Inorganica Chimica Acta, 64 (1982) L113–L114

Gibbs Free Energies of Transfer of Fe^{2+} from Water into Aqueous Methanol

M. J. BLANDAMER and J. BURGESS

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

Received October 27, 1981

Values of Gibbs free energies of transfer, ΔG^θ_{tr}, or transfer chemical potentials, $\delta_m\mu^\theta$, are available from many sources for the transfer of alkali metal cations from water into a variety of binary aqueous mixtures. Values for metal(II) cations, especially those of transition metals, are much rarer. However, the publication of stability constants for formation of the tris-1,10-phenanthrolineiron(II) cation, equation (1), in a range of methanol–water mixtures

$$Fe^{2+} + 3\ phen \overset{\beta_3}{\rightleftharpoons} Fe(phen)_3^{2+} \qquad (1)$$

[1] permits estimates to be made for $\delta_m\mu(Fe^{2+})$, as outlined in the following paragraphs, by using calculations based on equation (2).

$$\delta_m\mu^\theta(Fe^{2+}) = \delta_m\mu^\theta(Fephen_3^{2+}) - 3\delta_m\mu^\theta(phen) - \\ - RT\delta_m(\ln\beta_3) \qquad (2)$$

Values for $RT\delta_m(\ln\beta_3)$ can be calculated*, over the whole solvent composition range, from the published equilibrium constants [1]. Values for $\delta_m\mu^\theta$ (phen) are available [2] for solvent mixtures containing up to 25% methanol*, and can be extrapolated fairly safely up to about 40% methanol. Complications arise over values for $\delta_m\mu^\theta(Fephen_3^{2+})$, due to the need to make extra-thermodynamic assumptions in obtaining single ion values. In fact there are three ways of estimating $\delta_m\mu^\theta(Fephen_3^{2+})$ for transfer into aqueous methanol. The first set of estimates can be derived (Table I) from measured solubilities of the hexachlororhenate(IV) salt of this cation. This derivation involved the use of $\delta_m\mu^\theta$-$(ReCl_6^{2-})$ values [3], themselves derived from Wells's $\delta_m\mu^\theta(Cs^+)$ values [4]. The second series of estimates is derived (Table II) from solubilities of $Fe(phen)_3$-$(ClO_4)_2$ [5], again using Wells' single ion assumptions in the derivation of $\delta_m\mu^\theta(ClO_4^-)$. A third set of estimates is provided by van Meter and Neumann's calculations based on Born assumptions [5]. In Table III we derive values for $\delta_m\mu^\theta(Fe^{2+})$ from the first two sets of estimates, from measured solubilities. Values of $\delta_m\mu^\theta(Fe^{2+})$ derived from van Meter and Neumann's calculations for $\delta_m\mu^\theta(Fephen_3^{2+})$ do not agree well; we prefer to base our $\delta_m\mu^\theta(Fe^{2+})$ estimates on measured solubilities. Very similar values for $\delta_m\mu^\theta(Fe^{2+})$ can be derived from published stability constants for the $Fe(bipy)_3^{2+}$ cation in methanol–water mixtures [6], using solubilities of its BPh_4^- salt and $\delta_m\mu^\theta(BPh_4^-)$ values [7] based on Wells [4], at least for transfer between methanol–water mixtures (values for transfer from water agree less well, but there are reasons to suspect the reported solubility of $Fe(bipy)_3(BPh_4)_2$ in water). Obviously if one uses $\delta_m\mu^\theta(BPh_4^-)$ values based on the $\delta_m\mu^\theta$-$(BPh_4^-) = \delta_m\mu^\theta(AsPh_4^+)$ assumption [8], such as those of Tissier [9], agreement will not be satisfactory as Wells's transfer values differ markedly from $AsPh_4^+/BPh_4^-$ values.

Our Table III estimates for $\delta_m\mu^\theta(Fe^{2+})$ are compared with published estimates for $\delta_m\mu^\theta(M^{2+})$, where M = Ba^{2+}, Cd^{2+}, Zn^{2+} [4], and Hg^{2+} [3], in Fig. 1, in which all values are based on Wells's single ion data. It is interesting that the $\delta_m\mu^\theta(Fe^{2+})$ plots come in a position intermediate between the plot

---

*Throughout this letter all transfer quantities are on the molar scale, at 298.2 K, and solvent compositions are by volume before mixing.

TABLE I. Derivation of $\delta_m\mu^\theta(Fephen_3^{2+})$ from Hexachlororhenate(IV) Solubilities.

% MeOH	$[Fephen_3][ReCl_6]$		$\delta_m\mu^\theta(ReCl_6^{2-})$ (kJ mol^{-1})	$\therefore\delta_m\mu^\theta(Fephen_3^{2+})$ (kJ mol^{-1})
	10^6 soly (mol dm^{-3})	$\delta_m\mu^\theta$ (kJ mol^{-1})		
0	5.1			
10	8.0	−2.2	+2.8	−5.0
20	10.6	−3.6	+5.5	−9.1
30	18.0	−6.2	+6.7	−12.9
40	26.0	−8.0	+8.6	−16.6

0020-1693/82/0000-0000/$0.275

© Elsevier Sequoia/Printed in Switzerland

TABLE II. Derivation of $\delta_m\mu^\theta(\text{Fephen}_3^{2+})$ from Perchlorate Solubilities.

% MeOH	$\delta_m\mu^\theta([\text{Fephen}_3][\text{ClO}_4]_2)^a$ (kJ mol^{-1})	$2\delta_m\mu^\theta(\text{ClO}_4^-)^b$ (kJ mol^{-1})	$\therefore\delta_m\mu^\theta(\text{Fephen}_3^{2+})$ (kJ mol^{-1})
10	−2.4	+1.1	−3.5
20	−4.8	+2.2	−7.0
30	−7.5	+3.6	−11.1
40	−10.9	+5.3	−16.2

[a] By interpolation from ref. [5] results. [b] By interpolation of ref. [4] values, with appropriate conversion from mol fraction to molar scale and solvent compositions from weight percent to volume percent.

TABLE III. Derivation of $\delta_m\mu(\text{Fe}^{2+})$ from Fe(phen)_3^{2+} Data.

% MeOH	$RT\delta_m(\ln\beta_3)$ (kJ mol^{-1})	$3\delta_m\mu(\text{phen})$ (kJ mol^{-1})	$\delta_m\mu(\text{Fephen}_3^{2+})^a$ (kJ mol^{-1})		$\therefore\delta_m\mu(\text{Fe}^{2+})^a$ (kJ mol^{-1})	
			I	II	I	II
10	−2.4	−2.4	−5.0	−3.5	−0.2	+1.3
20	−4.0	−4.7	−9.1	−7.0	−0.4	+1.7
30	−5.4	−7.3	−12.9	−11.1	−0.2	+1.6
40	−8.4	(−10)	−16.6	−16.2	(+2)	(+2)

[a] I from ReCl_6^{2-} solubilities, II from ClO_4^- solubilities.

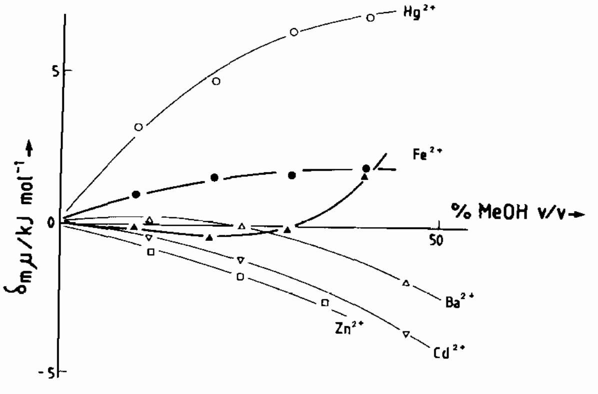

Fig. 1. Transfer chemical potentials for 2+ cations; for Fe^{2+} ● based on $\text{Fe((phen)}_3(\text{ClO}_4)_2$ solubilities, ▲ based on $\text{Fe(phen)}_3(\text{ReCl}_6)$ solubilities (*cf.* text).

for Hg^{2+} and the plots for the other ions. It would be useful now to obtain $\delta_m\mu^\theta(\text{Fe}^{2+})$ values by a more direct route, say from solubility measurements on a sparingly soluble salt of iron(II) such as the tetraphenylboronate, iodate, or oxalate, for confirmation. A reliable set of $\delta_m\mu(\text{Fe}^{2+})$ values for transfer to binary aqueous solvent mixtures is required for dissociation of solvent effects on reactivity into initial state and transition state components [10] for such reactions as inner-sphere reductions of cobalt(III) complexes by Fe^{2+} and formation reactions of Fe(bipy)_3^{2+} and Fe(phen)_3^{2+}. It would also be possible to use $\delta_m\mu^\theta(\text{Ni}^{2+}) = \delta_m\mu^\theta(\text{Fe}^{2+})$ in a parallel analysis of the important Eigen–Wilkins complex formation reaction of nickel(II). Such an analysis has been reported for H [11], but cannot be carried out for G until $\delta_m\mu^\theta(\text{Ni}^{2+})$ values are available.

References

1 G. Biswas, S. Aditya, A. Bhattacharyya and S. C. Lahiri, *J. Indian Chem. Soc., 54,* 1137 (1977).
2 J. Burgess and R. I. Haines, *J. Chem. Eng. Data, 23,* 196 (1978).
3 M. J. Blandamer, J. Burgess and R. I. Haines, *J. Chem. Soc. Dalton Trans.,* 607 (1980).
4 C. F. Wells, *J. Chem. Soc. Faraday Trans. I, 69,* 984 (1973).
5 F. M. van Meter and H. Neumann, *J. Am. Chem. Soc., 98,* 1382 (1976).
6 D. K. Hazra and S. C. Lahiri, *Analyt. Chim. Acta, 79,* 335 (1975).
7 M. J. Blandamer, J. Burgess and F. M. Mekhail, to be submitted to *Inorg. Chim. Acta.*
8 B. G. Cox, *Ann. Rep. Chem. Soc. (A),* 249 (1974) and refs. therein.
9 C. Tissier, *C.R. 286C,* 35 (1978).
10 M. J. Blandamer and J. Burgess, *Coord. Chem. Rev., 31,* 93 (1980).
11 M. J. Blandamer, J. Burgess, R. Sherry and R. I. Haines, *J. Chem. Soc. Chem. Commun.,* 353 (1980).