00 \pm 0.02^\circ\text{C}$ by passing thermostatted water through the outer jackets of the Ingold vessels. The emfs were measured by a digital voltmeter, Keithley 197, with an internal resistance of 2 GΩ. The difference in potential between Cd(s) and Cd(am) , 50.5 mV,^{34,35} was corrected for, while there is no potential difference between Zn(s) and Zn(am) .^{34,35}

Results

The experimentally determined electrode potentials of the zinc, cadmium, mercury(I) and mercury(II) couples *vs.* the reference $\text{Ag}^+/\text{Ag(s)}$ electrode in methanol, dimethyl sulfoxide, acetonitrile, pyridine and *N,N*-dimethylthioformamide after extrapolation of all concentrations to 1.00 mol dm^{-3} are summarized in Table 1. The standard electrode potentials of the couple $\text{Ag}^+/\text{Ag(s)}$ in the studied solvents *vs.* the normal hydrogen electrode, NHE, in water have been calculated from the Gibbs energies of transfer of the silver ion.^{14,15} These values and the experimentally obtained differences in electrode potential after extrapolation of all concentrations to 1.00 mol dm^{-3} have been used to calculate the standard electrode potentials of the zinc, cadmium, mercury(II) and mercury(I) couples in the studied solvents *vs.* NHE in water. These standard electrode potentials and the reproporation constants of mercury(I) in the different solvents are summarized in Table 1 and Fig. 1; the values in the very strongly electron-pair-donating solvent liquid ammonia are given for comparison. The Gibbs energies of transfer, $\Delta_t G^\ominus$, of the divalent metal ions studied are calculated from the standard electrode potentials, see Calculations section. The obtained $\Delta_t G^\ominus$ values are summarized in Table 2.

The enthalpies of solution, $\Delta_{\text{sol}} H^\ominus$, determined in this study and those taken from the literature are summarized in Table 3. The enthalpies of transfer for the trifluoromethylsulfonate ion determined previously are also included in Table 3. The enthalpies of transfer of the zinc, cadmium, mercury(II) and mercury(I) ions have been calculated as described in the Calculations section. The obtained enthalpies of transfer of the individual ions are given in Table 2, and the complete transfer thermodynamics of the studied metal ions are summarized in Table 2 and Fig. 2.

The Gibbs energies of transfer, $\Delta_t G^\ominus$, for the zinc, cadmium and mercury(II) ions have been reported previously

Table 2 Transfer thermodynamics, in kJ mol^{-1} , for some divalent metal ions from water to methanol (M), acetonitrile (AN), dimethyl sulfoxide (DMSO), pyridine (Py), *N,N*-dimethylthioformamide (DMTF) and liquid ammonia [$\text{NH}_3(\text{l})$]

	M			AN			DMSO		
	$\Delta_{\text{hyd}} G^\ominus$ ^a	$\Delta_{\text{hyd}} H^\ominus$ ^b	$T\Delta_{\text{hyd}} S^\ominus$	$\Delta_t G^\ominus$	$\Delta_t H^\ominus$	$T_t \Delta S^\ominus$	$\Delta_t G^\ominus$	$\Delta_t H^\ominus$	$T_t \Delta S^\ominus$
Zn^{2+}	−2024	−2063	−39	48.8	−46.8	−95.6	55.3	20.9 ^c	−34.4
Cd^{2+}	−1797	−1831	−34	36.6	−41.6	−78.2	36.4	9.0	−27.4
Hg^{2+}	−1822	−1845	−23	57.7	−23.8	−81.5	47.9	9.7	−38.2
Hg_2^{2+}				56.9	−105.3	−162.2	43.0	−50.9	−93.9
	Py			DMTF			$\text{NH}_3(\text{l})$ ^e		
	$\Delta_t G^\ominus$	$\Delta_t H^\ominus$	$T\Delta_t S^\ominus$	$\Delta_t G^\ominus$	$\Delta_t H^\ominus$	$T\Delta_t S^\ominus$	$\Delta_t G^\ominus$ ^f	$\Delta_t H^\ominus$	$T\Delta_t S^\ominus$
Zn^{2+}	−2.3	−85.6	−83.3	−34.4	−54.3	−19.9	−150		
Cd^{2+}	−13.2	−115.1	−101.9	−114.9	−91.9	+23.0	−154		
Hg^{2+}	−88.2	−158.2 ^a	−70.0	−191.9			−228	−235 ^g	−7
Hg_2^{2+}	−73.0								

^a Ref. 40. ^b Ref. 41. ^c Ref. 22 has reported the value 21.5 kJ mol^{-1} . ^d Ref. 22 has reported the value $−64.3 \text{ kJ mol}^{-1}$. ^e The temperature is $−33^\circ\text{C}$. ^f Ref. 39, the $\Delta_t G^\ominus$ value of proton from water to liquid ammonia has been determined to be $−96 \text{ kJ mol}^{-1}$, ref. 36–38. ^g Ref. 42 gives the value $−160 \text{ kJ mol}^{-1}$. ^h Ref. 2.

Table 3 Enthalpies of solution, $\Delta_{\text{sol}}H^\ominus/\text{kJ mol}^{-1}$, of metal trifluoromethylsulfonates in water (W), methanol (M), acetonitrile (AN), dimethyl sulfoxide (DMSO), pyridine (Py) and *N,N*-dimethylthioformamide (DMTF), and enthalpies of transfer, $\Delta_t H^\ominus$, for the trifluoromethylsulfonate ion from water to the solvents in this study at 25 °C

	W	M	AN	DMSO	Py	DMTF
Zn(CF ₃ SO ₃) ₂	−76.9 ± 0.6				−171.1 ± 1.3	−109.6 ± 1.3
	−79.9 ^a	−116.7 ^a	−54.8 ^a	−139.7 ^a		
Cd(CF ₃ SO ₃) ₂	−58.5 ± 0.3				−182.2 ± 2.1	−128.8 ± 0.7
	−61.3 ^a	−92.9 ^a	−48.1 ^a	−129.7 ^a		
Hg(CF ₃ SO ₃) ₂	−53.4 ± 0.9	−67.2 ± 1.4	−39.5 ± 0.5	−133.2 ± 1.8	−220.2 ± 8.6	
Hg ₂ (CF ₃ SO ₃) ₂	−37.0 ± 1.0	−132.3 ± 0.3	−83.7 ± 1.9	−111.7 ± 8.8		
CF ₃ SO ₃ [−]		+5.0 ^b	+2.1 ^b	+1.8 ^b	−4.3 ^b	10.8 ^b

^a Ref. 21. ^b Ref. 15.

by Gritzner *et al.*,^{6,10} who used the BCr assumption on their polarographic data. These $\Delta_t G^\ominus$ values are in some cases in good agreement with the values obtained in this study, using the TATB assumption, but in other instances large deviations are observed, see Table 4. These large differences do not seem to be caused by the different extrathermodynamic assumptions used.¹⁵

Discussion

The transfer thermodynamic functions of single ions give an overall view of the chemical bonds formed, broken and perturbed in the solvation and dehydration processes of the ion; this also includes the solvent bulk. It must be stressed that the transfer thermodynamics gives the difference between the solvation thermodynamics of an ion in the solvent under study and the reference solvent. It is therefore necessary to have a good knowledge of the properties and the bulk structure of the reference solvent. The choice of water as reference solvent is made because the amount of thermodynamic data in aqueous solution is very large, the properties and the bulk structure of water are well known,⁴³ and water is, indeed, the most commonly used solvent.

Several processes in the solvation of an ion affect the transfer thermodynamic functions. In the hypothetical reaction studied, $M^{2+}(\text{aq}) = M^{2+}(\text{solvent})$, (M^{2+} is a divalent metal ion) M^{2+} –solvent bonds are formed and M^{2+} –water bonds are broken. The bulk structures are affected by the introduction of ions to the solvent under study and the removal of ions from water. Solvent molecules have to be broken out of the bulk structure for the solvation of an ion, and thereby intermolecular forces between solvent molecules are broken. The more rigid the bulk structure, the more energy is required to break out a solvent molecule for solvation. Furthermore, fairly bulky solvated ions may not fit well into the bulk structure and will therefore affect the intermolecular solvent-solvent interactions close to it. For solvents with a pronounced bulk structure such as the protic solvents with intermolecular hydrogen bonds, and the sulfur donor solvents which seem to have intermolecular sulfur–sulfur inter-

actions,⁴⁴ the change in bulk structure affects the solvation thermodynamics and thereby also substantially affects the transfer thermodynamics.⁴⁵ The transfer thermodynamics of a single ion from water to another solvent do therefore include, as main contributions, the formation of new ion–solvate bonds, the break-up of the ion–hydrate bonds, the removal of solvent molecules from the bulk structure for the solvation and the effect of the bulk structure on the solvated ion.¹⁵ Exit of the ion from an aqueous solution makes the aqueous bulk structure returns to its basic unaffected state.

Methanol

Methanol is a protic solvent with physical and chemical properties close to those of water and it is considered to be a hard electron-pair donor. Methanol forms weaker hydrogen bonds than water, and only the hydrogen on the oxygen atom can participate in hydrogen bonding. This means that the methanol bulk structure is considerably less rigid than the aqueous one.⁴⁶ The electron-pair donor ability of methanol, $D_s = 18$, is almost the same as for water, $D_s = 17$.⁴⁷ The transfer thermodynamic functions show that the transfer of the zinc, cadmium, mercury(II) and mercury(I) ions from water to methanol is very unfavourable even though the process is markedly exothermic. This means that the entropy term of this process is very unfavourable, see Table 2. It can be assumed that the bond strength and energy in the metal ion–hydrate and –methanol solvate bonds as well as the bonding characteristics are similar.⁴⁷ The transfer thermodynamics observed are therefore very dependent on the extent to which the bulk structures are affected by the introduction of an ion, in this case a divalent metal ion. On the introduction of a metal ion, solvent molecules are broken out of the bulk structure for the solvation. The internal bulk structures are certainly affected when the fairly large solvated metal ion is fitted in. These processes are both endothermic, and the absolute value increases with increasing strength of the intermolecular forces and the degree of order of the bulk structure. This means that the aqueous bulk structure is energetically more affected by the introduction of an ion than the methanol bulk. The process studied with a metal ion leaving

Table 4 A comparison of the $\Delta_t G^\ominus$ values from acetonitrile (AN) to methanol (M), dimethyl sulfoxide (DMSO), pyridine (Py) and *N,N*-dimethylthioformamide (DMTF) obtained by the TATB and BCr extrathermodynamic assumptions

	M		DMSO		Py		DMTF	
	TATB	BCr	TATB	BCr	TATB	BCr	TATB	BCr
Ag ⁺	+29.7 ^a	+29.5 ^b	−11.9 ^a	−6.9 ^b	−34.8 ^a	−40.4 ^c	−78.4 ^d	−74.2 ^b
Zn ²⁺	−6.5		−104.2	−91.4 ^c	−57.6	−80.9 ^c	−89.7	−66.9 ^e
Cd ²⁺	+0.2	+34.9 ^e	−94.6	−85.2 ^c	−49.6	−83.0 ^e	−151.3	−78.6 ^e
Hg ²⁺	+9.8		−116.8	−60.6 ^b	−136.1	−106.7 ^c	−239.8	−161.2 ^b
Hg ₂ ²⁺	+13.9		−107.4		−116.0			

^a Ref. 15. ^b Ref. 8. ^c Ref. 6. ^d Ref. 15. ^e Ref. 10.

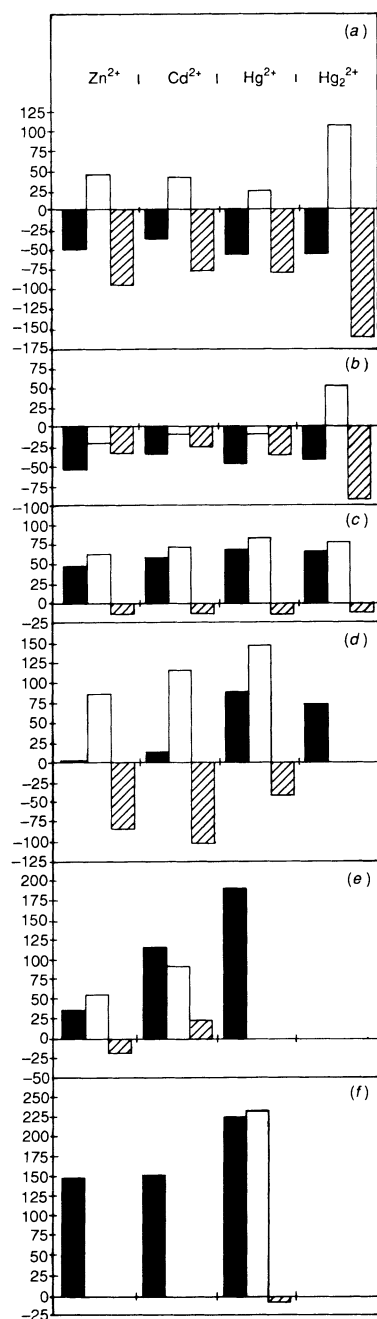


Fig. 2 The changes of Gibbs energy, $-\Delta_i G^\ominus$, (black), enthalpy, $-\Delta_i H^\ominus$, (white) and entropy, $T\Delta_i S^\ominus$, (hatched) in kJ mol^{-1} for the transfer of the zinc, cadmium, mercury(II) and mercury(I) ions from water to (a) methanol, (b) acetonitrile, (c) dimethyl sulfoxide, (d) pyridine and (e) *N,N*-dimethylthioformamide at 25°C and (f) to liquid ammonia at -33°C

an aqueous solution for a methanol solution is therefore expected to be significantly exothermic and the entropy of transfer to be markedly negative. The very large mercury(I) ion seems to affect the bulk structures substantially more than the other ions in this study, see Table 2.

The transfer thermodynamic functions from water to methanol of the alkali-metal ions display the same trends as the metal ions in this study, even though the absolute values for the alkali-metal ions are smaller than for the divalent ions in this study. This implies that the introduction of divalent ions affects the solvent bulk structure more than monovalent ions do. This is expected as the metal ions in this study are assumed to have a second solvation sphere, the number of

solvent molecules broken out of the bulk structure for solvation is possibly two or three times as many as that for the alkali-metal ions and the larger the ion is the more it will perturb the bulk structure.

Acetonitrile

Acetonitrile is an aprotic nitrogen donor solvent with weak and soft electron-pair donor properties.⁴⁸ Previous studies have shown that acetonitrile solvates the monovalent coinage metal ions particularly well,^{24,26} while the hard alkali-metal ions are weakly solvated in acetonitrile.^{5,14,15} The transfer thermodynamic pattern for the metal ions in this study to acetonitrile is close to that of methanol, even though the enthalpies and entropies of transfer to acetonitrile are markedly more positive than to methanol. It can be assumed that the acetonitrile molecules solvating the metal ions are less ordered than the corresponding water and methanol molecules because of the weaker solvate bonds. This can partly explain the more positive entropies of transfer to acetonitrile. However, an acetonitrile solution has probably about the same degree of total order as a methanol solution. This is maybe somewhat surprising since there is no hydrogen bonding in acetonitrile. However, spectroscopic and structural studies have indicated that acetonitrile can form dimers or larger aggregates,^{49,50} and that acetonitrile indeed has a fairly high degree of internal bulk order. The results in this study show that acetonitrile does not solvate soft divalent d^{10} metal ions, such as mercury(II), significantly more strongly than other divalent metal ions. This is supported by a solvation thermodynamic study of the mercury(II) halides, which showed that mercury(II) is weakly solvated by acetonitrile.⁵¹ It is of interest to note that the significant difference in the entropies of transfer to methanol and acetonitrile found for the metal ions in this study is not observed for the monovalent cations. The reason for this difference is not obvious.

Dimethyl sulfoxide

Dimethyl sulfoxide is an aprotic solvent with the possibility to coordinate either through its oxygen or sulphur atom. The ions under study all coordinate dimethyl sulfoxide through its oxygen atom as shown by spectroscopic and structural investigations.^{52,53} The dimethyl sulfoxide solvates and hydrates of the zinc, cadmium and mercury(II) ions are all octahedral.^{52,54,55}

Previous transfer thermodynamic studies have shown that dimethyl sulfoxide donating through its oxygen atom solvates both hard and soft cations (electron-pair acceptors) more strongly than does water.¹⁴⁻¹⁷ A vibration spectroscopic study has shown that the metal ion-dimethyl sulfoxide interactions of the metal ions in this study are stronger than the metal ion-water ones.⁵² The enthalpies of transfer are strongly exothermic and the entropies of transfer have small negative values, see Table 2. These small and negative entropies of transfer indicate that dimethyl sulfoxide has a pronounced bulk structure. Structural investigations on dimethyl sulfoxide solutions always reveal two very intense peaks at about 5.5 and 10 Å in the radial distribution function that correspond to intermolecular distances within the solvent bulk.^{52,56} It is, however, not fully understood how this bulk structure is built up. The large exothermic enthalpies of transfer indicate that solvate bonds do have a higher degree of covalency than the hydrate bonds. The transfer thermodynamic functions of the mercury(I) ion are similar to the other ions in this study. These also show that mercury(I) is more strongly solvated in dimethyl sulfoxide than hydrated in aqueous solution, even though mercury(I) is less stable in

comparison to mercury(II) in dimethyl sulfoxide than in water as shown by the disproportionation constants of mercury(I) in these solvents,²⁵ see Table 1.

Pyridine

Pyridine is an aprotic solvent donating through its nitrogen atom. The electron donating properties of the nitrogen donor solvents in this study, acetonitrile and pyridine, are indeed very different. Pyridine has strong electron-pair donor properties and it is regarded as a typical soft donor solvent with a fairly high D_s value of 38.⁴⁷ The zinc and cadmium ions are regarded as borderline acceptors which are only slightly more strongly solvated in pyridine than in water, while the soft mercury(II) ion is much more strongly solvated in pyridine than in water, see Table 2. All enthalpies of transfer are very exothermic indicating that the pyridine solvate bonds have a fairly high degree of covalency. The entropies of transfer are all very negative showing that the total order for the transfer of metal ions from an aqueous to a pyridine solution increases significantly. The pyridine-solvated mercury(II) ion is octahedral with a small second-order Jahn–Teller distortion in the solid state,⁵⁷ and most probably also in pyridine solution. In air this solvate easily loses four pyridines to form a very stable disolvate.⁵⁸ The solid pyridine solvates of zinc and cadmium also contain six pyridines per metal ion.⁵⁸ These solvates are certainly octahedral in both pyridine solution and in the solid state. Pyridine is without doubt the solvent in this study with the lowest degree of bulk order. Pyridine has furthermore a low relative permittivity, $\epsilon = 12.3$, which shows that bulk pyridine has low ability to reduce long-range coulombic interactions. In order to reduce the electric field around the ions as effectively as possible the dipoles of the pyridine molecules in a fairly large volume will be oriented towards the ion. This means that more pyridine molecules than those in the inner coordination sphere(s) to the metal ion will be electrostatically ordered around the ion. This effect increases, of course, with increasing charge density of the ion and decreasing relative permittivity of the solvent. A recently performed large angle X-ray scattering study on a pyridine solution of lead(II) trifluoromethylsulfonate shows two large peaks at 5.5 and 10 Å in the radial distribution function indicating a higher degree of order in this pyridine solution⁵⁹ than in pyridine solutions of uncharged and monovalent species where these peaks are much less intense.^{60–62} This observation supports the view that the introduction of a divalent ion with a higher charge density than the anions and monovalent cations to pyridine increases its bulk order substantially. It is not possible to determine the enthalpy of transfer for mercury(I) in pyridine as mercury(I) salts partly disproportionate at dissolution in pyridine.²⁵

N,N-Dimethylthioformamide

N,N-dimethylthioformamide is a sulfur donor solvent with a high relative permittivity implying that the solubility and the degree of dissociation of many salts is very high in this solvent. *N,N*-Dimethylthioformamide has pronounced soft electron-pair donor properties, $D_s = 52$,⁴⁷ and it will therefore solvate soft electron-pair acceptors, such as mercury(II) very well. Mercury(I) cannot be studied as it disproportionates completely into metallic mercury and mercury(II) in *N,N*-dimethylthioformamide. The zinc, cadmium and mercury(II) ions are all more strongly solvated in *N,N*-dimethylthioformamide than in water, and the strength of the solvation increases markedly with increasing softness of metal ion, associated with increasingly exothermic enthalpies

of transfer, see Table 2. The entropy of transfer is slightly negative for zinc while it is slightly positive for cadmium. One reason for this somewhat unexpected pattern may be that the hydrated zinc and cadmium ions are octahedral in aqueous solution,⁵² while the *N,N*-dimethylthioformamide-solvated zinc and cadmium ions are tetrahedral and octahedral, respectively.⁶³ The soft donor solvents, *N,N*-dimethylthioformamide and pyridine, discriminate between hard and soft electron-pair acceptors, and both pyridine and *N,N*-dimethylthioformamide solvate typical soft electron-pair acceptors very strongly, while typical hard metal ions such as sodium and potassium are weakly solvated in these solvents.¹⁵ The relatively small entropies of transfer strongly indicate that *N,N*-dimethylthioformamide has a fairly high degree of bulk order. Large-angle X-ray scattering studies on *N,N*-dimethylthioformamide solutions have indicated intermolecular sulfur–sulfur interactions at about 3.1 Å, which supports the view that *N,N*-dimethylthioformamide has a significant bulk structure.^{59,63} A vibration spectroscopic study of *N,N*-dimethylthioformamide-solvated mercury(II) halide complexes has shown that *N,N*-dimethylthioformamide is much more strongly coordinated to mercury in the solid state than in *N,N*-dimethylthioformamide solution,⁶⁴ indicating that in *N,N*-dimethylthioformamide solution the *N,N*-dimethylthioformamide molecules coordinated to mercury are also interacting with bulk solvent molecules. This weakens the interaction towards mercury, while in the solid state, where no such intermolecular *N,N*-dimethylthioformamide interactions are present, the *N,N*-dimethylthioformamide molecules exhibit a stronger electron-pair donor ability. This observation also indicates that *N,N*-dimethylthioformamide has a pronounced bulk structure and has previously also been found for the same systems in tetrahydrothiophene.⁶⁵

Liquid ammonia

Liquid ammonia is a protic solvent with very strong electron-pair donating properties.⁴⁷ Liquid ammonia solvates the zinc, cadmium and mercury(II) ions more strongly than any other solvent reported so far.^{4,5,14,15,66} Liquid ammonia seems to have an ability to solvate very soft metal ions like mercury(II) very well, $\Delta_r G^\ominus$ is about 35 kJ mol^{−1} more exergonic to liquid ammonia than to *N,N*-dimethylthioformamide, and typical hard acceptors such as the alkali-metal ions are equally well solvated in liquid ammonia and dimethyl sulfoxide.¹⁵ The zinc and cadmium ions are much more strongly solvated in liquid ammonia than in any other solvent reported, see Table 2 and ref. 1 and 2.

Conclusions

The solvation of an ion is, evidently, not only dependent on the characteristics of the formed ion–solvate bonds, but also on the bulk order and the strength of the intermolecular forces between the solvent molecules in the bulk. The present transfer thermodynamic data as well as those determined previously^{14,15} show very clearly that the Gibbs energies and the enthalpies of transfer counter balance each other in such a way that the entropies of transfer are surprisingly similar in each solvent. This shows that the bulk order properties of the solvent influence its solvation properties to a large extent. The solvent bulk order generally decreases on introduction of an ion into solvents with a well ordered bulk structure, *e.g.* protic solvents and sulfur donor solvents. Solvent molecules are forced out of the internal bulk structure for solvation and the solvated ions disturb the bulk structure as they are fairly large and do not fit into the cavities offered. The solvent order may, on the other hand, increase on introduction of an

ion into solvents with low bulk order and low relative permittivity as *e.g.* pyridine. The solvent molecules are then electrostatically ordered around the ions and the total bulk order increases. The pronounced soft donor solvents *N,N*-dimethylthioformamide and pyridine solvate soft metal ions very strongly and discriminate very significantly between soft and hard metal ions.

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