Pure & Appl. Chem., Vol. 60, No. 12, pp. 1743–1756, 1988.
Printed in Great Britain.

Recent aspects of single ion transfer properties

Gerhard Gritzner

Institut für Chemische Technologie Anorganischer Stoffe,
Johannes Kepler Universität, A-4040 Linz, Austria

Abstract - Gibbs energies, entropies and enthalpies of transfer for several cations and anions from acetonitrile into various solvents formed the basis for investigations on general trends in the interactions of solvent molecules with positively and negatively charged ions. Gibbs energies of transfer for Na^+, K^+, Rb^+, Cs^+, Cu^+, Tl^+ and Ag^+ obtained from different assumptions, experimental techniques and research groups together with a large number of recently published Gibbs energies of transfer for Li^+, Ba^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} based on the bis(biphenyl)chromium assumption - were employed to study the interactions of hard and soft donor solvents with hard, soft and borderline cations. Solvent effects on anions were deduced from the Gibbs energies of transfer for Cl^-, Br^-, I^- and SCN^-. Parameters proposed to account for hard and soft donor properties or for acceptor properties of the solvents were compared with the Gibbs energies of transfer. Parameters representing hard donor properties of solvents correlated with Gibbs energies of transfers for cations into hard solvents, but transfer properties of soft and borderline cations into soft solvents called for a different solvent parameter. The Gibbs energies of transfer for anions related to such solvent parameters that characterized acceptor properties. The solvent induced changes in the Gibbs energies of transfer of hard and soft cations as well as the respective data for anions were explained within the framework of a donor-acceptor model of ion-solvent interactions, including the principle of hard and soft acids and bases. The current status on enthalpies and entropies of transfer is discussed.

INTRODUCTION

Single ion transfer properties such as Gibbs energies, entropies and enthalpies of transfer are studied to obtain information on the changes in the interactions that cations and anions experience in different solvents. Single ion transfer properties are based on a reference state in solution, since Gibbs energies, enthalpies and entropies from a reference solvent into other solvents reflect the solvent induced changes much better than the Gibbs energies or enthalpies of solvation. Strictly thermodynamic measurements, however, yield such properties only for the transfer of electrolytes or molecules. Any separation of the experimental data for the interactions of the solvent molecules with salts into the respective contributions for the solvent-cation and the solvent-anion interactions must therefor employ a model and necessitates at least one extrathermodynamic assumption. Transfer properties of single ions are, as any single ion property, outside of the realm of strict thermodynamics. Despite their extrathermodynamic nature, single ion transfer properties, especially Gibbs energies of transfer have been successfully applied to correlate a large amount of seemingly unrelated data in solution chemistry. Single ion transfer properties have been employed to predict solubilities and to account for solvent induced changes in spectroscopic and redox properties. Gibbs energies of transfer for single ions were also found helpful in the understanding of solvent effects on reaction rates (ref. 1,2).

Several extrathermodynamic assumptions were proposed to calculate single ion transfer properties. They were extensively reviewed by Popovych (ref. 3), Parker and Alexander (ref. 4), Cox and Parker (ref. 5) and recently by Marcus

(ref. 6). These reviews allow a restriction to those assumptions and their underlying concepts and to the experimental techniques that formed the basis for the data on which the discussion in this article is based.
The Gibbs energies of transfer used were derived from the following three types of assumptions: (i) the reference electrolyte assumption, (ii) the assumption of a solvent independent reference redox system and (iii) the assumption of a negligible liquid junction potential.

The reference electrolyte assumption can be traced back to Born (ref. 7), who suggested that the Gibbs energies of solvation of potassium fluoride can be equally divided into the contributions of the K^+ and the F^- ions. This concept was expanded by Grunwald, Baughman and Kohnstam (ref. 8) proposing tetraphenylphosphonium tetraphenylborate, by Popovych, who suggested tris(isoamyl)butylammonium tetraphenylborate (ref. 9) and later by Arnett and McKelvey (ref. 10) and by Alexander and Parker (ref. 4, 11) recommending tetraphenylarsonium tetraphenylborate as the reference electrolyte. The assumption that the transfer properties of a 1:1 electrolyte consisting of a large symmetrical cation and a large symmetrical anion, both of similar size, can be equally assigned to the cation and the anion is generally backed up by the argument that the Born contributions of ion-solvent interactions for both cations and anions are a function of the reciprocal of the ionic radius, but independent of the charge of the ion. There is, however, no proof that the interactions of a cation and an anion of the same ionic radius with solvent molecules are equal. Actually, data presented in this paper do not support such a model. Experimental data for this assumption are obtained from solubility measurements. In such studies it is generally assumed, but not always examined that equilibrium was established between the solid and the liquid phase that no solvates were formed in the solid phase and that complete dissociation of the electrolyte prevailed in solution. Low solubilities are subject to considerable experimental error, large solubilities require some correction for ion-ion interactions.

The reference redox system as an extrathermodynamic assumption goes back to the search for a solvent independent redox system to establish a so-called universal scale of standard potentials. Pleskov's original proposal to employ the system $Rb^+/Rb(Hg)$ as such a system (ref. 12) was considerably improved by Koepp, Wendt and Strehlow (ref. 13), when they proposed the redox couples ferrocene/ferrocenium ion and cobaltocene/cobaltocenium ion. Other solvent independent redox systems were proposed later on (ref. 14), but besides ferrocene only bis(biphenyl)chromium(I)/(0) (ref. 15) was widely used. From emf measurements versus such reference redox systems one can obtain Gibbs energies of transfer from the well known relation $\Delta G_t^\circ = n F (E^\circ_S - E^\circ_{RS})$, where ΔG_t° is the Gibbs energy of transfer, E°_S is the standard electrode potential in the respective solvent and E°_{RS} the standard electrode potential in the reference solvent. Both electrode potentials should be measured versus the reference redox system in cells without liquid junction potentials. The arguments for the redox couples ferrocene/ferrocenium ion and bis(biphenyl)chromium(I)/(0) as solvent independent redox systems claim similar interactions of the solvent molecules with the oxidized and the reduced form of these redox couples. The differences of the interactions with the two forms of the redox system are assumed to be small and in the order of the experimental error of the measurements. In the case of bis(biphenyl)chromium, it was argued that the chromium atom is imbedded between the phenyl rings and that the solvent molecules will interact only with the phenyl rings of bis(biphenyl)chromium(0). In the oxidized form one can expect the positive charge to be delocalized over the four rings, again leading mainly to interactions of the solvent molecules with the phenyl rings (ref. 16). Most of the data were derived from polarographic and cyclovoltammetric measurements, with both the redox couple under investigation and the reference redox system being in the same electrolyte. In calculating Gibbs energies of transfer from polarographic data, it is assumed that the half-wave potentials of reversible or nearly reversible electrode processes are a good approximation for the standard electrode potentials and that any effects by the supporting electrolyte on the half-wave potentials of the ions studied are compensated by similar effects on the reference redox system.

The assumption that the liquid junction potential between two organic electrolyte solutions can be suppressed by a 0.1 mol dm^{-3} solution of tetraethylammonium picrate in either one of the nonaqueous solvents as suggested by Parker and Alexander (ref. 4) is the equivalent of KCl bridges used in aqueous systems (ref. 17). This assumption was employed by Parker and

coworkers in connection with the tetraphenylarsonium tetraphenylborate assumption and with nonaqueous bridge electrolytes (ref. 4,18,19). Unfortunately this assumption was later on rather indiscriminately used also with aqueous reference electrodes. Data are obtained from potentiometric measurements. The major concern about this assumption is that liquid junction potentials in general depend on the design of the junction and are thus not necessarily reproducible. Another worrisome point about this assumption is the dependence of the liquid junction potentials on the choice of the solvent used for the bridge electrolyte (ref. 20). Data obtained from the assumption of a negligible liquid junction potential therefor need confirmation by some other unrelated methods of obtaining Gibbs energies of transfer.

The enthalpies and entropies of transfer treated in this context were obtained from the tetraphenylarsonium tetraphenylborate assumption. Enthalpies of transfer obtained from calorimetric measurements for tetraphenylarsonium tetraphenylborate are equally divided into the anion and cation contributions of the reference electrolyte (ref. 10, 18). Entropies of transfer for single ions could also be derived from the temperature dependence of the Gibbs energies of transfer. Such data are accessible from the changes in electrode potentials measured versus a reference redox system in cells without transfer assuming that the electrode potentials of the reference redox system are independent of temperature. Unfortunately there are practically no data available from this approach. Comparisons of enthalpies of transfer derived from different experimental techniques based on different assumptions are therefor not really possible at this time.

As mentioned earlier transfer properties are referred to a reference solvent, in which the Gibbs energies, enthalpies and entropies of all ions are considered to be zero. The use of a reference solvent reflects much better the small energy changes due to ion-solvent interactions compared to the large changes in Gibbs energies or enthalpies connected with the transfer from the gaseous state into any condensed state.

Several reference solvents, such as methanol (ref. 19-21), acetonitrile (ref. 19, 22-26), N,N-dimethylformamide (ref. 1, 26-28) and water (ref. 18, 32-36) were used. There are arguments for and against each of these reference solvents. Recently water was strongly propagated as the "best" reference solvent based on the large amount of data available for aqueous solutions in general and on the importance of water in chemistry and biophysics (ref. 37, 38). Unfortunately, however, several of the reference substances used to obtain single ion transfer properties cannot be used in water. The redox potential of ferrocene in water is ambiguous; bis(biphenyl)chromium(0) is practically insoluble in this solvent (ref. 39). Conversion of data obtained from these assumptions to water as a reference solvent requires the subsequent application of two extrathermodynamic assumptions adding to the uncertainty of such data. The solubility product of tetraphenylarsonium tetraphenylborate is very small and thus difficult to measure (ref. 40-43). Furthermore water is a highly structured solvent. In view of these facts, it seems appropriate to choose a less structured solvent as a reference solvent, in which all reference substances can be easily measured. Acetonitrile and N,N-dimethylformamide are two such solvents. Acetonitrile was chosen in this paper and the following discussion concerns itself with Gibbs energies, entropies and enthalpies of transfer from this reference solvent into other pure solvents.

GIBBS ENERGIES OF TRANSFER

There are more data available for Gibbs energies of transfer than for the other transfer properties of single ions. Gibbs energies of transfer, derived from a variety of different assumptions employing different experimental techniques and reference solvents, are available from the literature. Some of the published data, however, were based on assumptions that did not receive wide acceptence and not all of the experiments, which lead to such data, were carried out in a reliable manner. Thus there is a considerable scatter in the published data (ref. 37). Values for Gibbs energies of transfer for a given ion and a given solvent can vary by as much as 20 kJ mol^{-1} and more (ref. 37). Such a variation in the values comes close to the changes observed for the transfer of the alkali metal ions for the solvents studied. Thus any evaluation of general principles in ion-solvent interactions cannot use all of the published data indiscriminately. In a recent attempt to derive at one single set for Gibbs energies, enthalpies and entropies of transfer,

preference was given to the tetraphenylarsonium tetraphenylborate assumption and to water as the reference solvent. Data from several other assumption were adjusted to the tetraphenylarsonium assumption by adding a constant to the values for the cations and substracting it from the anions. These constants depended on both the assumptions used and on the research groups. "Weighted" means of such adjusted values lead to a "selected" data set (ref. 37). Such a data set, mainly centered around one assumption, indeed provides single scales for Gibbs energies, entropies and enthalpies of transfer, but does not necessarily lead to reliable data, since experimental errors are not detected by a somewhat arbitrary "weighing" procedure. Furthermore one must keep in mind that due to the extrathermodynamic procedures involved in obtaining the data, "true" values for single ion properties are not accessible. Thus values for single ion transfer properties given to one tenth of a kJ mol^{-1} are at best an expression of the precission of the experimental techniques employed and should not be mistaken for the accuracy of such data. Rather then using these "selected" data the following approach is being used to shed light on general solvent-induced trends on the transfer properties of cations and anions: Gibbs energies of transfer derived from the tetraphenylarsonium tetraphenylborate assumption and the assumption of a negligible liquid junction potential by Parker and coworkers (ref. 1,18) and recently published values by Johnsson and Persson (ref. 32,33) were converted to acetonitrile as the reference solvent. These data are summarized in Tables 1 and 2 together with enthalpies of transfer from acetonitrile based on the tetraphenylarsonium tetraphenylborate assumption. Gibbs energies of transfer for cations as reported from these research groups can now be compared with the values for cations obtained from the bis(biphenyl)chromium assumption. The agreement between the data from these assumptions is quite good, the values are generally within 6 kJ mol^{-1}. This agreement must be considered very satisfactory considering both the different experimental techniques used and the extrathermodynamic nature of the assumptions. Fig. 1 exemplifies the agreement on hand of the Gibbs energies of transfer for Ag^+. The theoretical slope of one for this correlation is within the error limits of the calculated slope. There are, however, also a few notable discrepancies in the data given in Table 1. The values in tetramethylene sulfone, pyridine and tetrahydrothiophene differ by more than 10 kJ mol^{-1}, as do the values for Ag^+, Rb^+ and Cs^+ in propylene carbonate and for Ag^+ in formamide. These discrepancies call for remeasuring of the respective data points.

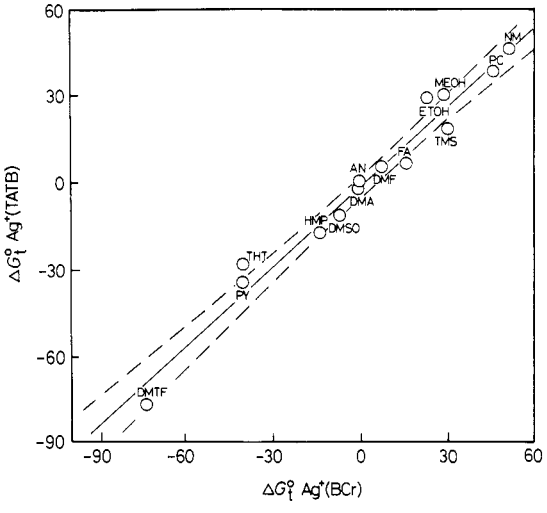

Fig. 1. Molar Gibbs energies of transfer of Ag^+ derived from the tetraphenylarsonium tetraphenylborate assumption ($\Delta \underline{G}_t^\circ$ Ag^+ (TATB)) and from the bis(biphenyl)chromium assumption ($\Delta \underline{G}_t^\circ$ Ag^+(BCr)). Reference solvent: acetonitrile. Abbreviations. AC: acetone, AM: ammonia, BF: benzoylfluoride, BL: butyrolactons, BN: benzonitrile, DEA: diethylacetamide, DEF: diethylformamide, DMA: dimethylacetamide,DMF: dimethylformamide, DMSO: dimethylsulfoxide, DMTF:dimethylthioformamide, ES: ethylene sulfite, ETDI: ethanediol, ETOH: ethanol, FA: formamide, HMP: hexamethylphosphoric triamide, HMTP: hexamethylthiophosphoric triamide, IBUN: isobutyronitrile, MEOH: methanol, NB: nitrobenzene, NM: nitromethane, NMF: N-methylformamide, NMP: N-methyl-2-pyrrolidinone, NMTP: N-methyl-2-thiopyrrolidinone, PAN: phenylacetonitrile, PC: propylene carbonate, PRN: propanenitrile, PY: pyridine, TDE: 2,2'-thiodiethanol, TFE: trifluoroethanol, THF: tetrahydrofurane, THT: tetrahydrothiophene, TMP: trimethyl phosphate, TMS: tetramethylene sulfone, TMU: tetramethylurea, W: water.

Since it is impossible to validate any assumption experimentally or theoretically we will never know, which assumption is best. Our confidence in published values for single ion transfer properties, however, will become greater, when studies based on different experimental techniques and employing different assumptions lead to similar values.

TABLE 1. Molar Gibbs energies of transfer in kJ mol^{-1} for several cations based on the tetraphenylarsonium tetraphenylborate assumption (first line)[a] and on the bis(biphenyl)chromium assumption (second line) as well as enthalpies of transfer (third line)[a] from acetonitrile as reference solvent at 25 °C.

Solvents	Na^+	K^+	Rb^+	Cs^+	Cu^+	Ag^+	Tl^+
Acetone	*	*	*	*	*	30	*
	-10	-6	-7	-6	56	28	-7
	*	*	*	*	*	*	*
Ammonia	-32	-21	-19	-21	-57	-78	*
	*	*	*	*	*	*	*
	-23	-2	0	*	*	-65	*
Acetonitrile	0	0	0	0	0	0	0
	0	0	0	0	0	0	0
	0	0	0	0	0	0b	0
N,N-Dimethyl-	*	-23	*	*	*	-3	*
acetamide	-25	-18	-12	-13	*	-1	-21
	*	*	*	*	*	*	*
N,N-Dimethyl-	-24	-18	-17	-14	*	5	-20
formamide	-22	-14	-13	-12	*	8	-21
	-20	-16	-15	*	*	14	*
Dimethyl	-28	-20	-18	-18	10	-12	-30
sulfoxide	-24	-17	-14	-15	15	-7	-29
	-15	-12	-10	*	30	-10	*
N,N-Dimethyl-	26	17	*	9	-55	-78	-25
thioformamide	21	20	14	6	-50	-74	-30
	*	*	*	*	*	*	*
Ethanol	*	10	*	*	*	29	*
	-5	4	4	3	*	24	-3
	*	*	*	*	*	*	*
Formamide	-22	-14	-12	-12	*	6	*
	*	*	*	*	27	17	-10
	-3	6	6	*	*	30	*
Hexamethylphos-	*	-25	*	*	*	-18	*
phoric triamide	-39	-19	-16	-14	*	-13	-34
	*	-35	*	*	*	*	*
Hexamethylthio-	*	*	*	*	*	*	*
phosphoric	30	*	*	*	-23	-57	-16
triamide	*	*	*	*	*	*	*
Methanol	-6	2	3	4	*	30	-5
	-10	-2	-1	1	*	30	-6
	-7	4	8	*	*	21	*
Nitromethane	*	15	*	*	*	46	*
	*	*	*	*	*	52	9
	*	*	*	*	*	*	*
N-Methyl-	*	*	*	*	*	7	*
formamide	-20	-11	-11	-8	*	9	-19
	*	*	*	*	*	*	*
N-Methyl-2-	-30	-22	-17	*	*	-2	*
pyrrolidinone	-34	-16	-14	-14	*	0	-25
	-26	-21	*	*	*	*	*
Propylene	1	-2	-10	-17	*	38	-1
carbonate	5	3	-1	-1	*	47	3
	6	2	0	*	*	40	*
Pyridine	1	-3	6	25	-30	-35	-11
	8[c]	-1[c]	-1[c]	-1[c]	-43[c]	-40[c]	-23[c]
	-17	0	-3	*	-55	-65	*
Tetrahydro-	19	*	*	*	22	-29	-2
thiophene	*	*	*	*	-31	-40	-12
	-12	*	*	*	-19	-55	*
Tetramethylene	-17	-12	-16	-15	*	18	*
sulfone	-3	-3	-4	-4	*	31	-7
	-2	-3	-4	*	*	39	*
2,2,2-Tri-	*	30	*	*	*	71	*
fluoroethanol	*	*	*	*	*	*	*
	*	*	*	*	*	*	*
Water	-14	-8	-7	-5	52	22	-9
	*	*	*	*	*	*	*
	13	23	24	*	72	41	*

[a]Ref. 1,18,32,33 [b]based on Ref. 33 [c]S.Sperker private communication

Gibbs energies of transfer of cations

The amount of data available for Gibbs energies of transfer of cations based on the bis(biphenyl)chromium assumption is much greater than for the tetraphenylarsonium tetraphenylborate assumption or any other assumption. Besides the values given in Table 1 there are data now available for Li^+, Na^+, K^+, Rb^+, Cs^+, Ba^{2+}, Cu^+, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Tl^+ and Pb^{2+} in up to 38 nonaqueous solvents (ref. 22-24, 26-30). The data set based on the bis(biphenyl)chromium assumption will therefor be used to search for general principles governing the interactions of solvent molecules with cations. The observation obtained from such investigations, however, agree with those obtained for the more limited number of Gibbs energies of transfer from the tetraphenylarsonium tetraphenylborate assumption.

Any evaluation of solvent effects on Gibbs energies of transfer of cations must first examine whether the interactions of solvents with all cations for which data are available are of the same general nature. To answer this question the Gibbs energies of transfer of the cations studied were plotted versus the Gibbs energies of transfer of the Na^+. A similar procedure was employed previously with a considerably smaller data base using the Gibbs energies of K^+ (ref. 31). The data for Na^+ were preferred here since there are more values - especially in soft solvents - available for Na^+ than for K^+. Such plots showed a linear relation between the values for Li^+, K^+, Rb^+, Cs^+, Ba^{2+} and Na^+ for all of the solvents studied (Fig. 2). A plot of Gibbs energies of transfer for Ag^+ versus the Gibbs energies of Na^+, however, clearly indicates the formation of two groups of solvents.(Fig. 3) The data for solvents, which donate via an oxygen atom in the molecule form one line. The values for nitriles, pyridine and the sulfur donor solvents, tetrahydrothiophene, hexamethylthiophosphoric triamide, N-methyl-2-thiopyrrolidinone and N,N-dimethylthioformamide clearly deviate from the line. Such a plot immediately brings to mind Pearsons's principle of hard and soft acids and bases (ref. 44) and its precursor, the division of cations into class(a) and class(b) cations by Ahrland, Chatt and Davies (ref. 45). The Ag^+-ion being a soft acceptor (soft-acid) or class(b) cation is capable of undergoing strong soft-soft interactions with the nitriles, pyridine and the solvents, which donate via the soft sulfur atom in the molecule. Dimethylsulfoxide, which was found to interact as a soft donor solvent in complexes with Pd^{2+}, Pt^{2+}, Ru^{3+} and Rh^{3+} (ref. 46,47) definitely acts as a hard donor solvent towards Ag^+. A similar plot with data from the tetraphenylarsonium tetraphenylborate assumption gives the same results, with water being on and ammonia being off the line for hard solvents.

Besides Ag^+, Cu^+ and Hg^{2+} are generally considered to be soft acceptors. Not surprisingly Cu^+ is the stable form in soft donor solvents and Cu^{2+} salts react in sulfur-donor solvents with solvent oxidation forming Cu^+. Data for

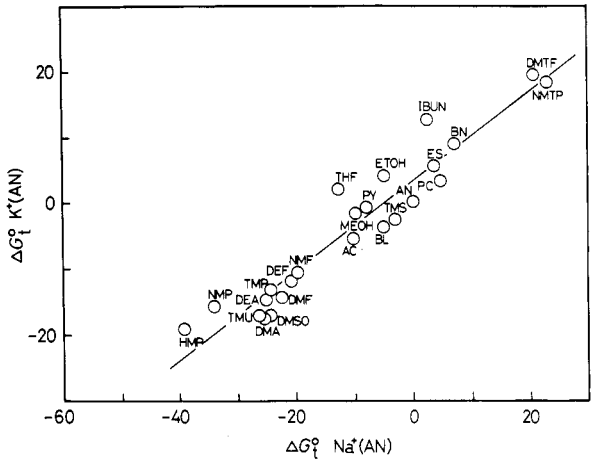

Fig. 2. Molar Gibbs energies of transfer of K^+ (ΔG_t° K^+ (AN)) versus molar Gibbs energies of transfer of Na^+ (ΔG_t° Na^+ (AN)) based on the bis(biphenyl)chromium assumption. Reference solvent: acetonitrile. Abbreviations for solvents are given in Fig. 1.

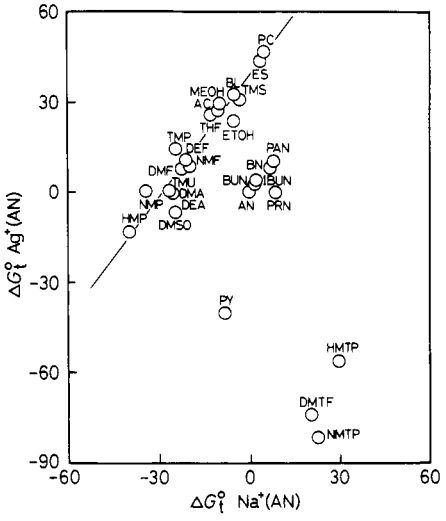

Fig. 3. Molar Gibbs energies of transfer of Ag^+ (ΔG_t° Ag^+ (AN)) versus molar Gibbs energies of Na^+ (ΔG_t° Na^+ (AN)) based on the bis(biphenyl)chromium assumption. Reference solvent: acetonitrile. Abbreviations of solvents are given in Fig. 1.

Cu^+ in hard solvents are scarce, since Cu^{2+} is the stable oxidation state in hard solvents. As observed for Ag^+ there is a linear relation between the Gibbs energies of transfer for Hg^{2+} and Na^+ in hard solvents. The data in nitriles deviate only slightly from this correlation, the values in N-methyl-2-thiopyrrolidinone, N,N-dimethylthioformamide, hexamethylthiophosphoric triamide and pyridine are not on the line. Similar observations are made for the Gibbs energies of Cd^{2+} as a function of the data for Na^+. The Gibbs energies of transfer for Tl^+, Zn^{2+}, Pb^{2+} for nitriles are pretty much on the line for hard solvents, the data in the sulfur donor solvents are definitely off the line.

These observations made for the Gibbs energies of transfer of cations follow the classifications of Pearson and Ahrland, Chatt and Davies. Data for hard or class(a) cations Li^+, K^+, Rb^+, Cs^+ and Ba^{2+} correlated for all solvents studied. Gibbs energies of transfer for typically soft or class(b) cations Ag^+, Cu^+ and Hg^{2+} showed deviations for nitriles, pyridine and the sulfur donor solvents. The cations Pb^{2+}, Zn^{2+}, Tl^+ and Cd^{2+} are best considered borderline acceptors. None of those show strong soft-soft interaction with nitriles. In the absence of any reliable quantitative measure for the hardness and softness of acceptors, however, assignments in the border region remain diffuse. Similarely it is not always easy to assign soft solvents. The nitriles appear to be very weak soft donor solvents, allowing soft-soft interactions only with soft acceptors such as Cu^+, Ag^+, Au^+ and possibly the noble metal cations.
Since the number of data for the Gibbs energies of transfer of Ag^+ is much larger than the number for the Gibbs energies of transfer of Na^+, data for the cations Zn^{2+}, Cd^{2+}, Hg^{2+}, Tl^+ and Pb^{2+} were plotted versus the respective data of Ag^+. Two lines, one line covering the data for hard and another line comprising the data for soft solvents, were observed (ref. 30,48). These correlation allowed a prediction of the Gibbs energies of transfer for any of these cations in solvents where such data were missing as long as data for Ag^+ are available. Furthermore in case of ambidentate solvents such as mercaptoethanol or 2,2'-thiodiethanol, which may interact via a hard donor atom or via a soft donor atom in the molecule, it is possible to assign the nature of the interaction, depending on which line the respective point will be. Thus 2,2'-thiodiethanol will act as a soft donor versus Tl^+, Pb^{2+}, Zn^{2+} and Cd^{2+} but as a hard donor versus Cu^{2+}.

Gibbs energies of transfer of anions

Solvent effects on the Gibbs energies of transfer of anions were evaluated by plotting the data for Br^-, I^-, SCN^- and ClO_4^- versus the Gibbs energies of transfer for Cl^-. As previously reported for a more limited set of data (ref. 1) linear correlations were observed for all of these data, showing that the solvent effects on these anions are of the same nature (Fig. 4), the data point for Br^- in tetrahydrothiophene may be an exception. The slopes obtained for the correlations for Cl^- (1.0), Br^- (0.67) and I^- (0.46) decrease in the same order as the electron affinities of the respective halogen atoms.

A grouping into hard-hard and soft-soft interactions, as found for the cations, was not observed for the anions and solvents studied. This is not surprising in view of the fact that none of the solvents studied has soft acceptor properties, thus only hard-hard interactions are possible for the systems investigated.

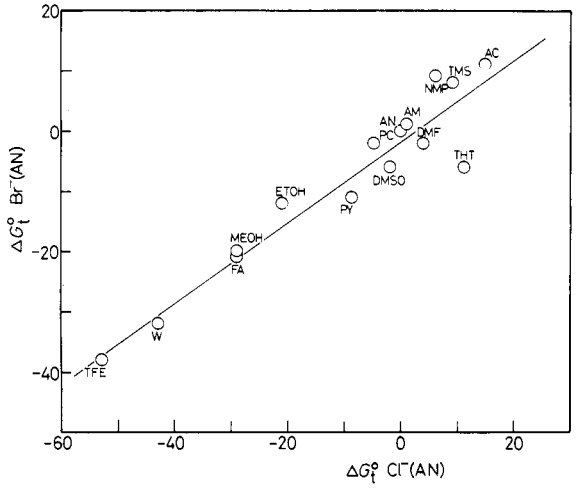

Fig. 4. Molar Gibbs energies of transfer of Br^- (ΔG_t° Br^- (AN)) versus molar Gibbs energies of transfer of Cl^- (ΔG_t° Cl^- (AN)) in kJ mol^{-1} based on the tetraphenylarsonium tetraphenylborate assumption. Reference solvent: acetonitrile. Abbreviations of solvents are given in Fig. 1.

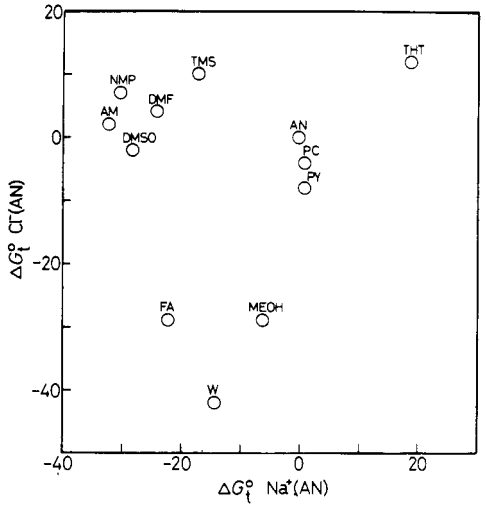

Fig. 5. Molar Gibbs energies of transfer of Cl^- (ΔG_t° Cl^- (AN)) versus molar Gibbs energies of Na^+ (ΔG_t° Na^+ (AN)) in kJ mol^{-1} based on the tetraphenylarsonium tetraphenylborate assumption. Reference solvent: acetonitrile. Abbreviations of solvents are given in Fig. 1.

Following the observation of the relations between the Gibbs energies of cations on one hand and the Gibbs energies of transfer of anions on the other it remains to investigate whether there is a correlation between the Gibbs energies of transfer for cations and anions. As shown in Fig. 5 no such correlations exist. One must therefor conclude that the interactions of solvents with cations and with anions are of different nature.

GIBBS ENERGIES OF TRANSFER AND SOLVENT PROPERTIES

The first model to account for ion-solvent interactions treated the energy changes that ions experience upon transfer from the gaseous state as the reference state into solution (Gibbs energies of solvation), mainly into the solvent water (Gibbs energies of hydration) (ref. 7). This model used the macroscopic dielectric constants of the solvents to characterize the solvents. This very crude approximation of ion-solvent interactions in the early days of solution chemistry, set a trend to employ macroscopic electrostatic solvent properties, such as the dielectric constants, the dipole moments (ref. 49,50), the quadrupole moments (ref. 51), the refractive indices etc. to describe ion-solvent interactions. Equations including several of the above mentioned parameters were proposed, augmented by other experimental parameters such as the ionic radius or the radius of the solvent molecules (ref. 52). Gibbs energies of transfer can in principle be calculated from equations for Gibbs energies of solvation by taking the difference of the Gibbs energies of solvation for the solvents of interest and the chosen reference solvent. A comparison of calculated and "experimental" data shows that the original Born equation does not yield Gibbs energies of transfer for cations that come even close to the "experimental" data; irregardless on whether such data are derived from the bis(biphenyl)chromium assumption or from the tetraphenylarsonium tetraphenylborate assumption (ref. 24). Correlation between Gibbs energies of transfer and the dipole moments for cations or anions do not exist either. It can be easily shown that even more sophisticated models based on macroscopic solvent properties will fail when asked to describe Gibbs energies of transfer from hard solvents into soft solvents. As shown in Table 3 Gibbs energies for the transfer from N,N-dimethylformamide into N,N-dimethylthioformamide are positive for alkali metal ions but negative for Ag^+ and Hg^{2+}. Data for other soft cations such as Au^+, Pd^{2+}, Pt^{2+}, Ir^{3+} and other noble metal cations are missing at present, but one can safely predict that they will follow the general trends observed for Ag^+ and Hg^{2+}. None of these equations will yield positive values for one group of cations and negative values for another group.

All of the models, which are based on electrostatic principles, are in the mainstream of classical physics and generally ignore the vast amount of chemical knowledge about the interactions of ions with neutral or charged ligands. The observed changes in Gibbs energies of transfer and thus ion-solvent interactions, however, can be easily accounted for, if one employs "chemical models". Chemists in explaining reactions or complex formation with organic or inorganic ligands always considered the ability of ions, atoms or molecules to accept or donate electron-pairs. Cations are definitely Lewis-type electron-pair acceptors (Lewis acids) and all of the solvents referred

to in this study do possess a lone electron-pair for such interactions. Lone electron-pairs for most of the solvents studied are located on oxygen atoms, in some cases on nitrogen atoms, on halogen atoms or on sulfur atoms. All solvents will thus qualify as Lewis-type electron-pair donors (Lewis bases). Anions on the other hand are Lewis-type electron-pair donors. The acceptor properties of the investigated solvents, however, are generally due to more or less acidic hydrogen atoms in the solvent molecules, since data for solvents, which could act as true electron-pair acceptors are not available

TABLE 2. Molar Gibbs energies (first line) and enthalpies of transfer (second line) in kJ mol^{-1} for several anions based on the tetraphenylarsonium tetraphenylborate assumption from acetonitrile as reference solvent at 25 °C.[a]

Solvents	Cl^-	Br^-	I^-	SCN^-	$CF_3SO_3^-$	ClO_4^-
Acetone	15	11	12	*	*	*
	*	*	*	*	*	*
Ammonia	2	1	6	*	*	*
	-15	-24	-22	*	*	*
Acetonitrile	0	0	0	0	0	0
	0	0	0	0	0	0
N,N-Dimethyl-	7	*	2	4	*	*
acetamide	*	*	*	*	*	*
N,N-Dimethyl-	4	-2	0	4	*	-4
formamide	1	-5	-7	*	-6	-4
Dimethyl	-2	-6	-10	-4	*	-6
sulfoxide	-2	-5	-6	-3	-1	-1
Ethanol	-21	-12	0	*	*	*
	*	*	*	*	*	*
Formamide	-29	-21	-11	2	*	*
	-17	-10	0	*	-1	6
Hexamethylphos-	17	*	16	9	*	*
phoric triamide	*	*	*	*	*	*
Methanol	-29	-21	-12	-7	*	1
	-12	-4	5	0	2	15
Nitromethane	-10	*	-2	-4	*	*
	*	*	*	*	*	*
N-Methylformamide	-21	-16	*	*	*	*
	*	*	*	*	*	*
N-Methyl-2-	7	9	5	13	*	*
pyrrolidinone	4	1	5	*	*	*
Propylene	-4	-2	-1	-3	*	*
carbonate	8	9	6	*	*	*
Pyridine	-8	-11	0	7	*	12
	7	3	-1	-2	-5	-3
Tetrahydro-	12	-6	*	*	*	*
thiophene	5	4	-10	12	13	12
Tetramethylene	10	8	2	4	*	*
sulfone	6	4	-2	*	*	*
2,2,2-Trifluoro-	-52	-38	-21	*	*	*
ethanol	*	*	*	*	*	*
Water	-42	-32	-19	-13	*	-4
	-20	-8	7	3	-2	16

[a]Ref. 1, 18, 32, 33

TABLE 3. Molar Gibbs energies of transfer in kJ mol^{-1} for several cations from N,N-dimethylformamide into N,N-dimethylthioformamide based on the tetraphenylarsonium tetraphenylborate assumption (first line)[a] and on the bis(biphenyl)chromium assumption (second line).

Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Tl^+	Zn^{2+}	Cd^{2+}	Pb^{2+}	Hg^{2+}
64	50	37	*	23	-87	-4	*	*	*	*
63	43	34	27	18	-82	-9	9	-14	2	-124

[a]Ref. 31

at this time. However, the donor-acceptor concept for interactions between solvents and solutes can be expanded beyond electron-pair donation and electron-pair acceptance by taking partial charge transfer into account. Thus the formation of hydrogen bonds by the solvent molecules towards donors, such as the anions, can be included in this model.

The acceptance of models based on chemical experience to solution chemistry was slow. The main reason was surely the lack of suitable parameters to quantize donor and acceptor properties of solvents. The donor number proposed by Gutmann in 1964 was a major breakthrough in this area (ref. 53,54), with the acceptor number following in 1974 (ref. 54,55). With the introduction of these parameters, it became possible to describe the hard donor properties and the hard acceptor properties of solvents. From the large number of solvent parameters published, several were found to characterize the donor properties, others represented the acceptor properties of solvents. Parameters, which also reflect hard donor properties are the B-parameter (ref. 56-58), the β-parameter (ref. 59,60), the D_H-parameter (ref. 61), the BF_3-parameter (ref. 62) the solvatochromic shift of acetylacetonato(tetramethylethylenediamine)copper(II) perchlorate (ref. 63) or the coordinating power of solvents (ref. 64). Although these parameters carry different names, it can be shown that they all correlate more or less linearly with the donor numbers. The quality of these additional parameters to account for the hard donor properties of solvents depends mainly on the reference substances chosen. It can be further shown that the Gibbs energies of transfer for cations will correlate with the donor number and related parameter as long as only hard donor solvents are taken into account (ref. 26,30). It is therefor quite obvious that the same phenomena of ion-solvent interactions are described by different wording bringing confusion rather than clarity to solution chemistry.
While Gibbs energies of transfer for hard donor solvents have been available for a considerable number of solvents for some time, such data for soft solvents became only very recently available to a larger extend. Probably data in N,N-dimethylthioformamide were the first values reported for a very soft donor solvent (ref. 31). Additional studies in such solvents as N-methylthiopyrrolidinone (ref. 22), hexamethylthiophosphoric triamide (ref. 65), tetrahydrothiophene (ref. 28,32) clearly showed that these solvents are capable of strong interactions with soft acceptor, but that they interact weakly with hard acceptors. Strong interactions, however, with soft acceptors but weak interactions with hard acceptors cannot be described by one parameter for solvent donor properties. The concept of hard and soft acids and bases was essentially of a very qualitative nature. With the data now available it is possible to describe the soft donor properties of solvents in a quantitative way. Several new parameters were recently published describing the interaction of such solvents with soft acceptors. Two such parameters, namely the D_S-parameter (ref. 66) and a parameter based on the Gibbs energies of transfer of Ag^+ (ref. 65,67) were put forward in 1985. The latter parameter, restricted to soft solvents, led to the SP-parameter (ref. 48). The μ-parameter followed (ref. 68). The spectroscopic scale of soft basicity may be seen as a possible precursor to these three parameters (ref. 69). Since these parameters were proposed only recently it appears appropriate to describe them briefly prior to a comparison with the Gibbs energies of transfer. The D_S-parameter is derived from the difference in the symmetric stretching vibration frequency of the $HgBr_2$ molecule in the gas phase and in solution measured by Raman spectroscopy (ref. 61, 70). It should be used to describe the interactions of soft cations with both hard and soft solvents. The SP-parameter is obtained by adding 25 to the positive numerical values of the Gibbs energies of transfer for Ag^+ from benzonitrile into other solvents. The addition of 25 to the data allows inclusion of even weaker soft solvents than benzonitrile on this scale in case data for such solvents become available. Taking positive values assures that larger values of the SP-parameter correspond an increase in the softness of the solvents. The SP-parameter should only be used for soft-soft interactions between solvents and cations, since it was observed that the interaction of soft cations with hard donor solvents can be described with parameters for hard donor properties of solvents. The μ-parameter is a modification on using the Gibbs energies of transfer of Ag^+ in estimating the soft donor properties of the solvents. Its values are calculated by substracting the Gibbs energies of Ag^+ from the mean of the sum of the Gibbs energies of transfer for Na^+ and K^+ from water as the reference solvent, divided by 100. The spectroscopic scale of soft basicity was based on the solvent induced shift of the stretching frequency of iodine cyanide in the IR-spectrum as a measure of the softness of solvents. The number of soft solvents for which both Gibbs energies of transfer and values

for the spectroscopic scale of soft basicity are available is more or less restricted to acetonitrile and pyridine. Thus no evaluation of this parameter on basis of the Gibbs energies of transfer is possible. The D_S-, the SP- and the μ-parameters, however, were evaluated with respect to their ability to reflect the observations made for the Gibbs energies of transfer of Ag^+, Hg^{2+} and some borderline cations. It was found that the D_S-parameter correlates Gibbs energies of transfer for both Ag^+ (r: 0.944 s: 12 n: 31) and Hg^{2+} (r: 0.972 s: 17 n: 20) quite well. Correlation between Gibbs energies of transfer for borderline acceptors such as Tl^+, Cd^{2+} or Pb^{2+} and the D_S-parameter yield one line for hard solvents, with the values for sulfur donor solvents deviating (ref. 30,48). The SP-parameter, which was restricted to soft solvents will account for the Gibbs energies of transfer for both soft and borderline cations from acetonitrile into soft solvents (ref. 29,30). Correlation coefficients for the Gibbs energies of transfer for Ag^+ and Hg^{2+} are better than 0.98. Correlations between the μ-parameter and the Gibbs energies of transfer of Ag^+ (r: 0.901 s: 16 n: 26) and Hg^{2+} (r: 0.851 s: 44 n: 15) are not as good as those observed for the D_S or the SP-parameters. Correlations with the "selected" values for the Gibbs energies of transfer of Ag^+ (r: 0.876 s: 16 n: 18) are worse than those for the data based on the bis(biphenyl)chromium assumption; multiple linear regressions employing both the μ- and the β-parameters improve the correlation coefficient to 0.927.
It is worthwhile to note that for hard solvents the D_S-values, μ-values and the values of the spectroscopic scale of soft basicity depend linearly on the donor numbers of the solvents.

Gibbs energies of transfer of the anions studied correlate well with the acceptor numbers of the solvents (ref. 1). Similar correlations can also be obtained with the E_T-values (ref. 71-73) and with those solvent parameters, which were found to depend linearely on E_T-values (ref. 73) such as the Y-values (ref. 74,75) or the Z-values (ref. 76). All of these parameters as well as the α-parameter (ref. 77) are in one way or another primarily a measure of the acceptor properties of the solvents. Although the E_T-values were originally proposed as a measure of solvent polarity, they were shown to correlate with the acceptor numbers of solvents (ref. 55) and were also used as a measure of solvent acceptor properties (ref. 78-81). No correlation for the Gibbs energies of transfer for the anions and either the reciprocal of the dielectric constant or the dipole moments was found. Anions are donors themselves interacting with the acceptor sites of the solvent molecules. Thus correlations between the Gibbs energies of transfer of anions and the donor numbers are neither expected nor were they observed. For similar reasons there are no correlations between the Gibbs energies of transfer of cations and the acceptor numbers of solvents.

ENTHALPIES OF TRANSFER

The number of solvents and ions, for which enthalpies of transfer are available is considerably smaller than the data set for Gibbs energies of transfer. Data for soft donor solvents are limited to ammonia, pyridine, acetonitrile and tetrahydrothiophene. Values for other sulfur donor solvents are not available at this time. The data for the cations and anions, which will be discussed, originate exclusively from the tetraphenylarsonium tetraphenylborate assumption. Additional support for these values from other assumptions, as in the case of the Gibbs energies of transfer, is currently not at hand. Enthalpies of transfer, as all single ion properties irregardless of the assumption used, rely on the independence of cation and anion solvation of the respective counterions at infinite dilution. Yet agreement between the enthalpies of transfer for a given cation derived from salts with different anions can vary by 10 kJ mol^{-1} and more, especially when one has to resort to measurements of heats of precipitation rather than to heats of solution (ref. 82). Slow rates of dissolution of salts in nonaqueous solvents can lead to some uncertainty of the data (ref. 83). With this limitations in mind a picture on what we know at present about solvent effects and the mutual dependence or independence of enthalpies of transfer will be given based on the enthalpies of transfer of Na^+, K^+, Rb^+, Ag^+, Cl^-, Br^- and I^-. Data for linear regressions between Gibbs energies and enthalpies of transfer are summarized in Table 4.

Good correlations between the respective Gibbs energies and enthalpies of transfer were observed only for Ag^+ and Cl^- and to a lesser degree for K^+ and Br^-. The correlation coefficients for Gibbs energies and enthalpies of Na^+ and I^-, respectively, were below 0.5. Enthalpies of transfer thus follow the

Gibbs energies of transfer for a given ion only in a very general way becoming more negative with a decrease in Gibbs energies.

TABLE 4. Linear correlations between molar Gibbs energies and enthalpies of transfer of several cations and anions.[a]

Y	X	intercept a_1	slope a_2	correlation coefficient r	standard error s	number of solvents
$\Delta G_t°$ Na^+	$\Delta H_t°$ Na^+	-	-	0.381	15	12
$\Delta G_t°$ K^+	$\Delta H_t°$ K^+	-9.99	0.428	0.669	7	12
$\Delta G_t°$ Rb^+	$\Delta H_t°$ Rb^+	-	-	0.467	9	10
$\Delta G_t°$ Ag^+	$\Delta H_t°$ Ag^+	-2.52	0.728	0.912	15	11
$\Delta G_t°$ Cl^-	$\Delta H_t°$ Cl^-[b]	-4.43	1.615	0.893	8	11
$\Delta G_t°$ Br^-	$\Delta H_t°$ Br^-[b]	-6.31	1.355	0.625	10	11
$\Delta G_t°$ I^-	$\Delta H_t°$ I^-	-	-	0.498	8	11
$\Delta H_t°$ K^+	$\Delta H_t°$ Na^+	4.76	0.759	0.805	7	11
$\Delta H_t°$ Rb^+	$\Delta H_t°$ Na^+	5.16	0.582	0.647	9	10
$\Delta H_t°$ Ag^+	$\Delta H_t°$ Na^+[c]	30.27	1.318	0.810	12	7
$\Delta H_t°$ Rb^+	$\Delta H_t°$ K^+	1.00	0.992	0.985	2	10
$\Delta H_t°$ Br^-	$\Delta H_t°$ Cl^-[d]	-3.50	1.320	0.976	2	9
$\Delta H_t°$ I^-	$\Delta H_t°$ Cl^-	-	-	0.164	9	12
$\Delta H_t°$ Cl^-	$\Delta H_t°$ Na^+	-	-	0.241	10	12
$\Delta H_t°$ Ag+	$\Delta H_t°$ Br-	-	-	0.241	43	11

[a] $Y = a_1 + a_2 X$ [b] without ammonia [c] without acetonitrile, ammonia, pyridine and tetrahydrothiophene [d] without formamide, methanol and water.

The enthalpies of transfer for Na^+, K^+, Rb^+ and Ag^+ in hard donor solvents show roughly a linear dependence on each other, although some correlation coefficients are as low as 0.65. The values for Ag^+ for the soft solvents tetrahydrofurane, pyridine, ammonia and acetonitrile, however, clearly deviate from the linear relation between the enthalpies of transfer for Na^+ and Ag^+ into hard solvents. Correlations between the enthalpies of transfer of Cl^- and Br^- are limited to solvents that do not posses any expressed acceptor properties and solvent structures. Correlations between the enthalpies of transfer for I^- and Cl^- could not be observed. In the absence of any relations between the enthalpies of transfer for cations on one side and anions on the other it must be concluded that the enthalpies of transfer for cations are affected by different ion-solvent interactions than the enthalpies of transfer for anions.

ENTROPIES OF TRANSFER

Entropies of transfer have always been related to changes in the structure of the solvents due to the dissolution of ions and to changes in the translational freedom of solvent molecules under the influence of ions (ref. 18,33,35,83). Cox and Parker developed a model to describe these effects based on entropies of transfer from "ideal" into real solvents (ref. 84). Within this concept the entropy of dissolution of a crystalline salt in a hypothetical, ideal, noninteracting solvent with the same molecular weight and same density as the real solvent under consideration was calculated, assuming amongst others that (i) the entropy of an ion in a crystall lattice is independent of the lattice containing that ions and that (ii) the entropy of solution for the tetraphenylarsonium ion is equal to that of the tetraphenylborate ion. The entropies of transfer for single ions from this hypothetical state in an ideal solvent into the real solvent are then taken to calculate "minimum solvation numbers" and to discuss ion- induced changes in the solvent structures. Marcus recently published solvation numbers for several cations and anions obtained from calculated entropies of solvation (ref. 85), building on Ulich's approach (ref. 86) for the calculation of such data. The values generally vary between 0 and 6, depending on the ion and the solvent and agree with the data obtained from conductivities. Only the values in methanol are exceptionally large; solvation numbers as high as 30 were reported for Zn^{2+} and Cd^{2+}.

Entropies of transfer have been discussed individually for each ion and solvent in the past (ref. 18,33,87). General conclusions cannot be readily

drawn from the available data, but correlations between the entropies of transfer of Ag^+ and Na^+ include the solvents acetonitrile, tetrahydrothiophene and pyridine. At least from these data it appears that a separation into soft-soft and hard-hard interactions does not occur for the entropies of transfer. More data are required before this observation can be generalized. The solvent-induced changes in the entropies of transfer for Cl^-, Br^- and I^- showed a loose mutual dependence (r~0.88, s~9), but were independent of the changes in entropies of transfer for cations. A more detailed picture on solvent effects on entropies of transfer requires additional data, preferably from different assumptions and a better understanding of the structural changes of solvents by cations and anions.

Acknowledgement

Part of the work reported was supported by the Fonds zur Förderung der wissenschaftlichen Forschung (Austria).

REFERENCES

1. A. J. Parker, U. Mayer, R. Schmid and V. Gutmann, J. Org. Chem., 43, 1843 (1978)
2. A. J. Parker, Chem. Rev., 69, 1 (1969)
3. O. Popovych, Crit. Rev. Anal. Chem., 1, 73 (1970)
4. A. J. Parker and R. Alexander, J. Am. Chem. Soc., 90, 3313 (1968)
5. B. G. Cox and A. J. Parker, J. Am. Chem. Soc., 95, 402 (1973)
6. Y. Marcus, Ion Solvation, Wiley (1985)
7. M. Born, Z. Phys., 1, 45 (1920)
8. E. Grunwald, G. Baughman and G. Kohnstam, J. Am. Chem. Soc., 82, 5801 (1960)
9. O. Popovych and A. J. Dill, Anal. Chem., 41, 456 (1969)
10. E. M. Arnett and D. R. McKelvey, J. Am. Chem. Soc., 88, 2598 (1966)
11. B. G. Cox, A. J. Parker and W. E. Waghorne, J. Am. Chem. Soc., 95, 1010 (1973)
12. W. A. Pleskov, Usp. Khim., 16, 254 (1947)
13. H. M. Koepp, H. Wendt and H. Strehlow, Z. Elektrochem., 64, 483 (1960)
14. G. Gritzner and J. Kuta, Pure Appl. Chem., 56, 461 (1984) and references cited
15. G. Gritzner, J. Phys. Chem., 90, 5478 (1986) and references cited
16. J. Böck and G. Gritzner, Z. Phys. Chem. (Wiesbaden), 130, 181 (1982)
17. N. Bjerrum and E. Larsson, Z. Phys. Chem., 127, 358 (1927)
18. B. G. Cox, G. R. Hedwig, A. J. Parker and D. W. Watts, Aust. J. Chem., 27, 477 (1974)
19. R. Alexander, A. J. Parker, J. H. Sharp and W. E. Waghorne, J. Am. Chem. Soc., 94, 1148 (1972)
20. R. Alexander and A. J. Parker, J. Am. Chem. Soc., 89, 5549 (1967)
21. I. M. Kolthoff and M. K. Chantooni Jr., J. Phys. Chem., 76, 2024 (1972)
22. G. Gritzner, Inorg. Chim. Acta, 24, 5 (1977)
23. G. Gritzner and E. Geyer, Z. Phys. Chem. (Wiesbaden), 125, 7 (1981)
24. G. Gsaller and G. Gritzner, Z. Phys. Chemie (München), 138, 137 (1983)
25. J. W. Diggle and A. J. Parker, Electrochim. Acta, 18, 975 (1973)
26. G. Gritzner, J. Chem. Soc. Faraday Trans. 1, 82, 1955 (1986)
27. S. Sperker, G. Gsaller, H. Marek and G. Gritzner, J. Solution Chem., 17, 35 (1988)
28. G. Gritzner and S. Sperker, J. Solution Chem. in print
29. G. Gritzner and G. Kraml, submitted for publication
30. G. Gritzner, J. Chem. Soc. Faraday Trans. 1, 84, 1047 (1988)
31. R. Alexander, D. A. Owensby, A. J. Parker and W. E. Waghorne, Aust. J. Chem., 27, 933 (1974)
32. M. Johnsson and I. Persson, Inorg. Chim. Acta, 127, 15 (1987)
33. M. Johnsson and I. Persson, Inorg. Chim. Acta, 127, 25 (1987)
34. A. Lewandowski, Electrochim. Acta, 29, 547 (1984), ibid., 30, 311 (1985), ibid., 31, 59 (1986)
35. G. R. Hedwig, D. A. Owensby and A. J. Parker, J. Am. Chem. Soc., 97, 3888 (1975)
36. J. F. Coetzee and W. K. Istone, Anal. Chem., 52, 53 (1980)
37. Y. Marcus, Pure Appl. Chem., 55, 977 (1983)
38. Y. Marcus, Pure Appl. Chem., 57, 1103 (1985)
39. G. Gritzner, Monatsh. Chem., 106, 947 (1975)
40. I. M. Kolthoff and M. K. Chantooni Jr., J. Am. Chem. Soc., 93, 7104 (1971)

41. O. Popovych, A. Gibofsky and D. H. Berne, Anal. Chem., 44, 811 (1972)
42. J. I. Kim, J. Phys. Chem., 82, 191 (1978)
43. J. I. Kim, Bull. Soc. Chim. Belg., 95, 435 (1986)
44. R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963)
45. S. Ahrland, J. Chatt and N. R. Davies, Q. Rev. Chem. Soc., 12, 265 (1958)
46. F. A. Cotton, R. Francis and W. D. Horrocks Jr., J. Phys. Chem., 64, 1534 (1960)
47. J. Selbin, W. E. Bull and L. H. Holmes Jr., J. Inorg. Nucl. Chem., 16, 219 (1961)
48. G. Gritzner, Z. Phys. Chem. (München), 158, 99 (1988)
49. J. D. Bernal and R. H. Fowler, J. Chem. Phys., 1, 515 (1933)
50. D. O. Eley and M. G. Evans, Trans. Faraday Soc., 34, 1093 (1938)
51. H. F. Halliwell and S. C. Nyburg, Trans. Faraday Soc., 58, 1126 (1963)
52. A. D. Buckingham, Disc. Faraday Soc., 51, 1418 (1955)
53. V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett., 2, 257 (1966)
54. V. Gutmann, The Donor Acceptor Approach to Molecular Interactions (Plenum, New York, 1978) and references cited
55. U. Mayer, V. Gutmann and W. Gerger, Monatsh. Chem., 106, 1235 (1975)
56. I. A. Koppel and V. A. Palm, in Advances in Linear Free Energy Relationships, ed. N. B. Chapman and J. Shorter (Plenum, New York, 1972)
57. T. Kagiya, Y. Sumida and T. Inoue, Bull. Chem. Soc., Jpn., 41, 767 (1968)
58. A. G. Burden, G. Collier and J. Shorter, J. Chem. Soc. Perkin Trans. II, 1627 (1976)
59. M. J. Kamlet and R. W. Taft, J. Am. Chem. Soc., 98, 377 (1976)
60. M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, J. Org. Chem., 48, 2877 (1983)
61. I. Persson, Pure Appl. Chem., 58, 1153 (1986)
62. P.-C. Maria and J.-F. Gal, J. Phys. Chem., 89, 1296 (1985)
63. R. W. Soukup and R. Schmid, J. Chem. Ed., 62, 459 (1985)
64. M. Munakata, S. Kitagawa and M. Miyazima, Inorg. Chem., 24, 1638 (1985)
65. G. Kraml and G. Gritzner, J. Chem. Soc. Faraday Trans. 1, 81, 2875 (1985)
66. M. Sandström, I. Persson and P. L. Goggin, Proceedings Seventh International Symposium on Solute-Solute-Solvent Interactions, (Reading, U.K.) 2 - 10 (1985)
67. G. Gritzner, Proceedings Seventh International Symposium on Solute-Solute-Solvent Interactions, (Reading, U.K.) 2 - 21 (1985)
68. Y. Marcus, J. Phys. Chem., 91, 4422 (1987)
69. C. Laurence, M. Queignec-Cabanetos, T. Dziembowska, R. Queignec and B. Wojtkowiak, J. Am. Chem. Soc., 103, 2567 (1981)
70. I. Persson, M. Sandström and P. L. Goggin, Inorg. Chim. Acta, 129, 183 (1987)
71. K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, Justus Liebigs Ann. Chem., 661, 1 (1963)
72. C. Reichardt and E. Harbusch-Görnert, Justus Liebigs Ann. Chem., 721 (1983)
73. C. Reichardt, Angew. Chem. Int. Ed., 4, 29 (1965)
74. E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948)
75. S. G. Smith, A. H. Fainberg and S. Winstein, J. Am. Chem. Soc., 83, 618 (1961)
76. E. M. Kosower, J. Am. Chem. Soc., 80, 3253 (1958)
77. R. W. Taft and M. J. Kamlet, J. Am. Chem. Soc., 98, 2886 (1976)
78. T. M. Krygowski and W. R. Fawcett, J. Am. Chem. Soc., 97, 2143 (1975)
79. W. R. Fawcett and T. M. Krygowski, Can. J. Chem., 54, 3283 (1976)
80. T. M. Krygowski, J. P. Radomski, A. Rzeszowiak, P. K. Wrona and C. Reichardt, Tetrahedron, 37, 119 (1981)
81. S. Glikberg and Y. Marcus, J. Solution Chem., 12, 255 (1983)
82. S. Ahrland and S.-I. Ishiguro, Inorg. Chim. Acta, 142, 277 (1988)
83. S. Ahrland, Pure Appl. Chem., 54, 1451 (1982)
84. B. G. Cox and A. J. Parker, J. Am. Chem. Soc., 95, 6879 (1973)
85. Y. Marcus, J. Solution Chem., 15, 291 (1986)
86. H. Ulich, Z. Electrochem., 36, 497 (1930)
87. A. J. Parker, Electrochim. Acta, 21, 671 (1976)