# Letters

## Transfer chemical potentials for $Fe^{2+}$ from water into aqueous methanol

There are many data available for transfer chemical potentials ($\delta_m\mu^\ominus$) for alkali-metal cations from water into binary aqueous solvent mixtures, some data for alkaline-earth and $d^{10}$ metal cations, but very few for cations of the transition elements. The Note of Lahiri and co-workers[1] concerning $\delta_m\mu^\ominus(Fe^{2+})$ for transfer from water into aqueous methanol was therefore of interest. Unfortunately that Note contains several errors, including (*a*) incorrect calculation of solubility products, (*b*) the notion that transfer chemical potentials for electrolytes can be calculated with equal validity from solubilities and from solubility products [*i.e.* the assumption $\delta_m\mu^\ominus(\text{salt}) = -RT \ln (\text{solubility in mixture/solubility in water}) = -RT \ln (K_{sp} \text{ in mixture}/K_{sp} \text{ in water})$], (*c*) a lack of appreciation of the need to allow for the contribution of the anion's transfer chemical potential, and (*d*) an error of sign in the key equation (7), where $-\Delta G^\ominus_{t(FeL_3{}^{2+})}$ should read $+\Delta G^\ominus_{t(FeL_3{}^{2+})}$.

With reference to (*c*), the calculation presented in ref. 1 requires that the transfer chemical potential for perchlorate, $\delta_m\mu^\ominus(ClO_4^-)$, is zero for all methanol–water solvent mixtures. This extra-thermodynamic assumption is, except in water-rich mixtures, poor for a hydrophilic ion such as perchlorate. Even in the event that $\delta_m\mu^\ominus(ClO_4^-)$ is zero, estimates of $\delta_m\mu^\ominus(Fe^{2+})$ based on this assumption should be internally consistent. This is not the case for the results of ref. 1, and hence doubt is cast on the associated calculations. In ref. 1 the four estimates by the four different routes for $\delta_m\mu^\ominus(Fe^{2+})$ for transfer to a given solvent mixture are, for instance, −12.3, −9.3, +8.4, and +18.4 kJ mol$^{-1}$ for transfer to 34.4% (by weight) methanol.* We therefore present in this Letter corrected derivations for $\delta_m\mu^\ominus(Fe^{2+})$ from the experimental results reported in ref. 1, *viz.* solubilities of the perchlorates of $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ and of the ligands 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy).

The essential stages in our calculations are set out in the Table,[2-7] which shows solubility products (molar scale) and transfer chemical potentials for the salts $[FeL_3][ClO_4]_2$ (L = bipy or phen), and then transfer chemical potentials for the two cations using values for perchlorate on the $AsPh_4^+ \equiv BPh_4^-$ (t.a.t.b.) and $PPh_4^+ \equiv BPh_4^-$ (t.p.t.b.) assumptions. The transfer chemical potential for the $Fe^{2+}$ cation can then be calculated from the overall stability constants for tris-ligand complex formation, $\beta_3$, and the transfer chemical potentials for the complexes and the ligands by the formula (i).[7] Here $-RT\delta_m \ln \beta_3 = +RT\delta_m\Delta G^\ominus$; in equation (3) of ref. 1 this equilibrium is written in the instability (dissociation) constant form rather than in the more usual stability constant form. There has to be some mixing of data at 295 and 298 K in obtaining $\delta_m\mu^\ominus(Fe^{2+})$ values from the published data, but the discrepancies are $\ll$ 1 kJ mol$^{-1}$.

$$\delta_m\mu^\ominus(Fe^{2+}) = \delta_m\mu^\ominus(FeL_3{}^{2+}) - 3\delta_m\mu^\ominus(L) - RT\delta_m \ln \beta_3 \quad \text{(i)}$$

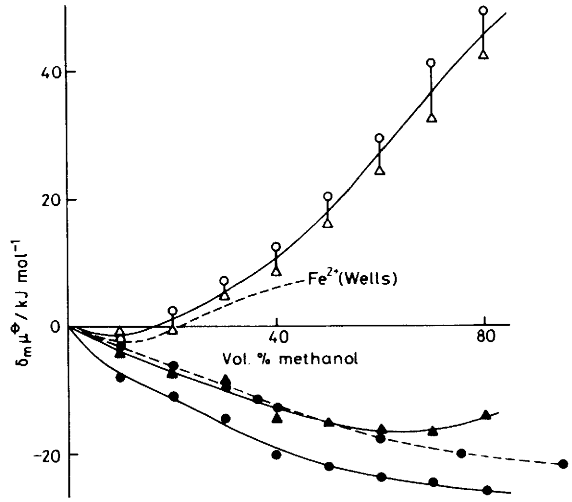

**Figure 1.** Transfer chemical potentials for $[Fe(bipy)_3]^{2+}$ (▲), $[Fe(phen)_3]^{2+}$ (●), and $Fe^{2+}$ (○,△); (——) t.a.t.b. single ion assumption, (– – –) single ion assumption of Wells

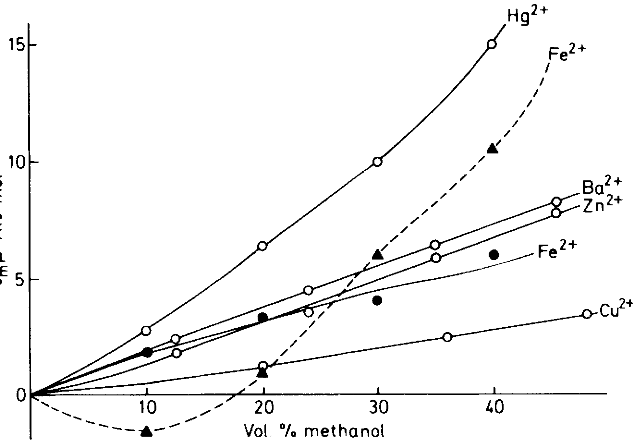

**Figure 2.** Transfer chemical potentials for $M^{2+}$ cations. (– – –) from Figure 1 (see text)

Figure 1 shows the transfer chemical potentials for the $[FeL_3]^{2+}$ cations from the Table, with the values of van Meter and Neumann[2] for $[Fe(phen)_3]^{2+}$ for comparison, and the values for $\delta_m\mu^\ominus(Fe^{2+})$ derived in the Table. The two sets of values agree tolerably well, considering difficulties in measuring solubilities and determining stability constants for such extremely stable complexes. We have also included in Figure 1 a plot of $\delta_m\mu^\ominus(Fe^{2+})$ values derived in an analogous manner, but using the $\delta_m\mu^\ominus(ClO_4^-)$ values of Wells.[8] Comparison of this plot for mean $\delta_m\mu^\ominus$ with the mean $\delta_m\mu^\ominus(Fe^{2+})$ plot from the values of the Table shows the relatively small effect of single ion assumptions in this particular system. Activity corrections also have a relatively small effect on $\delta_m\mu^\ominus(Fe^{2+})$ values. Use of the correction factors of van Meter and Neumann[2] has no significant effect over the range 0—30% methanol, then increases $\delta_m\mu^\ominus(Fe^{2+})$ by 0.4, 1.1, and 2.4 kJ

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* Such comparisons for mixtures containing a higher proportion of methanol are subject to errors in columns seven or eight of their Table 3: *e.g.* the average of −16.0 and −16.0 is quoted as −14.2.

**Table.** Derivation of $\delta_m\mu^\ominus(Fe^{2+})$ for transfer from water in methanol–water mixtures; values for transfer parameters in kJ mol$^{-1}$ on the molar scale at *295* K

| Methanol (wt. %) | $10^9K_{sp}$ | | $\delta_m\mu^\ominus$ | | | $\delta_m\mu^\ominus$ | |
|---|---|---|---|---|---|---|---|
| | $[Fe(bipy)_3]$-$[ClO_4]_2$ | $[Fe(phen)_3]$-$[ClO_4]_2$ | $[Fe(bipy)_3]$-$[ClO_4]_2$ | $[Fe(phen)_3]$-$[ClO_4]_2$ | $2\delta_m\mu^\ominus(ClO_4^-)$[a] | $[Fe(bipy)_3]^{2+}$ | $[Fe(phen)_3]^{2+}$ |
| 0 | 21.44 | 0.365[b] | | | | | |
| 8.0 | 93.57 | 6.912 | −3.61 | −7.22 | +0.6 | −4.2 | −7.8 |
| 16.4 | 294.24 | 18.97 | −6.42 | −9.69 | +1.0 | −7.4 | −10.7 |
| 25.2 | 402.18 | 88.75 | −7.19 | −13.48 | +1.0 | −8.2 | −14.5 |
| 34.4 | 7 263 | 1 140 | −14.29 | −19.74 | +0.4 | −14.7 | −20.1 |
| 44.1 | 9 326 | 2 791 | −14.90 | −21.94 | +0.2 | −15.1 | −22.1 |
| 54.2 | 14 131 | 4 604 | −15.92 | −23.16 | +0.4 | −16.3 | −23.6 |
| 64.7 | 9 242 | 4 146 | −14.88 | −22.91 | +1.8 | −16.7 | −24.7 |
| 75.9 | 1 647 | 3 662 | −10.65 | —22.60 | +3.4 | −14.1 | −26.0 |

| Methanol (wt. %) | $\delta_m\mu^\ominus$ | | $RT\delta_m \ln \beta_3$ | | $\Delta G^\ominus_{t(Fe^{2+})}$[e] | |
|---|---|---|---|---|---|---|
| | 3bipy | 3phen | bipy[c] | phen[d] | From bipy | From phen |
| 8.0 | −3.8 | −3.4 | +0.5 | −2.4 | −0.9 | −2.0 |
| 16.4 | −8.1 | −9.2 | +0.9 | −4.0 | −0.2 | +2.5 |
| 25.2 | −13.8 | −16.0 | 0 | −5.4 | +5.6 | +6.9 |
| 34.4 | −20.2 | −24.1 | −3.3 | −8.4 | +8.8 | +12.4 |
| 44.1 | −26.3 | −31.0 | −5.3 | −11.3 | +16.5 | +20.2 |
| 54.2 | −32.0 | −36.8 | −9.1 | −16.3 | +24.8 | +29.5 |
| 64.7 | −37.1 | −42.0 | −12.6 | −23.8 | +33.0 | +41.1 |
| 75.9 | −42.6 | −47.3 | −15.2 | −28.0 | +42.7 | +49.3 |

[a] At 298.2 K, from refs. 3 and 4. [b] *cf.* $K_{sp} = 2.6 \times 10^{-9}$ (ref. 2). [c] Stability constants from ref. 5. [d] Stability constants from ref. 6. [e] Calculated as in text.[7]

mol$^{-1}$ (*i.e.* by 3, 4, and 5%) as the methanol content increases to 40, 60, and 80%.

The values for $\delta_m\mu^\ominus(Fe^{2+})$ in the Table are plotted in Figure 2, in the form of the mean values from bipy and phen taken from Figure 1, in context with other $\delta_m\mu^\ominus(M^{2+})$ values. The other plot for $\delta_m\mu^\ominus(Fe^{2+})$ in Figure 2 is derived from $\delta_m\mu^\ominus[Fe(phen)_3{}^{2+}]$ values[9] calculated from $[Fe(phen)_3][ReCl_6]$ and $[Fe(phen)_3][ClO_4]_2$ solubilities on the t.a.t.b./t.p.t.b assumption,* solubilities of phen published earlier,[10] and the same set of stability constants. The $\delta_m\mu^\ominus$ plots for $Ba^{2+}$, $Zn^{2+}$, and $Hg^{2+}$ in Figure 2[4,11] are all on the t.a.t.b. single ion assumption, while the $\delta_m\mu^\ominus(Cu^{2+})$ values[12,†] are based on a negligible liquid-junction-potential assumption which is stated to be close to the t.a.t.b./t.p.t.b. assumptions. It will be seen that all the $\delta_m\mu^\ominus(M^{2+})$ plots are, as one would expect, of the same general shape, implying preferential solvation by water in the mixed solvents. The plot for $Fe^{2+}$ derived from Lahiri's[1] solubilities deviates somewhat from the general trend. This may be ascribed to uncertainties in the measured solubilities (*cf.* Figure 1); a difference of a factor of two in solubilities in one solvent mixture corresponds to 5.2 kJ mol$^{-1}$ in $\delta_m\mu^\ominus([FeL_3][ClO_4]_2)$, which in water-rich mixtures means a difference of nearly 5.2 kJ mol$^{-1}$ in $\delta_m\mu^\ominus(Fe^{2+})$ as $\delta_m\mu^\ominus(ClO_4^-)$ is close to zero.

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**Lahiri and co-workers reply.** In the context of the comments of Blandamer and Burgess we now state the following errors in our previous Note.[1]

(*i*) $-\Delta G^\ominus_{t(FeL_3{}^{2+})}$ in equation (7) should be $+\Delta G^\ominus_{t(FeL_3{}^{2+})}$.

(*ii*) The solubility product of $[Fe(bipy)_3][ClO_4]_2$ at 25.2 wt. % methanol given as 2 007.95 should be 207.95.

(*iii*) the values for $Fe^{2+}$ (using phen) from 44.7, 54.2, 64.1, and 75.9 wt.% methanol, given as −16.00, −17.5, −19.3, and −23.5 respectively (Table 3, column eight), should be −12.3, −12.8, −10.6, and −11.8.

(*iv*) The *A* values used in the calculation of the activity coefficients ($f_{ClO_4}$ and $f_{FeL_3{}^{2+}}$) are erroneously taken to be the same throughout the whole composition range.

As regards point (*a*) of the Letter, it should be noted that

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* We used the single ion assumption of Wells[8] in ref. 7.

† Another recently published set of $\delta_m\mu^\ominus(Cu^{2+})$ values (A. Lewandowski, *Electrochim. Acta*, 1984, **29**, 547) are in close agreement with ref. 12.

**Table.** Transfer free energy changes in kJ mol$^{-1}$ (molar scale)

| Methanol (wt. %) | Activity solubility product ($10^9K_{sp}$) at 295 K | | $\Delta G^{\ominus}_{t([FeL_3][ClO_4]_2)}$ (295 K) | | $3\Delta G^{\ominus}_{t(L)}$ (295 K) | | $\Delta\Delta G^{\ominus}_1$ for the reaction (298 K) $[FeL_3]^{2+} \rightleftharpoons Fe^{2+} + 3L$ | | $\Delta G^{\ominus}_{t(Fe^{2+})}$* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | [Fe(bipy)$_3$]-[ClO$_4$]$_2$ | [Fe(phen)$_3$]-[ClO$_4$]$_2$ | bipy | phen | bipy | phen | bipy | phen | Using bipy | Using phen |
| 0 | 13.2 | 0.284 | | | | | | | | |
| 8.0 | 50.02 | 4.55 | −3.26 | −6.80 | −3.8 | −3.4 | 0.6 | −2.4 | 1.1 (0.8) | −5.8 (−6.2) |
| 16.4 | 129.17 | 11.24 | −5.58 | −9.02 | −8.1 | −9.2 | 0.7 | −4.0 | 3.2 (2.4) | −3.8 (−4.5) |
| 25.2 | 160.62 | 42.12 | −6.12 | −12.26 | −13.8 | −16.0 | 0.0 | −5.4 | 7.7 (6.6) | −1.7 (−2.9) |
| 34.4 | 1 550.24 | 342.87 | −11.68 | −17.40 | −20.2 | −24.1 | −2.8 | −8.4 | 5.2 (3.1) | −1.7 (−4.1) |
| 44.1 | 1 583.14 | 633.50 | −11.73 | −18.90 | −26.3 | −31.0 | −5.3 | −11.3 | 9.3 (6.1) | +0.8 (−2.2) |
| 54.2 | 1 661.81 | 765.99 | −11.85 | −19.37 | −32.0 | −36.8 | −9.1 | −16.3 | 11.0 (7.0) | +1.1 (−2.7) |
| 64.7 | 897.43 | 618.25 | −10.34 | −18.41 | −37.1 | −42.0 | −12.8 | −23.8 | 14.0 (9.4) | −0.2 (−4.7) |
| 75.9 | 193.69 | 333.70 | −6.58 | −17.33 | −42.6 | −47.3 | −15.6 | −28.0 | 20.4 (16.3) | 2.5 (−2.8) |

* Values in parentheses are those obtained using the concentration solubility product values of $[FeL_3][ClO_4]_2$.

Burgess and Blandamer have calculated the concentration solubility product ($K_{sp} = 4S^3$) instead of the activity solubility product ($K_{sp} = 4S^3f^2_{ClO_4^-}f_{FeL_3^{2+}}$ or $K = 4S^3f^3_{\pm}$) given in our paper. We have recalculated the activity solubility product values using the Debye–Hückel equation $-\log f_{\pm} = (AZ + Z - \sqrt{\mu})/(1 + \sqrt{u})$ (taking $Ba'$ to be equal to 1 in the solvent mixtures, where $B$ = Debye-Hückel constant and $a'$ = ion size parameter). Appropriate $A$ values for the different mixed solvents have been recalculated. There may be some uncertainties in the calculated values of the activity coefficients of the ions but this is unavoidable.

Since the equilibrium constants and the absorption coefficients of the $[FeL_3]^{2+}$ complexes are generally known to be independent of anions, we considered the solubilities of the $[FeL_3]^{2+}$ complexes to be independent of anions. We have tried to calculate the transfer chemical potential of $Fe^{2+}$ ion using the extra-thermodynamic assumption that the transfer chemical potential of $[FeL_3]^{2+}$ can be regarded to be independent of anions; *i.e.* $\Delta G^{\ominus}_{t(ClO_4^-)}$ has been taken to be zero in the solvent mixtures. Moreover, since $ClO_4^-$ appears on both sides of equation (1), the contribution of $\Delta G^{\ominus}_{t(ClO_4^-)}$ should be

$$[FeL_3][ClO_4]_2 \rightleftharpoons Fe[ClO_4]_2 + 3L \qquad (1)$$

automatically cancelled out. However, since $[FeL_3][ClO_4]_2$ is an electrolyte, it is logical that the solubility product of $[FeL_3][ClO_4]_2$ should be used in calculating the transfer chemical potentials of $[FeL_3][ClO_4]_2$. Equation (3) of ref. 1 should therefore be treated with caution.

For equation (1) we can write (2a)—(2c).

$$\Delta\Delta G^{\ominus}_{t(1)} = \Delta G^{\ominus}_{t(Fe[ClO_4]_2)} + 3\Delta G^{\ominus}_{t(L)} - \Delta G^{\ominus}_{t([FeL_3][ClO_4]_2)} \qquad (2a)$$

$$= \Delta G^{\ominus}_{t(Fe^{2+})} + 2\Delta G^{\ominus}_{t(ClO_4^-)} + 3\Delta G^{\ominus}_{t(L)} - \Delta G^{\ominus}_{t(FeL_3^{2+})} - 2\Delta G^{\ominus}_{t(ClO_4^-)} \qquad (2b)$$

$$= \Delta G^{\ominus}_{t(Fe^{2+})} + 3\Delta G^{\ominus}_{t(L)} - \Delta G^{\ominus}_{t(FeL_3^{2+})} \qquad (2c)$$

If we use the activity solubility product of $[FeL_3][ClO_4]_2$ in equation (2b), the contributions of $\Delta G^{\ominus}_{t(ClO_4^-)}$ automatically cancel out and equation (2c) is obtained. Thus, there is no question of 'a lack of appreciation of the need to allow for the contribution of the anions transfer chemical potential.' Rather if the transfer chemical potential of $[FeL_3]^{2+}$ is used (as done by Blandamer and Burgess), the results would be vitiated as the contribution due to $2\Delta G^{\ominus}_{t(ClO_4^-)}$ [fifth term of (2b)] is eliminated but the second term of (2b) remains. Thus the use of experimentally determined values of $\Delta G^{\ominus}_{t(1)}$, $\Delta G^{\ominus}_{t(L)}$, and $\Delta G^{\ominus}_{t([FeL_3][ClO_4]_2)}$ would give us the value of $\Delta G^{\ominus}_{t(Fe^{2+})}$ from the experimental results without any extra thermodynamic assumptions.

We have used two different routes for the estimation of $\Delta G^{\ominus}_{t(Fe^{2+})}$ and the results obtained are likely to be different. However, this does not mean that the transfer chemical potentials can be calculated with equal validity from solubilities and from solubility products [point (*b*) of Burgess and Blandamer].

It is true there are difficulties in measuring solubilities and determining the stability constants for extremely stable complexes such as $[FeL_3][ClO_4]_2$, as rightly pointed out by Blandamer and Burgess. However, by suitable choice of the systems particularly involving monovalent ions, transfer chemical potentials of ions can be derived without extra thermodynamic assumptions.

The equation (i) used by Blandamer and Burgess for the calculation of transfer chemical potential of $Fe^{2+}$ is erroneous as the third term on the right-hand side should be positive using the usual stability constant form, since $\Delta\Delta G^{\ominus}_{t(instability)} = -\Delta\Delta G^{\ominus}_{t(stability)} = RT\delta_m \ln \beta_3$. Thus, the values of $\delta_m\mu(Fe^{2+})$ given by Blandamer and Burgess are erroneous.

We are extremely sorry that errors appeared in our previous Note.[1] We appreciate the Letter of Blandamer and Burgess which has enabled us to scrutinize and evaluate this work afresh. The modified values of $\Delta G^{\ominus}_{t(Fe^{2+})}$ are given in the Table. The discrepancies in these values of $\Delta G^{\ominus}_{t(Fe^{2+})}$ may be ascribed to combined uncertainties in the measured solubilities and the stability constant values.

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