# Temperature Coefficients of Half-wave Potentials and Entropies of Transfer of Cations in Aprotic Solvents

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Temperature coefficients of polarographic half-wave potentials for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Tl<sup>+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, bis(biphenyl)chromium(i) tetraphenylborate, ferrocene and perylene have been derived from measurements *vs*. Ag/Ag<sup>+</sup> (0.01 mol dm<sup>-3</sup>) electrodes kept at 25 °C in 0.1 mol dm<sup>-3</sup> solutions of tetrabutylammonium perchlorate in dimethyl sulphoxide, *N*,*N*-dimethylformamide, hexamethylphosphoric triamide and propylene carbonate. Entropies for the above mentioned redox couples and for Ag<sup>+</sup> were calculated for reversible electrode reactions on the basis of the assumption of a negligible thermal diffusion potential. This assumption was also employed to calculate single-ion entropies of transfer from *N*,*N*-dimethylformamide into dimethyl sulphoxide, propylene carbonate and hexamethylphosphoric triamide.

Transfer properties, such as Gibbs energies, entropies and enthalpies of transfer, offer a better understanding of solventsolute interactions. Transfer properties of salts and neutral molecules are thermodynamic quantities, which can be obtained from experiment. Gibbs energies of transfer, for instance, can be derived from solubility or electrochemical measurements, and enthalpies of transfer from calorimetric studies. The separation of transfer properties for salts into cation and anion contributions, however, requires extrathermodynamic assumptions. Suitable assumptions and their scientific justification have been discussed in several publications.<sup>1-6</sup> Individual ion contributions for Gibbs energies of transfer were obtained by applying either the reference electrolyte assumption or the reference redox system assumption or the assumption of a negligible liquid-junction potential. The most widely used reference electrolyte is tetraphenylarsonium tetraphenylborate.<sup>5,7</sup>

Bis(biphenyl)chromium(I)/(0)<sup>6,8-10</sup> and to a lesser degree ferrocene/ferrocenium<sup>11</sup> served as reference redox couples.<sup>12</sup> Enthalpies of transfer for cations and anions were almost exclusively derived from the reference electrolyte assumption employing tetraphenylarsonium tetraphenylborate. Entropies of transfer were calculated from the difference of the Gibbs energies and the enthalpies of a given ion.<sup>4,13-22</sup> Such data therefore include the uncertainties of the estimations of the single-ion Gibbs energies and the single-ion enthalpies. Entropies of reactions are directly accessible from the temperature dependence of electrode potentials. Data for singleion transfer entropies from such direct measurements, however, are very scarce. Here we report studies on the temperature dependence of polarographic half-wave potentials of reversible electrode reactions and the calculation of entropies for half-cell reactions, as well as transfer entropies of cations from N,N-dimethylformamide into dimethyl sulphoxide, propylene carbonate and hexamethylphosphoric tramide derived from these investigations. The values are based on the assumption of a negligible thermal diffusion potential between the hot and cold parts of a non-isothermal cell in 0.1 mol dm<sup>-3</sup> solutions of tetrabutylammonium perchlorate in the respective non-aqueous solvents. This assumption was previously used for measuring the entropies of the electrode reactions of Mn<sup>3+</sup>/Mn<sup>2+</sup> couples,<sup>23</sup> metal ion complexes,<sup>23-30</sup> organometallic compounds,<sup>31-33</sup> copper proteins,<sup>34</sup> several aromatic hydrocarbons, heteroaromatic compounds, nitrobenzenes and benzophenones,<sup>35-37</sup> quinones<sup>38</sup> and

semiqinones,<sup>39,40</sup> and recently tetranuclear iron-sulphur cluster compounds,<sup>41</sup> but to our knowledge this assumption has not yet been applied to estimate single-ion transfer entropes.

#### Experimental

#### Materials

All solvents were purified by pre-drying over molecular sieves followed by double distillation under vacuum. The first distillation was performed in the presence of  $CaH_2$  as drying agent. The first and last 15–20% of the solvents was discarded in each distillation.

The alkali-metal perchlorates, as well as  $Ba(ClO_4)_2$  and the trifluoromethane sulphonates of Tl<sup>+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>, were prepared as described elsewhere.<sup>42</sup>

Tetrabutylammonium perchlorate (purum, Fluka) was recrystallized from water. Tetraheptylammonium perchlorate was prepared as described previously.<sup>43</sup> Both tetrabutylammonium perchlorate and tetraheptylammonium perchlorate were dried in vacuum at 60 °C for 24 h. Perylene (>99%, Fluka) was used without further purification.

#### **Apparatus and Procedures**

The preparation of the electrolyte solutions was carried out in a glove box under the exclusion of moisture and oxygen. Polarographic and voltammetric measurements were carried out using a three-electrode arrangement in the cell already published<sup>42</sup> with the use of a UAP4 pulse polarograph in combination with a PRT 30-01 potentiostat (all Tacussel-Solea, France) and a 733 Servogor X-Y recorder (BBC Goerz, Austria). The capillary had flow rates between 0.4648 and 0.4667 mg s<sup>-1</sup> at a mercury column height of 65 cm in the solvents studied. A special reference-electrode compartment, shown in Fig. 1, was used in the experiments, containing a silver wire in contact with a 0.01 mol dm<sup>-3</sup>  $AgCF_3SO_3$  solution in 0.1 mol dm<sup>-3</sup> tetrabutylammonium perchlorate as supporting electrolyte. The top part was thermostatted at  $25.0 \pm 0.05$  °C. The same supporting electrolyte at the same concentration was always used in the reference and the measuring half cell to avoid any liquid-junction potentials. 0.1 mol dm<sup>-3</sup> tetraheptylammonium perchlorate solutions in hexamethylphosphoric triamide were employed for the study of the alkali-metal cations, since the polaro-



Fig. 1 Reference electrode: (a) silver wire, (b) thermistor, (c) sintered aluminium oxide diaphragm

graphic reductions of these cations were irreversible in tetrabutylammonium perchlorate solutions. The compounds of interest were dissolved at concentrations of 0.001 mol dm<sup>-3</sup> in solutions of tetrabutylammonium perchlorate (0.1 mol  $dm^{-3}$ ) in the respective solvents and studied by d.c. and pulse polarography (pulse duration 40 ms, level 50 mV, drop duration 0.6 s, delay 0.5 s, scan rate  $2-5 \text{ mV s}^{-1}$ ) using the following cell:

Connections of the external leads to the mercury and platinum electrodes in cell (A) and to the silver wires in cell (B) were made at 25 °C to avoid the formation of thermocouples. The measurements were performed at 10 °C intervals for the

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temperature range 15-65 °C. The temperature dependence of the potential of the studied redox couple was measured by pulse polarography. The temperatures in both half cells were measured with Pt-100 resistors with an accuracy of 0.05 °C. At the end of each run the measurements were repeated at 25 °C and compared with the initial measurements at 25 °C to check that the potential of the reference cell had not changed. The half-wave potentials for the reduction of bis(biphenyl)chromium(I) and perylene, as well as the oxidation of ferrocene, were also measured using cyclic voltammetry (mercury or platinum electrodes, scan rate  $50-200 \text{ mV s}^{-1}$ ).

The data for the silver/silver(I) couple were obtained from potentiometric measurements in cell (B):

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At least two independent measurements were performed for each data set. The temperature dependence of the half-wave potentials was analysed by linear regression. Correlation coefficients of 0.99 or better were obtained, the standard deviations for the slopes were smaller than 0.02 mV K<sup>-1</sup>. The slopes from independent measurements agreed to within 0.04 mV  $K^{-1}$  or better. This uncertainty in the estimation of the slopes leads to precisions of better than  $\pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$  for monovalent and  $\pm 6 \text{ kJ mol}^{-1}$  for divalent cations in the reaction entropies and  $\pm 0.9$  kJ mol<sup>-1</sup> for monovalent and +1.7 kJ mol<sup>-1</sup> for divalent cations in the 298 $\Delta$ , S<sup>o</sup> values. The reversibility of the electrode reactions was checked by examining  $E_{1/4} - E_{3/4}$  values and the half-widths of the peaks in pulse polarography.

#### Results

Half-wave potentials as well as temperature coefficients derived from measurements vs. the  $Ag/Ag^+$  (0.01 mol dm<sup>-3</sup>) electrode at 25 °C in 0.1 mol dm<sup>-3</sup> solutions of tetrabutylammonium perchlorate in the respective solvents are listed in Table 1. The entropies for the half-cell reactions,  $\Delta_r S^0 = (S^0_{red} - S^0_{ox})$ , are summarized in Table 2. Entropies of

Table 1 Polarographic half-wave potentials (V) at 298 K, measured vs. the  $Ag/Ag^+$  (0.01 mol dm<sup>-3</sup>) electrode, and temperature coefficients (mV K<sup>-1</sup>) in 0.1 mol dm<sup>-3</sup> solutions of tetrabutylammonium perchlorate in several non-aqueous solvents<sup>a</sup>

	DMSO		РС		DMF		НМР	
	E <sub>1/2</sub>	dE/dT	<i>E</i> <sub>1/2</sub>	dE/dT	E <sub>1/2</sub>	dE/dT	<i>E</i> <sub>1/2</sub>	dE/dT
Li <sup>+</sup>	irr	irr	-2.743	1.57	-2.764	2.11		
Na <sup>+</sup>	-2.343	0.85	-2.581	1.09	-2.470	1.11	2.418 <sup>b</sup>	0.78
K *	- 2.343	0.68	-2.694	0.64	-2.500	0.78	2.130 <sup>b</sup>	0.65
Rb <sup>+</sup>	-2.324	0.46	-2.727	0.48	-2.477	0.58	2.280 <sup>b</sup>	0.60
Cs <sup>+</sup>	-2.331	0.24	-2.713	0.31	-2.445	0.36	2.251 <sup>b</sup>	0.51
$Ag^+$	0.000	0.40	0.000	0.37	0.000	0.30	0.000	0.68
TĨ⁺	-0.793	0.73	-1.002	0.75	-0.850	0.86	0.750	0.71
Cu <sup>2+</sup>	с		irr	irr	-0.407	1.85	0.353	0.90
Zn <sup>2+</sup>	irr	irr	irr	irr	-1.412	2.31	irr	irr
Cd <sup>2+</sup>	-0.995	1.58	-0.967	1.80	-0.993	1.92	0.832	1.93
Ba <sup>2+</sup>			-2.434	1.88	-2.425	1.77	2.368	1.53
Pb <sup>2+</sup>	-0.793	1.15	-0.842	1.53	-0.848	1.59	0.732	1.76
<b>B</b> Cr <sup>d</sup>	-0.961	0.46	-1.505	0.43	-1.116	0.63	0.891	0.56
fc <sup>e</sup>	0.171	0.43	-0.377	0.45	0.014	0.62	2.030	0.61
perf	- 1.891	0.20	-2.452	0.00	-2.104	0.00	1.885	0.40

<sup>a</sup> DMSO, dimethyl sulphoxide; PC, propylene carbonate; DMF, N,N-dimethylformamide; HMP, hexamethylphosphoric triamide.<sup>b</sup> 0.1 mol dm<sup>-3</sup> tetraheptylammonium perchlorate; 'Poorly resolved double wave. 'Bis(biphenyl)chromium(1) tetraphenylborate. 'Ferrocene. <sup>f</sup> Perylene. irr: irreversible.

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**Table 2** Molar reaction entropies  $(\Delta_r S^0 = S^0_{red} - S^0_{ox})$  in J K<sup>-1</sup> mol<sup>-1</sup> from half-wave potentials of reversible electrode reactions based on the assumption of a negligible thermal diffusion potential in several non-aqueous solvents<sup>*a*</sup>

	DMSO	PC	DMF	НМР
Li <sup>+</sup>		151	204	
Na <sup>+</sup>	82	105	107	72
Κ+	66	62	75	63
Rb⁺	44	46	56	58
Cs <sup>+</sup>	23	30	35	49
Ag <sup>+</sup>	39	36	32	66
TĨ⁺	70	72	83	69
Cu <sup>2+</sup>			357	174
Zn <sup>2+</sup>			446	
Cd <sup>2+</sup>	305	347	371	372
Ba <sup>2+</sup>		363	342	295
Pb <sup>2+</sup>	222	295	307	340
BCr <sup>b</sup>	44	41	61	54
fc <sup>c</sup>	41	43	60	59
per <sup>d</sup>	19	0	0	39

<sup>a</sup> Abbreviations of solvents are given in Table 1. <sup>b</sup> Bis(biphenyl) chromium(1) tetraphenylborate. <sup>c</sup> Ferrocene. <sup>d</sup> Perylene.

transfer were calculated from the slopes with N,N-dimethylformamide as reference solvent and are given as  $298\Delta_t S^0$  in Table 3 following common practice for transfer entropies.

## Discussion

Polarographic half-wave potentials for reversible electrode reactions are related to standard electrode potentials by the following equation:<sup>44</sup>

$$E_{1/2} = E^0 + (RT/nF)\ln(f_{ox}/f_{red})$$
$$- (RT/2nF)\ln(D_{ox}/D_{red})$$

Temperature coefficients of polarographic half-wave potentials of reversible electrode processes are the same as for standard electrode potentials, provided that the ratios (not the individual values) of the activity coefficients of the oxidized and the reduced forms of the redox couple and the ratios of the diffusion coefficients of the oxidized and the reduced species do not change with temperature. Since changes in the ratios are unlikely, the temperature dependence of the halfwave potentials will be employed to calculate reaction entropies. 2601

The measured temperature coefficients  $dE_{1/2}/dT$  across the non-isothermal cells (A) and (B) consist of the temperature coefficients of the Galvani potentials of the redox couple under study ( $dE_G/dT$ ), of the potential across the hot and cold parts of the mercury working electrode (Thomson effect,  $dE_T/dT$ ) and of the thermal diffusion potential across the hot and cold parts of the electrolyte solution (Soret effect,<sup>45</sup>  $dE_s/dT$ ).

$$\mathrm{d}E_{1/2}/\mathrm{d}T = \mathrm{d}E_{\mathrm{G}}/\mathrm{d}T + \mathrm{d}E_{\mathrm{T}}/\mathrm{d}T + \mathrm{d}E_{\mathrm{S}}/\mathrm{d}T$$

The Thomson effect in the temperature range 0–100 °C was calculated to be 14  $\mu$ V K<sup>-1</sup> for mercury and 6  $\mu$ V K<sup>-1</sup> for platinum.<sup>23</sup> This contribution is well below experimental error. The neglect of the Thomson effect is therefore fully justified. Although only relative rather than absolute values for  $dE_s/dT$  are available from studies in aqueous solutions, estimation of the Soret effect yielded values <50  $\mu$ V K<sup>-1</sup>, and probably even smaller than 20  $\mu$ V K<sup>-1</sup>.<sup>23,46-50</sup> Such contributions are well below the experimental precision and can be neglected. It is this neglect of the Soret effect, which forms the basis for the extra-thermodynamic assumption, by the very nature of extra-thermodynamic assumptions, escapes proof or disproof. Following the arguments mentioned before, reaction entropies for half-cell reactions are calculated from:

$$nF(dE^{0}/dT) = -S^{0}(M^{z+}) + S^{0}(M^{(z-n)+})$$
$$= (S^{0}_{red} + S^{0}_{ox})$$
$$= \Delta_{r}S^{0}$$

The  $\Delta_r S^0$  values for the redox couples studied show the following sequence:

$$\begin{array}{l} Zn^{2+} > Cd^{2+} > Cu^{2+} > Ba^{2+} > Pb^{2+} > Li^+ > \\ Na^+ > Tl^+ > K^+ > Rb^+ > Cs^+ \approx Ag^+ \end{array}$$

The entropy for the reduction of perylene to the monovalent radical anion in N,N-dimethylformamide has been reported to be  $-10 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273 K<sup>36</sup> in 0.1 mol dm<sup>-3</sup> Bu<sub>4</sub>NBF<sub>4</sub>, whereas we found a value of zero. Entropies for the oxidation of ferrocene have been measured before and found to be 59<sup>31</sup> and 52<sup>41</sup> J K<sup>-1</sup> mol<sup>-1</sup> in N,N-dimethylformamide and 52<sup>31</sup> and 45<sup>41</sup> J K<sup>-1</sup> mol<sup>-1</sup> in dimethyl sulphoxide. Our data are 60 J K<sup>-1</sup> mol<sup>-1</sup> for N,N-dimethylformamide and 41 J K<sup>-1</sup> mol<sup>-1</sup> for dimethyl sulphoxide. Although some of the entropies of reaction for the above mentioned systems were obtained from measurements

**Table 3** Molar  $298\Delta_t S^0$  values (kJ mol<sup>-1</sup>) from N,N-dimethylformamide as reference solvent, based on the assumption of a negligible thermal diffusion potential in several non-aqueous solvents<sup>a</sup> together with literature data derived from the tetraphenylarsonium tetraphenylborate assumption

	DMSO			PC		HMP	
	this work	li	t.	this work	lit.	this work	lit.
Li <sup>+</sup>		12.5 <sup>b</sup>	10.8°	15.5	2.5°		
Na <sup>+</sup>	7.5	9.8*	8.7°	0.6	0.8 <sup>c</sup>	9.5	
K +	2.9	7.6*	7.1°	4.0	2.9 <sup>c</sup>	3.7	-11.5°
Rb <sup>+</sup>	3.5	6.1 <sup>b</sup>	5.0°	2.9	7.1°	-0.6	
Cs <sup>+</sup>	3.5	6.1 <sup>b</sup>	7.9°	1.4	13.8°	-4.3	
Ag <sup>+</sup>	-2.9	0.0 <sup>c</sup>		-2.0	-7.1°	-10.9	
TI <sup>+</sup>	3.7			3.2		4.3	
Cu <sup>2+</sup>						54.6	
Zn <sup>2+</sup>		19.8 <sup>d</sup>					$-10.6^{d}$
Cd <sup>2+</sup>	19.6	12.6 <sup>d</sup>		6.9		-0.6	-44.5 <sup>d</sup>
Ba <sup>2+</sup>		10.8 <sup>d</sup>		-6.3		13.8	
Pb <sup>2+</sup>	25.3			3.5		-9.8	

<sup>a</sup> Abbreviations of solvents are given in Table 1. <sup>b</sup> Ref. 14. <sup>c</sup> Ref. 15. <sup>d</sup> Ref. 16.

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vs. aqueous reference electrodes and thus included liquidjunction potentials between the aqueous and non-aqueous phase,<sup>31</sup> agreement to within 10 J K<sup>-1</sup> mol<sup>-1</sup> is observed. This agreement between different research groups employing different electrochemical techniques and different supporting electrolytes is within the order of the experimental precision and thus surely supports confidence in the obtained entropy data.

Entropies for the reduction of bis(biphenyl)chromium(I) tetraphenylborate in tetraethylammonium perchlorate solutions were reported to be 96 J K<sup>-1</sup> mol<sup>-1</sup> in N,N-dimethyl-formamide, 85 J K<sup>-1</sup> mol<sup>-1</sup> for propylene carbonate and 96 J K<sup>-1</sup> mol<sup>-1</sup> for dimethyl sulphoxide.<sup>30</sup> These data are considerably greater than the values measured by us (61 J K<sup>-1</sup> mol<sup>-1</sup> in N,N-dimethylformamide, 41 J K<sup>-1</sup> mol<sup>-1</sup> in propylene carbonate and 44 J K<sup>-1</sup> mol<sup>-1</sup> in dimethyl sulphoxide), and also greater than the reaction entropies reported for ferrocene and di(benzene)chromium. In view of the good agreement observed for the reaction entropies for ferrocene and bis(biphenyl)chromium in this study, we feel that our data are more reliable than the previously published values.

Transfer entropies for single ions can be obtained from the differences in the reaction entropies *via* the following relation:

$$\Delta_{t} S^{0} = (S^{0}_{red} - S^{0}_{ox})_{S} - (S^{0}_{red} - S^{0}_{ox})_{R}$$
$$= (\Delta_{t} S^{0})_{R} - (\Delta_{t} S^{0})_{S}$$

where the subscript S represents the solvent and R the reference solvent, in this case N,N-dimethylformamide. The entropies of the reduced forms are the entropies of the respective metal amalgams. These values are independent of the nature of the solvent, their difference equals zero. Since entropies of transfer are calculated from the difference of the temperature coefficients for a given electrode reaction in two solvents, contributions of the Thomson effect cancel and contributions from the Soret effect should at least partially cancel. The precision of the entropies of transfer for cations should therefore be better than the precision of the reaction entropies.

The entropies of transfer for the cations were converted to 298 $\Delta$ , S<sup>o</sup> values and compared with literature data obtained from differences of  $\Delta_t H^0$  and  $\Delta_t G^0$  obtained from the tetraphenylarsonium tetraphenylborate assumption. Surprisingly good agreement was found for the entropies of transfer into dimethyl sulphoxide and for most of the cations into propylene carbonate. The data for monovalent cations in diemethylformamide and for Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Ag<sup>+</sup> in propylene carbonate agree to within 5 kJ mol<sup>-1</sup>. Considering that  $\Delta_t G^0$  and  $\Delta_t H^0$  values obtained by different research groups may each differ by 5 kJ  $mol^{-1}$  and more, the good agreement of our data with the literature values is very encouraging. Discrepancies were observed for Li<sup>+</sup> and Cs<sup>+</sup> in propylene carbonate and for the two data points available for hexamethylphosphoric triamide, namely for  $K^+$  and Cd<sup>2+</sup>. The disagreement for hexamethylphosphoric triamide must be assigned to the difficulties in measuring enthalpies in this solvent, owing to the very slow dissolution rates.<sup>16</sup> The results of this study clearly show that measurements of the temperature dependence of half-wave potentials of reversible systems offer an alternative method for obtaining single-ion transfer entropies.

Financial support by the Fonds zur Förderung der wissenschaftlichen Forschung (Austria) is gratefully acknowledged. A.L. thanks the Austrian Ministry of Science and Research for the invitation to work at the Johannes Kepler University.

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