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# Gibbs Free Energies of Transfer ($\Delta G^{\circ}_{tr}$) for Alkali Metal Ions and $Tl^+$

G. GRITZNER

*Institute of Inorganic Chemistry, Technische Universität Wien, Getreidemarkt 9, A-1060 Vienna, Austria*

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*Employing bisbiphenylchromium(I)/bisbiphenylchromium(0) as a reference redox system the polarographic behaviour of alkali metal ions and* $Tl^+$ *has been studied in butyrolactone, N-methylpyrrolidinone(2), N-methylthiopyrrolidinone(2), ethanol and acetonitrile. Based on the half wave potentials* versus *the above mentioned reference redox system, Gibbs free energies of transfer have been calculated for these solvents as well as for fourteen other solvents for which half wave potentials have been already published. Acetonitrile was chosen as a reference solvent. The difference in half wave potentials between ferrocene and bisbiphenylchromium(I) is reported for fourteen solvents. The half wave potential of the bisbiphenylchromium(I) reduction has also been measured in acetonitrile* versus *the Ag/0.01 molar* $AgClO_4$ *electrode in molar tetraethylammonium perchlorate solutions in acetonitrile. Gibbs free energies of transfer based on the bisbiphenylchromium assumption are compared with data obtained from the tetraphenylarsonium tetraphenylborate assumption in those solvents for which such data are available. The bisbiphenylchromium assumption and the effect of solvent parameters on the Gibbs free energy of transfer of alkali metal ions and* $Tl^+$ *are discussed.*

## Introduction

Estimations of changes in Gibbs free energies of single ions on transfer from one solvent to another ($\Delta G^{\circ}_{tr}$) have received considerable attention as a measure of ion–solvent interactions and review articles have recently summarized the state of the art [1–3]. Reasonable explanations of changes in properties of ions in different solvents have been presented and a better understanding of solvation in solvent mixtures has been achieved [4–6]. Data of Gibbs free energies of transfer ($\Delta G^{\circ}_{tr}$) have been calculated based on various extrathermodynamic assumptions [7–17]. Such assumptions are necessary because Gibbs free energies of single ions are not accessible on the basis of rigorous thermodynamics. The extrathermodynamic assumptions most widely used presently are (a) the assumption that the experimentally obtainable Gibbs free energies of transfer for salts consisting of ions with large radii can equally be divided between cation and anion [8–10] (*e.g.* tetraphenylarsonium tetraphenylborate), (b) the assumption that the redox potential of large organometallic compounds such as a ferrocene and bisbiphenylchromium is independent of the nature of the solvent [11–14], and (c) the assumption of negligible diffusion potential upon employing a salt bridge containing tetraethylammonium picrate in any non aqueous solvents [15–17]. Although much progress has been made in this area of research, there is still some discrepancy about the data obtained for $\Delta G^{\circ}_{tr}$ depending on the extrathermodynamic assumption used as well as on the experimental procedures employed.

Alkali metal ions and $Tl^+$ when studied by polarographic methods were found to undergo reversible one electron reductions to the metal amalgams on the dropping mercury electrode in a variety of solvents [18–31]. Since the reduced form is the same in all solvents, namely the respective metal amalgam, the polarographic half wave potential of these ions is affected only by the interaction of the solvent with the metal ions [12]. The half wave potentials of these ions with respect to bisbiphenylchromium(I) iodide (BBCrI) and bisbiphenylchromium(I) tetraphenylborate respectively, therefore offer experimental data for an estimation of $\Delta G^{\circ}_{tr}$ values. Half wave potentials *versus* $BBCr^+[E_{1/2BBCr}]$ for the mentioned ions in ethanol (EtOH), butyrolactone (BL), N-methylpyrrolidinone(2) (NMP) and N-methylthiopyrrolidinone have been measured in this study and are reported together with $E_{1/2BBCr}$ in a variety of solvents.

Choosing acetonitrile (AN) as a reference solvent the $\Delta G^{\circ}_{tr}$ values obtained via the BBCr assumption will be compared with values obtained by other assumptions in solvents for which such data have been published.

Experimental data collected during the study will enable a conversion of data obtained with either $Rb^+$ [32] or ferrocene or $BBCr^+$ as reference redox systems and with data obtained via the assumption of negligible diffusion potentials upon employing a suitable salt bridge. The possibilities of experimental errors in evaluating $E_{1/2}$ *versus* aqueous reference electrodes during studies in non aqueous solutions will be stressed.

## Experimental

The polarographic data for the alkali metal perchlorates and $TlClO_4$ in AN, BL and NMP as well as the data for ferrocene and the $BBCr^+$ in AN, BL, NMP, propylenecarbonate (PC), dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), methanol (MeOH), EtOH, 1,2-dichloroethane (DCE), dichloromethane (DCM), nitromethane (NM), tetramethylene sulfone (TMS) and N-methylthiopyrrolidinone(2) (NMTP) were obtained in an experimental setup described previously [33]. Bisbiphenylchromiumtetraphenylborate (BBCrTPB) was made by reacting bisbiphenylchromium iodide (BBCrI) dissolved in AN with sodium tetraphenylborate dissolved in water. Upon evaporating most of the AN the precipitate was filtered and washed with distilled water. Recrystallisation from AN yielded yellow–orange plates (from MeOH yellow–orange needles).
*Anal.* Calc.: C: 84.82, H: 5.93. Found: C: 84.64, H: 5.99.

Silver perchlorate was dried at 130 °C and $10^{-3}$ mm Hg.

Tetraethylammonium picrate ($et_4Npic$) was prepared by neutralizing picric acid with tetraethylammonium hydroxide in water followed by crystallization from a hexane–EtOH mixture. Anhydrous perchlorates of the alkali metals and $Tl^+$ were used, tetraethylammonium perchlorate ($et_4NClO_4$), tetrabutylammonium perchlorate ($bu_4NClO_4$) and tetrabutylammonium iodide ($bu_4NI$) served as supporting electrolytes.

BL was dried over molecular sieves and twice distilled at 80 °C under reduced pressure. Both BL and NMP were treated with carbon black prior to the final distillation step. Both solvents were distilled prior to use. The purification of NMTP has been reported recently [34]. All other solvents were purified according to methods published elsewhere and subjected to several distillations as final purification steps [33]. The water content analyzed by the Karl Fischer method was below $10^{-4}$ molar.

The following reference electrodes were used in this study:
Ag/AgCl sat. aqueous KCl/
Ag/0.01 molar $AgNO_3$ in AN (Pleskov Electrode)/,
Ag/0.01 molar $AgNO_3$, 0.1 molar $et_4NClO_4$ in AN/,
Ag/0.01 molar $AgNO_3$, 0.02 molar $et_4NClO_4$ in AN/ [35].

In some experiments a 0.1 molar solution of $et_4Npic$ in AN was used as a salt bridge. The difference in half wave potentials between $BBCr^+$ and the ion studied was measured by first recording the $E_{1/2}$ *versus* the external reference electrode. Upon addition of $BBCr^+$ the waves of both the $BBCr^+$ and the ion studied were recorded at least twice to obtain the difference in $E_{1/2}$. Effects of the BBCrI on the alkali metal ions in the solvents studied were not observed. $BBCr^+$ and ferrocene were studied by classical polarography and slow scan cyclic voltammetry (10–30 mV/sec) following the above outlined procedure. All measurements were carried out at 25 ± 0.02 °C.

## Results

Although the $E_{1/2}$ for the alkali metal ions and $Tl^+$ have been previously reported [24], the $E_{1/2BBCr}$ were again measured in 0.1 molar solutions of $et_4NClO_4$ in AN, since this solvent was chosen as a reference solvent. The $E_{1/2BBCr}$ were found to be $-1.20$ for $LiClO_4$, $-1.11_8$ V for $NaClO_4$, $-1.22_3$ for $KClO_4$, $-1.22_4$ for $RbClO_4$, $-1.20_7$ for $CsClO_4$ and $+0.48_0$ for $TlClO_4$. The $E_{1/2}$ for the alkali metal perchlorates rounded to the nearest one hundredth of a Volt agree within 10 mV with the values previously reported [24]. Since those data have also been rounded to one hundredth of a Volt the actual differences in $E_{1/2}$ between the two studies may well be less than 10 mV.

The $E_{1/2BBCr}$ in EtOH for $LiClO_4$, $NaClO_4$ and $TlClO_4$ were obtained in 0.1 molar $bu_4NClO_4$ solutions and are listed in Table I. Millimolar solutions of KI and RbI in 0.1 molar $bu_4NI$ had to be used to obtain $E_{1/2BBCr}$ values since the perchlorates of these two ions were not soluble in EtOH. Reversible diffusion controlled one-electron reductions were observed for all ions studied, BBCrI serving as a reference redox system.

The polarographic behaviour of $LiClO_4$, $NaClO_4$, $KClO_4$ and $TlClO_4$ in NMP has been described recently, the data for $RbClO_4$ and $CsClO_4$ are added in this work. Reversible one electron processes were observed, the limiting current of the polarographic wave being in either case controlled by diffusion. The Tomeš test yielded 56 mV for both $RbClO_4$ and $CsClO_4$. The $E_{1/2}$ values are listed in Table I together with $E_{1/2BBCr}$ already published.

In BL the alkali metal perchlorates and $TlClO_4$ yielded a single polarographic wave each corresponding to a one electron reduction to the metal amalgam. The $E_{1/2BBCr}$ are listed in Table I. Reversible behaviour was found for $Na^+$ (Tomeš test 57 mV), $K^+$ (T.t. 56 mV), $Rb^+$ (T.t. 55 mV), $Cs^+$ (T.t. 53 mV) and $Tl^+$ (T.t. 58 mV); nearly reversible behaviour was found for $Li^+$ (T.t. 67 mV).

As in EtOH, KI and RbI had to be studied in 0.1 molar $bu_4NI$ solutions in NMTP due to the insolubility of the perchlorates of these two ions in this solvent. The $E_{1/2BBCr}$ are listed in Table I. The Tomeš test for $Rb^+$ was 58 mV and for $K^+$ 60 mV. The

TABLE I. Half Wave Potentials of Alkali Metal Perchlorates and $TlClO_4$ in 0.1 Molar Solutions of Tetraethylammonium Perchlorate (0.08 molar in methanol) in Various Solvents at 25 °C (Reference system $BBCr^+/BBCr^0$).

| | $LiClO_4$ | $NaClO_4$ | $KClO_4$ | $RbClO_4$ | $CsClO_4$ | $TlClO_4$ |
|---|---|---|---|---|---|---|
| N,N-dimethylthioformamide (DMTF) [18] | −0.97 | −0.91 | ins | ins | ins | +0.17 |
| N-methylthiopyrrolidinone(2) (NMTP) [31] | −1.03[c] | −0.95 | −1.05[b] | −1.09[b] | ins | +0.15 |
| Benzylfluoride (BF) [23] | n.a. | n.a. | n.a. | n.a. | n.a. | +0.55 |
| Nitromethane (NM) [19] | s.r. | s.r. | s.r. | s.r. | s.r. | +0.55 |
| Nitrobenzene (NB) [27] | s.r. | s.r. | s.r. | s.r. | s.r. | +0.54 |
| Benzonitrile (BN) [24] | −1.13 | −1.05 | −1.16 | −1.18 | −1.16 | n.a. |
| Acetonitrile (AN) | −1.20 n.r. | −1.12 | −1.22 | −1.22 | −1.21 | +0.48 |
| Propylenecarbonate (PC) [19, 21, 24] | −1.25 | −1.09 | −1.21 | −1.23 | −1.22 | +0.52 |
| Butyrolactone (BL) | −1.34 n.r. | −1.17 | −1.26 | −1.26 | −1.25 | +0.41 |
| Ethylene sulfite (ES) [19, 20] | n.a. | n.a. | n.a. | n.a. | n.a. | +0.47 |
| Acetone (AC) [22] | −1.4 irr. | −1.22 | −1.28 | −1.30 | −1.27 | +0.41 |
| Methanol (MEOH) [24, 29] | −1.49[a] | −1.22 | −1.24 | −1.23 | −1.20 | n.a. |
| Ethanol (EtOH)[b] | −1.46 | −1.17 | −1.18 | −1.18 | n.a. | +0.42 |
| Trimethylphosphate (TMP) [19, 30] | n.a. | −1.37 | −1.36 | −1.35 | n.a. | +0.31 |
| N,N-dimethylformamide (DMF) [19] | n.a. | −1.37 | −1.39 | −1.37 | n.a. | +0.25 |
| N-methylpyrrolidinone(2) (NMP) [31] | inact. | −1.47 | −1.39 | −1.37 | −1.35 | +0.23 |
| N,N-dimethylacetamide (DMA) [24–26] | inact. | −1.38 | −1.40 | −1.36 | −1.35 | n.a. |
| Dimethylsulfoxide (DMSO) [19, 24] | n.a. | −1.37 | −1.40 | −1.37 | n.a. | +0.18 |
| N,N-diethylformamide (DEF) [24] | −1.78 n.r. | −1.39 | −1.41 | −1.37 | −1.36 | n.a. |

[a] Close to reduction of supporting electrolyte. [b] 0.1 molar tetrabutylammonion iodide, metal salts as iodides. [c] 0.1 molar tetrabutylammonium perchlorate. n.a., Not available. s.r., Solvent reduction preceding reduction of the ion. inact., Polarographically inactive. irr., Irreversible reduction. n.r., Nearly reversible reduction. ins., insoluble.

$E_{1/2BBCr}$, for NaI in 0.1 molar $bu_4NI$ was found to be $-0.95_5$ V.

Both ferrocene and $BBCr^+$ were studied in AN by classical polarography on the DME and by cyclic voltammetry on the stationary platinum electrode using a silver/0.01 molar silver perchlorate electrode in 0.02 molar $et_4NClO_4$ solutions in AN as a reference electrode. The $E_{1/2}$ values and the $1/2\,(E_{pa} + E_{pc})$ values agreed within 2 mV. The $E_{1/2}$ for ferrocene in 0.02 molar $et_4NClO_4$ *versus* the above mentioned reference electrode was +89 mV. The $E_{1/2}$ for $BBCr^+$ *versus* the same electrode was −1030 mV. The value of 89 mV for ferrocene differs by only 3 mV from the value reported in the literature [35]. This is well within the limits of experimental error. Since polarographic $E_{1/2}$ in non aqueous solvents are generally rounded to the nearest one hundredth of a Volt a value of 0.09 V will result from either study.

The difference in $E_{1/2}$ and $1/2\,(E_{pa} + E_{pc})$ values respectively for ferrocene and $BBCr^+$ are listed in Table II. The Tomeš test for the $BBCr^+$ reduction yielded 57 mV in TMS, 58 mV in EtOH, 59 mV in BL, 60 mV in DCM and 63 mV in DCE indicating reversible or nearly reversible behaviour. The polarographic behaviour in the other solvents studied has been described previously [18, 24, 31, 37, 38]. The Tomeš test for the ferrocene wave gave 56 mV in TMS, 67 mV in EtOH, 63 mV in DCE, 57 mV in BL and 82 mV in DCM. The reduction of ferrocene in DCM is irreversible. The differences in $E_{pa}$ and $E_{pc}$ for $BBCr^+$ were between 65 and 90 mV at 30 mV $sec^{-1}$, the deviation from the theoretical value of 59 mV largely being caused by the uncompensated resistance between the tip of the capillary of the reference electrode and the working electrode [36]. There may well be also a contribution due to a beginning deviation from strictly reversible behaviour at this scan rate. Similar effects have been observed in the case of ferrocene [35]. Studies presently under way in our laboratory show that the iodide ion can interact in some cases with the metal complexes studied. The well known adsorption of the iodide ion on the mercury electrode further supported a change to BBCr TPB as an alternative compound. TBP was chosen because other anions such as $ClO_4^-$ and $NO_3^-$ did not yield stable compounds. The variations in $\Delta E_{1/2}$ between BBCrI and BBCrTPB are within the limits of experimental error indicating that any possible ion pair formation between $BBCr^+$ and $I^-$ must be quite small. The values previously reported [37, 38] for PC and AN were found to be about 10 mV higher than those measured in this investigation. This discrepancy may well have been caused by the less refined three-electrode system previously employed. The difference in $E_{1/2}$ between ferrocene and BBCrI in ethanol was measured in 0.1 molar solutions of $bu_4NClO_4$, resulting in a more accurate value for this solvent. Measurements in AN using 0.1 molar solutions of $et_4NClO_4$ and $bu_4NClO_4$ as well

TABLE II. Differences in $E_{1/2}$ and $1/2(E_{pa} + E_{pc})$ Values for Ferrocene and Bisbiphenylchromium Tetraphenylborate (Bisbiphenylchromium iodide respectively) in 0.1 Molar Tetraethylammonium Perchlorate Solutions in Several Solvents as well as Solvent Parameters

| Solvent | $\Delta E_{1/2}$ (ferrocene BBCr) | | $\epsilon$[d] | $\mu$[e] | DN [43, 45][f] | AcN [55][g] |
|---|---|---|---|---|---|---|
| | BBCrTPB | BBCrI | | | | |
| 1,2-dichloroethane (DCE) | $1.13_1$[a] | – | 10.1 | | 0 | 16.7 |
| Dichloromethane (DCM) | $1.14_8$[a]<br>$1.15_2$[b] | | 9.0 | | | 20.4 |
| Nitromethane (NM) | $1.11_2$ | $1.11_4$ [37, 38] | 35.9 | 3.46 | 2.7 | 20.5 |
| Nitrobenzene (NB) | | 1.13 [37] | 34.8 | | 4.4 | 14.8 |
| Acetonitrile (AN) | $1.11_8$<br>$1.11_9$[a]<br>$1.11_9$[c] | $1.12_1$ | 38.0 | 3.92 | 14.1 | 18.9 |
| Propylene carbonate (PC) | $1.11_4$ | $1.11_3$ | 69 | 4.98 | 15.1 | 18.3 |
| Butyrolactone (BL) | $1.11_2$ | $1.11_5$ | 39.1 | | | |
| Acetone (AC) | | 1.13 [22] | 20.7 | 2.88 | 17.0 | 12.5 |
| Methanol (MeOH) | $1.13_4$ | $1.13_3$ | 32.6 | 1.70 | 19 | 41.3 |
| Ethanol (EtOH) | $1.13_4$ | $1.13_8$[a] | 24.6 | 1.69 | | 37.1 |
| N,N-dimethylformamide (DMF) | $1.12_7$ | 1.13 [37, 38] | 36.1 | 3.82 | 26.6 | 16.0 |
| N-methylpyrrolidinone(2) (NMP) | $1.12_6$ | $1.12_7$ | 32 | 4.09 | 27.3 | 13.3 |
| Dimethylsulfoxide (DMSO) | $1.12_3$ | $1.12_3$ [37, 38] | 45 | 3.96 | 29.8 | 19.3 |
| Tetramethylene sulfone (TMS) | $1.11_4$ | – | 42.0 | 4.81 | 14.8 | |

[a] 0.1 molar tetra-n-butylammonium perchlorate. [b] Saturated solution of tetraethylammonium perchlorate. [c] 0.02 molar tetraethylammonium perchlorate. [d] $\epsilon$ = Dielectric constant. [e] $\mu$ = Dipole moment. [f] DN = Donor number. [g] AcN = Acceptor number.

TABLE III. Calculated Molar Gibbs Free Energies of Transfer in kJoules gIon$^{-1}$ for Alkali Metal Ions and $Tl^+$ Based on the Bisbiphenylchromium Assumption. Reference Solvent: Acetonitrile.

| | DN[a] | $\epsilon$[b] | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ | $Tl^+$ |
|---|---|---|---|---|---|---|---|---|
| N,N-dimethylthioformamide (DMFT) | | 47.8 | +22.2 | +20.3 | n.a. | n.a. | n.a. | −29.9 |
| N-methylthiopyrrolidinonc(2) (NMTP) | | 47.5 | +16.4 | +16.4 | +16.4 | +12.5 | n.a. | −31.8 |
| Benzylfluoride (BF) | 2.0 | 22.7 | n.a. | n.a. | n.a. | n.a. | n.a. | +6.8 |
| Nitromethane (NM) | 2.7 | 35.9 | n.a. | n.a. | n.a. | n.a. | n.a. | +6.8 |
| Nitrobenzene (NB) | 4.4 | 34.8 | n.a. | n.a. | n.a. | n.a. | n.a. | +5.8 |
| Benzonitrile (BN) | 11.9 | 25.2 | +6.8 | +6.8 | +5.8 | +3.8 | +4.8 | n.a. |
| Acetonitrile (AN) | 14.1 | 38.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Propylenecarbonate (PC) | 15.1 | 69.0 | −4.8 | +2.9 | +1.0 | −1.0 | −1.0 | +3.9 |
| Butyrolactone (BL) | | 39.1 | −13.5 | −4.8 | −3.9 | −3.9 | −3.9 | −6.8 |
| Ethylene sulfite (ES) | 15.3 | 41.0 | n.a. | n.a. | n a. | n.a. | n.a. | −1.0 |
| Acetone (AC) | 17.0 | 20.7 | n.a. | −9.7 | −5.8 | −7.7 | −5.8 | −6.7 |
| Methanol (MeOH) | 19.0 | 32.6 | −28.0 | −9.7 | −1.9 | −1.0 | +1.0 | n.a. |
| Ethanol (EtOH) | | 24.6 | −25.1 | −4.8 | +3.9 | +3.9 | n.a. | −5.8 |
| Trimethylphosphate (TMP) | 23.0 | 20.6 | n.a. | −24.1 | −13.5 | −12.5 | n.a. | −16.4 |
| N,N-dimethylformamide (DMF) | 26.6 | 36.1 | n.a. | −24.1 | −16.4 | −14.5 | n.a. | −22.2 |
| N-methylpyrrolidinone(2) (NMP) | 27.3 | 32.0 | n.a. | −33.8 | −16.4 | −14.5 | −13.5 | −24.1 |
| N,N-dimethylacetamide (DMA) | 27.8 | 38.9 | n.a. | −25.1 | −17.4 | −13.5 | −13.5 | n.a. |
| Dimethylsulfoxide (DMSO) | 29.8 | 45.0 | n.a. | −24.1 | −17.4 | −14.5 | n.a. | −29.0 |
| N,N-diethylformamide (DEF) | 32.0 | | −56.0 | −26.1 | −18.3 | −14.5 | −14.5 | n.a. |

[a] DN = Donor number. [b] $\epsilon$ = Dielectric constant.

as 0.02 molar solutions of $et_4NClO_4$ showed that the $E_{1/2}$ values are not influenced by varying the concentration of the supporting electrolyte nor by changing from $et_4NClO_4$ to $bu_4NClO_4$. Similar results were recently also obtained in nitromethane [38].

In our experimental set up, designed for minimum leakage between the aqueous and the non aqueous phase it was observed that the phase boundary potential in a given experiment changed very little with time. The $E_{1/2}$ of $BBCr^+$ *versus* the aqueous KCl

TABLE IV. A Comparison of Gibbs Free Energies of Transfer in kJoules gIon$^{-1}$ for Alkali Metal Ions and Tl$^+$ Based on the Tetraphenylarsonium Tetraphenylborate Assumption and Data Calculated in this Paper. Reference Solvent: Acetonitrile.

| Solvent | Methanol | | | | Dimethylformamide | | | |
|---|---|---|---|---|---|---|---|---|
| Ion | Ref. 7 | This Work | Ref. 40 | Δ[a] | Ref. 7 | This Work | Ref. 40 | Δ |
| Li$^+$ | −25.9 | −28.0 | n.a. | 2.1 | −39.3 | n.a. | n a. | |
| Na$^+$ | −5.4 | −9.7 | −5.3 | 4.3 | −24.3 | −24.1 | −22.8 | −0.2 |
| K$^+$ | +2.1 | −1.9 | +2.3 | 4.0 | −17.6 | −16.4 | −17.7 | −1.2 |
| Rb$^+$ | +3.3 | −1.0 | +3.4 | 4.3 | −16.7 | −14.5 | −17.1 | −2.2 |
| Cs$^+$ | +4.6 | +1.0 | +4.6 | 3.6 | −14.2 | n.a. | −14.3 | |
| Tl$^+$ | −5.0 | n.a. | −5.1 | | −20.5 | −22.2 | −20.6 | −1.7 |
| | Dimethylsulfoxide | | | | N-Methylpyrrolidinone(2) | | | |
| Li$^+$ | −44.4 | n.a. | n.a. | | n.a. | n.a. | | |
| Na$^+$ | −27.6 | −24.1 | −27.4 | −3.5 | −30.1 | −33.8 | | +3.7 |
| K$^+$ | −20.1 | −17.4 | −20.0 | −2.7 | −21.7[b] | −16.4 | | −5.3 |
| Rb$^+$ | −17.6 | −14.5 | −17.7 | −3.1 | −16.7 | −15.5 | | −1.2 |
| Cs$^+$ | −17.6 | n.a. | −17.7 | | n.a. | −13.5 | | |
| Tl$^+$ | −29.7 | −29.0 | −29.7 | −0.7 | n.a. | −24.1 | | |
| | Propylenecarbonate | | | | | | | |
| | Ref. 7 | This Work | Δ | | | | | |
| Li$^+$ | −5.8 | −4.8 | −1.0 | | | | | |
| Na$^+$ | +1.3 | +2.9 | −1.6 | | | | | |
| K$^+$ | −2.1 | +1.0 | −3.1 | | | | | |
| Rb$^+$ | −9.6 | −1.0 | −8.6 | | | | | |
| Cs$^+$ | −17.2 | −1.0 | −16.2 | | | | | |
| Tl$^+$ | −1.3 | +3.9 | −5.2 | | | | | |

[a] Δ = Difference between $\Delta G^\circ_{tr}$ from Ref. 7 and data collected in this work. [b] 26.0 according to Ref. 17.

saturated Ag/AgCl electrode served as an indicator. Variations of this value in independent experiments however have been observed. In this study values between −0.694 V and −0.703 V were obtained from eight independent experiments in EtOH (average value −0.696 V, standard deviation 4 mV) *versus* the above mentioned aqueous electrode. The values in BL ranged from −0.678 to −0.692 V (six experiments, average value −0.685 V, standard deviation 5 mV) and from −0.662 V to −0.697 V in AN (ten experiments, average value −0.681 V, standard deviation 10 mV). Although reasonable agreement of the $E_{1/2}$ values of BBCr$^+$ *versus* the aqueous reference electrode has been frequently observed within a series of measurements, an examination of the data collected in this laboratory has shown that variations as great as 0.1 V occurred in various solvents including AN [36]. The phase boundary potential between the aqueous and the non aqueous phase is a poorly defined quantity [12] and an aqueous reference electrode without a suitable combination of salt bridges should not be used as a reference electrode for reporting polarographic $E_{1/2}$ in non aqueous solvents. The use of a reference redox system such as BBCr$^+$ or ferrocene is strongly recommended.

## Discussion

Molar Gibbs free energies of transfer ($\Delta G^\circ_{tr}$) calculated on the basis of the BBCr assumption are listed in Table III. The $\Delta G^\circ_{tr}$ values in a given solvent show a general shift to more positive values in going from Li$^+$ to Cs$^+$. Acetonitrile was chosen as a reference solvent; a solvent that has been previously selected as a reference solvent [3]. Water, another commonly used reference solvent, could not be employed since the reduction of BBCr$^+$ in water is overlapped by adsorption phenomena of both the oxidized and the reduced form. Furthermore BBCr$^0$ is insoluble in water [39].

A comparison of the data calculated in this paper with recently reported data employing the tetraphenylarsonium tetraphenylborate assumption (TPAs TPB) is given in Table IV. Excellent agreement is observed in several cases. About 5 kJoules gIon$^{-1}$ is the presently accepted variation of data obtained by employing different extrathermodynamic assumptions [3]. Discrepancies in $\Delta G^\circ_{tr}$ values of more than 5 kJoules gIon$^{-1}$ exist for Rb$^+$ and Cs$^+$ in PC. The dramatic variation in $\Delta G^\circ_{tr}$ values for K$^+$, Rb$^+$ and Cs$^+$ as obtained on the basis of the TPAsTPB assumption in PC seems unlikely and a reestimation of these data in PC may well be necessary.

It is of considerable interest to search for a correlation of the $\Delta G^\circ_{tr}$ values with solvent parameters. Born's theory employing purely electrostatic considerations predicts a dependence of the $\Delta G^\circ_{tr}$ values on the reciprocal of the dielectric constant. No such correlation can be found in the data presented, not even for a given ion. Expanded models including ion–dipole, ion–quadrupole and induced dipole interactions have been developed for water as a solvent. Although very good agreement between calculated and experimental data has been obtained, assumptions still had to be made about the solvation sphere and the interactions of the solvent molecules [41]. Such information is not available for most non aqueous solvents. The method of adjusting ion size parameters, however, requires experimental data [42] not presently available for non aqueous solvents.

A good general relationship exists between the $\Delta G^\circ_{tr}$ for a given ion and the donor number. The donor number, an empirical parameter derived from the $\Delta H$ value of the reaction of a solvent with $SbCl_5$ in 1.2 dichloroethane, has already been successfully employed to describe Lewis type donor interactions of solvents [43]. In case of hard–hard interactions it can be said in a general way that the greater the donor number of the solvent the more negative the $\Delta G^\circ_{tr}$ value. There are of course some deviations since entropy contributions are not in all cases small enough to allow a direct comparison of a $\Delta H$ term with a $\Delta G$ term. The observed correlation, however, strongly suggests a treatment of ion–solvent interactions within the concept of extended Lewis type acceptor–donor interactions rather than on electrostatic principles. Solvent parameters obtained from interactions of the solvent with a suitable model substance should be preferred over physical parameters obtained from the pure solvent [43–45].

Two of the solvents, namely DMTF and NMTP, exhibit their donor properties via the sulfur atom in the molecules and can therefore be classified as soft donor solvents [46]. This finds its expression in the large positive $\Delta G^\circ_{tr}$ values for the alkali metal ions compared to the negative $\Delta G^\circ_{tr}$ value for $Tl^+$.

Unfortunately donor numbers for hard–soft interactions such as the interaction of the alkali metal ions with the two solvents are not yet available. Soft interactions will have to be treated separately within the framework of donor–acceptor interactions and empirical solvent parameters will have to be obtained.

Each experimental method in obtaining $\Delta G^\circ_{tr}$ values for single ions has its advantages and its disadvantages. Polarographic and voltammetric procedures in connection with a reference redox system yield, once such methods have been established at a laboratory, readily obtainable results. It is however necessary that polarographically reversible electrode reactions or at least nearly reversible reactions occur to allow the calculation of $\Delta G^\circ_{tr}$ from $E_{1/2}$. The necessity of employing a supporting electrolyte – usually 0.1 molar solutions – affects the activity coefficient of the species studied. Care must also be taken that no complex formation between the supporting electrolyte and the ion studied occurs. Ion pair formation of alkali metal perchlorates, if any, was found negligible [52, 54]. The supporting electrolyte affects the activity coefficient of both the metal ions studied and the $BBCr^+$, thus largely cancelling the effect of the supporting electrolyte on the activity coefficient in calculating $\Delta G^\circ_{tr}$ values. For the ions studied the effect of ion pair formation and the activity coefficient should be less than 1 kJoule $gIon^{-1}$.

The alkali metal ions and $Tl^+$ have been studied by independent research groups at various times in several solvents by polarographic methods [48–54]. $Rb^+$ was found to be an ion studied by many of them. Data with respect to $Rb^+$ – one of the earliest extrathermodynamic assumptions [32] – are summarized in Table V. In most cases the data agree within 0.01 V, with some data differing by 0.02 V and only few by 0.03 Volts. This variation in $E_{1/2}$ converted to kJoules $gIon^{-1}$ would cause variations of 0.9, 1.8 and 2.7 kJoules $gIon^{-1}$, respectively. This agreement is very good considering that the data were collected over a reasonably long time period in which polarographic techniques changed considerably. Starting with a two electrode system and separate measurements of the reference redox system, the procedures have advanced to using a three electrode system with a simultaneous determination of the reference redox system. The comparison of data shown in Table V does add confidence to the $E_{1/2}$ values reported in Table I although occasional errors in the $E_{1/2}$ in earlier studies caused by not making simultaneous measurements of the ions studied and the reference redox system could have occurred.

The difference in $E_{1/2}$ values between $BBCr^+$ and ferrocene ($\Delta E_{1/2}$) should be constant within the limits of experimental error. The observed deviation of ± 12 mV from the average value of 1.124 V is somewhat larger than the experimental error of ± 4 mV. No relation was found between the $\Delta E_{1/2}$ values and any of the following solvent parameters: dielectric constant, dipole moment, donor number [43] and acceptor number [55]. It is felt that these small variations must be due to specific solute–solvent interactions not accessible by general solvent parameters. It is largely $\pi$-type bonding between the chromium in the formal oxidation states of +I and 0 respectively and one of the rings each of the bisbiphenyl molecules that forms the two partners of this reference redox system. Any effect due to the

TABLE V. A Comparison of $E_{1/2}$ of Alkali Metal Ions and $Tl^+$ in Five Solvents Employing $Rb^+/Rb(Hg)$ as a Reference Redox System.

| Solvent | Acetonitrile (AN) | | | | Benzonitrile (BN) | | | Acetone (AC) | |
|---|---|---|---|---|---|---|---|---|---|
| Ion | Ref. 51 | Ref. 24 | Ref. 54 | This Work | Ref. 59 | Ref. 51 | Ref. 24 | Ref. 51 | Ref. 22 |
| $Li^+$ | +0.03 | +0.03 | 0.00 | +0.02 | +0.06 | +0.06 | +0.05 | n.a. | −0.10 |
| $Na^+$ | +0.13 | +0.12 | +0.11 | +0.10 | +0.12 | +0.14 | +0.13 | +0.07 | +0.07 |
| $K^+$ | +0.02 | +0.02 | +0.01 | 0.00 | n.a. | n.a. | +0.02 | 0.00 | +0.02 |
| $Rb^+$ | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $Cs^+$ | +0.01 | +0.02 | +0.02 | +0.01 | n.a. | n.a. | +0.02 | n.a. | +0.03 |
| $Tl^+$ | +1.71 | n.a. | n.a. | +1.70 | n.a. | | n.a. | n.a. | +1.71 |

| | Methanol (MeOH) | | Ethanol (EtOH) | |
|---|---|---|---|---|
| | Ref. 48 | Ref. 24 | Ref. 48 | This Work |
| $Li^+$ | −0.27 | −0.26 | −0.27 | −0.28 |
| $Na^+$ | +0.02 | +0.01 | +0.03 | +0.01 |
| $K^+$ | −0.01 | −0.01 | 0.00 | 0.00 |
| $Rb^+$ | 0.00 | 0.00 | 0.00 | 0.00 |
| $Cs^+$ | +0.04 | +0.03 | 0.00 | n.a. |
| $Tl^+$ | n.a. | n.a. | n.a. | +1.50 |

$Cr^+$ different from $Cr^0$ should spread over all four rings and thus be very modest. The solvent–solute interaction for this reference redox system should therefore be very small and nearly equal for the oxidized and the reduced form. This assumption is supported by the very low solubility of BBCrTPB in the solvents studied. Although both ferrocene and BBCr represent suitable reference redox systems, for reasons mentioned above BBCr should be slightly the better one. BBCr has also been preferred in this laboratory because the reduction of BBCr occurs at more negative potentials than the oxidation of ferrocene allowing the use of the dropping mercury electrode in all the solvents studied. In DMTF and in NMTP ferrocene could not be used at all since the oxidation of the solvent preceeds the oxidation of ferrocene. In acetic acid [56] and in dichloromethane the electrode reaction of ferrocene was found to be irreversible making ferrocene unsuitable as a reference redox system in these two solvents.

While it has been shown conclusively that $BBCr^+$ cannot be used in water as a reference system such detailed studies for ferrocene are lacking. $\Delta G^\circ_{tr}$ values based on the redox potential for ferrocene in water have shown considerable deviations from data collected by other methods, but good agreement has been obtained when water was omitted as a solvent [57]. Arguments recently put forward about the inadequacy of the ferrocene–ferrocinium assumption for estimating $\Delta G^\circ_{tr}$ values unfortunately are based on water as a solvent [58].

The agreement of the $\Delta G^\circ_{tr}$ data calculated from $E_{1/2BBCr}$ values with the results obtained on the basis of the TPAs–TPB assumption is in most cases as good as or even better than the agreement of other extrathermodynamic assumptions. This shows that the BBCr assumption is an equally acceptable method to study single ion Gibbs free energies of transfer.

Since extrathermodynamic assumptions are necessary in estimating $\Delta G^\circ_{tr}$ values of single ions, it is important that several independent methods of determination are employed. It is hoped that the data obtained on the basis of the BBCr assumption will confirm data obtained by other methods when they agree and cause reconsideration of the data obtained by either method when a discrepancy beyond the variation of 5 kJoules $gIon^{-1}$ occurs.

Careful experiments limit the experimental uncertainty of $\Delta G^\circ_{tr}$ obtained from $E_{1/2}$ to 1 kJoule $gIon^{-1}$. A comparison of $\Delta G^\circ_{tr}$ values obtained from independent methods should then also lead to a better understanding of the systematic errors introduced by the extrathermodynamic assumptions.

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