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# Thermodynamic Parameters for the Transfer of Ions From Water to Propylene Carbonate

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There are large discrepancies between various recorded values for the free energy of transfer of the alkali metal cations from water to propylene carbonate. Using the known enthalpies of transfer given by *Krishnan* and *Friedman*, and the entropy correlation introduced by *Abraham*, these discrepancies are resolved in favour of the values obtained by *Courtot-Coupez et al.* and those due (indirectly) to *Gritzner*. This enables, for the first time, a reasonably reliable set of free energies, entropies, and enthalpies of transfer to be constructed.

*(Keywords: Free energies, enthalpies, and entropies of transfer; Ions, thermodynamic of transfer; Propylene carbonate; Transfer of ions)*

*Thermodynamische Parameter für die Übertragung von Ionen von Wasser in Propylencarbonat*

Die verschiedenen veröffentlichten Werte für die freie Enthalpie der Übertragung von Alkalimetallkationen von Wasser in Propylencarbonat zeigen große Unstimmigkeiten. Diese Unstimmigkeiten können zugunsten der Werte von *Courtot-Coupez* et al. und der (indirekten) von *Gritzner* behoben werden, wenn man die bekannten Werte für die Übertragungsenthalpie von *Krishnan* und *Friedman*, und die von *Abraham* eingeführte Entropiekorrelation benützt. Es ist nun zum ersten Mal möglich, relativ zuverlässige Werte für die freie Energie, Entropie und Enthalpie auszuarbeiten.

## Introduction

Although propylene carbonate (*PC*) is a well-known dipolar aprotic solvent[1], there is as yet no accepted set of free energy data for ions in this solvent. *Gritzner*[2] has recently determined single-ion free energies of transfer from acetonitrile (*AN*) to a number of solvents, including *PC*, and has pointed out that there are considerable discrepancies between his results and previous work for transfer of the ions $Rb^+$ and $Cs^+$. These

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discrepancies must be due to errors in the determinations in *PC*, because it has been known for many years that similar anomalies occur in the transfer of $Rb^+$ and $Cs^+$ from water to *PC*[3]. *Gritzner*'s values for the *AN* to *PC* transfer may be combined with the well-established[4–7] values for transfer from water to *AN*, to yield another set of values for the water to *PC* transfer (Table 1). This set may be compared with the more important sets previously reported[3,6,8–14], all recalculated to the mol fraction scale and with $\Delta G_t^\circ(\mathrm{Br}^-)$ set equal to 7.4 kcal mol⁻¹*. Values reported by *Matsuura* and *Umemoto*[12] are not in accord with those of any other workers. The remaining sets fall into two groups—those of *Salomon*[9] and *Parker*[6] in which $\Delta G_t^\circ(\mathrm{Rb}^+) = -3.0$ and $\Delta G_t^\circ(\mathrm{Cs}^+) = -5.0$ kcal mol⁻¹, and those of *Courtot-Coupez* et al.[3,11,13] where $\Delta G_t^\circ(\mathrm{Rb}^+) = -1.6$ and $\Delta G_t^\circ(\mathrm{Cs}^+) = -2.0$ kcal mol⁻¹. The indirect values of *Gritzner*[2] agree well with those of *Courtot-Coupez* for the alkali metal cations. Although values of $\Delta G_t^\circ(\mathrm{B}Ph_4^-)$ in Table 2 are not very consistent, a recent study by *Kim*[15] yields for $\Delta G_t^\circ(Ph_4\mathrm{As}^+ + Ph_4\mathrm{B}^-)$ a value of —18.9 kcal mol⁻¹, after conversion to the mol fraction scale, in excellent agreement with *Parker*'s value[6] of —18.8 kcal mol⁻¹.

Table 1. *Free energies of transfer of Ions relative to* $Na^+$, *in kcal mol*⁻¹ *at 298 K*

| Ion | Water → *AN* [ref.[4–7]] | *AN* → *PC* [ref.[2]] | Water → *PC*[a] |
|---|---|---|---|
| $Li^+$ | 3.8 | —1.8 | 2.0 |
| $Na^+$ | 0.0 | 0.0 | 0.0 |
| $K^+$ | —1.4 | —0.5 | —1.9 |
| $Rb^+$ | —1.8 | —0.9 | —2.7 |
| $Cs^+$ | —2.1 | —0.9 | —3.0 |
| $Tl^+$ | —1.1 | 0.2 | —0.9 |

[a] Calculated form the previous two columns.

## Results and Discussion

There seems no obvious way of choosing between the various sets of values in Table 2 from the free energy data alone. There is, however, available a self-consistent set of ionic enthalpies of transfer[16], so that if

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* 1 cal = 4.184 J; the value of 7.4 kcal mol⁻¹ has been chosen so that the single-ion free energies of transfer are compatible with the calculated entropies (see later).

Table 2. *Free energies of transfer of ions from water to PC, on the mol fraction scale in kcal mol*$^{-1}$ *at 298 K*[a]

| Ion | *Kuznetsov*[8] (1969)[b] | *Salomon*[9] (1970) | *Butler*[10] (1971) | *Courtot-Coupez*[3,11] (1971/72) | *Parker*[6] (1974) | *Matsuura*[12] (1974) | *Courtot-Coupez*[13] (1974/75) | *Salomon*[14] (1975/76) | *Gritzner*[2] (1977)[b,c] |
|---|---|---|---|---|---|---|---|---|---|
| $Li^+$ | 3.2 | 3.6 | 3.1 | 3.6 | 3.6 | −0.6 | 3.0 | | 3.1 |
| $Na^+$ | 1.1 | 1.2 | 0.5 | 1.0 | 1.5 | −2.3 | 1.1 | | 1.1 |
| $K^+$ | −0.7 | −1.0 | −0.9 | −1.0 | −0.7<br>(−1.5)[d] | −4.0 | −1.0 | | −0.8 |
| $Rb^+$ | −1.2 | −3.1 | | −1.7 | −2.8 | −3.6 | −1.5 | | −1.6 |
| $Cs^+$ | −1.6 | −5.2 | | −2.2 | −5.0 | −3.7 | −2.0 | | −1.9 |
| $Tl^+$ | | | | | 0.4 | −3.6 | −1.2 | | 0.2 |
| $Ag^+$ | | | | 2.2 | 1.7 | −2.3 | 2.3 | 2.1 | |
| $Ph_4As^+$ | | | | | −10.6 | | | | |
| $Cl^-$ | | 9.4 | 9.9 | 10.0 | 9.3 | 9.5 | 10.2 | 10.1 | |
| $Br^-$ | | 7.4 | | 7.4 | 7.4 | 7.4 | 7.4 | 7.4 | |
| $I^-$ | | 4.7 | | 4.1 | 4.5 | 4.6 | 3.6, 4.1 | 2.5, 4.1 | |
| $Ph_4B^-$ | | | −9.7 | | −8.2 | | −10.5 | | |

[a] Where necessary, recalculated from the molar or molal scale, and expressed relative to a value of 7.4 for $Br^-$.

[b] Relative to a value of 1.1 for $Na^+$.

[c] From Table 1.

[d] *D. A. Owensby*, *A. J. Parker*, and *J. W. Diggle*, J. Amer. Chem. Soc. **96**, 2682 (1974).

**Table 3.** *Calculation of entropies of transfer (in cal $K^{-1}$ $mol^{-1}$) and free energies of transfer (in kcal $mol^{-1}$) from water to PC, on the mol fraction scale at 298 K*

| Ion | $I_w^{a}$ | $\Delta S_t^{o\,b}$ | $\Delta H_t^{o\,c}$ | $\Delta G_t^{o\,d}$ |
|---|---|---|---|---|
| $Li^+$ | —15 | —9 | 0.73 | 3.4 |
| $Na^+$ | —12 | —12 | —2.44 | 1.1 |
| $K^+$ | —9 | —15 | —5.24 | —0.8 |
| $Rb^+$ | —10 | —14 | —5.87 | —1.7 |
| $Cs^+$ | —11 | —13 | —6.40 | —2.5 |
| $Ag^+$ | —9[e] | —15 | —2.30[f] | + 2.2 |
| $Me_4N^+$ | —27 | + 3 | —3.89 | —4.8 |
| $Et_4N^+$ | —42 | 18 | + 0.17 | —5.2 |
| $Pr_4N^+$ | —58 | 34 | 2.79 | —7.3 |
| $Bu_4N^+$ | —71 | 47 | 4.39 | —9.6 |
| $Cl^-$ | —12 | —12 | 6.31 | 9.9 |
| $Br^-$ | —10 | —14 | 3.24 | 7.4 |
| $I^-$ | —9 | —15 | —0.78 | 3.7 |
| $ClO_4^-$ | —9 | —15 | —3.93 | 0.5 |

[a] From ref.[4]. [b] Calculated from equation (1) with $E = -24$. [c] From ref.[16]. [d] From the $\Delta S_t^o$ and $\Delta H_t^o$ values in the previous two columns. [e] Ref.[18]. [f] From data given in ref.[6].

the corresponding entropies could be obtained, a set of free energies of transfer could be calculated and compared with those in Table 2. Some years ago[4], I showed that single-ion entropies of transfer from water to a variety of solvents could be correlated through equation (1),

$$\Delta S_t^o(\text{Ion}) = E - I_W \tag{1}$$

and more recent work[17, 18] has confirmed the usefulness of this equation. In (1), $E$ is a constant for a given solvent, and $I_W$ is a constant for a given ion; values of $I_W$ are known for a large number of ions[4, 18] and are given in Table 3. Since there is good agreement between various workers on values of $\Delta G_t^o$ for the ions $Li^+$, $Na^+$, $K^+$, $Cl^-$ and $Br^-$, it is possible to obtain $\Delta S_t^o$ values for these ions and to deduce the value of $E$ for *PC* in equation (1). It is found that $E = -24$ cal $K^{-1}$ $mol^{-1}$, using data for the 5 ions above. Then knowing the value of $E$, equation (1) can be used in reverse to deduce $\Delta S_t^o$ values for the other ions. Then combination with the known $\Delta H_t^o$ values[16] will yield a set of $\Delta G_t^o$ values that should be reasonably self-consistent; details of these calculations are in Table 3. It is immediately clear that the deduced values of $\Delta G_t^o$ are in excellent agreement with the observed values of *Courtot-Coupez*[3, 11, 13] and of *Gritzner*[2], so that an unambiguous choice can be made with respect to the conflicting values for $Rb^+$, $Cs^+$, and to some extent $Ag^+$ and $I^-$.

Table 4. *Comparison of calculated and observed free energies of transfer from water to PC, on the mol fraction scale in kcal mol*$^{-1}$ *at 298 K*

| Ion | Calc.[a] | *Courtot-Coupez*[3,11,13] | *Gritzner*[2] |
|---|---|---|---|
| $Li^+$ | 3.4 | 3.3 | 3.1 |
| $Na^+$ | 1.1 | 1.1 | 1.1 |
| $K^+$ | —0.8 | —1.0 | —0.8 |
| $Rb^+$ | —1.7 | —1.6 | —1.6 |
| $Cs^+$ | —2.5 | —2.1 | —1.9 |
| $Ag^+$ | + 2.2 | + 2.2 | |
| $Cl^-$ | 9.9 | 10.1 | |
| $Br^-$ | 7.4 | 7.4 | |
| $I^-$ | 3.7 | 3.9 | |

[a] Table 3.

Table 5. *Transfer of ions from water to PC using the* $Ph_4As^+/Ph_4B^-$ *assumption, on the mol fraction scale*[a] *at 298 K*

| Ion | $\Delta G_t^\circ$/kcal mol$^{-1}$[b] | $\Delta H_t^\circ$/kcal mol$^{-1}$[c] | $\Delta S_t^\circ$/cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| $Li^+$ | 4.6 | 0.73 | —13.0 |
| $Na^+$ | 2.3 | —2.44 | —15.9 |
| $K^+$ | 0.4 | —5.24 | —18.9 |
| $Rb^+$ | —0.5 | —5.87 | —18.0 |
| $Cs^+$ | —1.3 | —6.40 | —17.1 |
| $Ag^+$ | 3.4 | —2.30[d] | —19.1 |
| $Me_4N^+$ | —3.6 | —3.89 | —1.0 |
| $Et_4N^+$ | —4.0 | + 0.17 | + 14.0 |
| $Pr_4N^+$ | —6.1 | 2.79 | 29.8 |
| $Bu_4N^+$ | —8.4 | 4.39 | 42.9 |
| $Ph_4As^+$ | —9.4[e] | —3.49 | 19.8 |
| $Cl^-$ | 8.7 | 6.31 | —8.0 |
| $Br^-$ | 6.2 | 3.24 | —9.9 |
| $I^-$ | 2.5 | —0.78 | —11.0 |
| $ClO_4^-$ | —0.7 | —3.93 | —10.8 |
| $Ph_4B^-$ | —9.4[e] | —3.49 | + 19.8 |

[a] To convert to the molar scale, add 0.91to the $\Delta G_t^\circ$ value for each ion and substract 3.1 from the $\Delta S_t^\circ$ value for each ion.

[b] From Table 3, with an adjustment of 1.2 kcal mol$^{-1}$ to cationic values and from anionic values.

[c] Ref. 16.

[d] See Table 3.

[e] From refs.[6,15].

It has been noted previously[4, 18] that equation (1) does not reproduce values of $\Delta S_t^\circ$ for $Ph_4As^+$ and, especially, $Ph_4B^-$ for transfer from water to a number of solvents. This is the case also for *PC*, where the discrepancy is about 4 cal $K^{-1}$ $mol^{-1}$. In order to convert the $\Delta S_t^\circ$ and $\Delta G_t^\circ$ values in Tables 3 and 4 to values using the $Ph_4As^+/Ph_4B^-$ assumption, an adjustment of ± 4 cal $K^{-1}$ $mol^{-1}$ has to be made to cationic and anionic entropy values, and one of ± 1.2 kcal $mol^{-1}$ to the corresponding free energy values. The final set of single-ion values is given in Table 5. On this scale, the general trend of $\Delta G_t^\circ$ values resembles that in acetonitrile, with values for the alkali metal cations being positive or slightly negative. This contrasts greatly with values in solvents such as *DMF* and *DMSO* where the $\Delta G_t^\circ$ values for the alkali metal cations are very negative (see for example Table 6 where values for the water to *DMSO* transfer are given). The strong solvation of these small cations and especially $Ag^+$ in *DMSO* does not extend to the larger organic ions for which very similar $\Delta G_t^\circ$ values are observed in *PC* and *DMSO*.

Table 6. *Comparison of free energies of transfer of ions from water to PC and DMSO, in kcal mol*$^{-1}$ *on the mol fraction scale at 298 K*

| Ion | Water → *PC*[a] | Water → *DMSO*[4, 6] |
|---|---|---|
| $Na^+$ | 2.3 | −4.1 |
| $K^+$ | 0.4 | −3.7 |
| $Ag^+$ | 3.4 | −8.8[6] |
| $Me_4N^+$ | −3.6 | −2.1 |
| $Et_4N^+$ | −4.0 | −4.3[b] |
| $Pr_4N^+$ | −6.1 | −6.0[b] |
| $Ph_4As^+$ | −9.4 | −9.7[c] |
| $Cl^-$ | 8.7 | 8.4 |
| $Br^-$ | 6.2 | 5.4 |
| $I^-$ | 2.5 | 2.0[4], 1.4[6] |
| $ClO_4^-$ | −0.7 | 0.1[4], −1.1[6] |
| $Ph_4B^-$ | −9.4 | −9.7[c] |

[a] From Table 5.

[b] Estimated values using data in ref.[4].

[c] *Kim*[15] also gives this value.

Returning to equation (1), the value of $E$ assigned to any solvent is a direct numerical measure of the absolute entropies of the simple univalent cations and anions in that solvent. The more negative is $E$, the more negative are the ionic entropies by that amount, so that $E$ is an interesting and informative solvent parameter. In Table 7 are collected the values of $E$ obtained to date, together with the solvent structural parameter, $\Delta T$ (bp) introduced by *Criss*[19,20] who predicted ionic entropies of transfer from water by an equation that can be restated as equation (2). There is a general trend between $E$ and $\Delta T$ (bp)

Table 7. *Values of the solvent entropic parameter, E, in cal $K^{-1}$ $mol^{-1}$, and the solvent structural parameter* $\Delta T$ (bp)

| Solvent | $E$ (ref.[4]) | $\Delta T$ (bp) (ref.[20]) |
|---|---|---|
| Water | $\simeq -11^{a}$ | 174 |
| Formamide | $-17$ | 162 |
| *NMF* | $-20$ | 128 |
| Methanol | $-22$ | 117 |
| *PC* | $-24$ | 151 |
| *DMSO* | $-25$ | 135 |
| Ethanol | $-25$[18] | 97 |
| 1-Propanol | $-29$[18] | 84[18] |
| *AN* | $-30$ | 105 |
| *DMF* | $-32$ | 98 |
| Acetone | $-35$ | 62 |
| Ammonia | $-35$ | 57 |
| 1,2-Dichloroethane | $-44$[17] | $\sim 0$ |

[a] There is no defined value for $E$ in the case of water, but for simple alkali metal cations and halide anions an average value of $-11$ cal $K^{-1}$ $mol^{-1}$ may be taken.

$$\Delta S_t^{\circ}(\text{Ion}) = 0.21\, \Delta T\,(\text{bp}) \qquad (2)$$

that reflects the known usefulness of equation (2) in predicting entropies of transfer. It is evident, however, that the $\Delta T$ (bp) value for *PC* is larger than expected, so that equation (2) does not work very well for transfers from water to *PC*. There is almost no connection between values of $E$ and parameters of solvent basicity such as *Gutmann*'s donor number[21] or *Koppel*'s basicity values[22]. As pointed out by *Criss*[19], solvent basicity seems to play only a minor role in influencing ionic entropies.

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