HOKKAIDO UNIVERSITY

Title	ESTIMATION OF THE SURFACE POTENTIAL OF WATER
Author(s)	NOTOYA, R.; MATSUDA, A.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 30(2), 107-109
Issue Date	1983-02
Doc URL	http://hdl.handle.net/2115/25133
Type	bulletin (article)
File Information	30(2)_P107-109.pdf

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 30, No. 2, pp. 107 to 110 (1982)

— Note —

ESTIMATION OF THE SURFACE POTENTIAL OF WATER

By

R. NOTOYA*) and A. MATSUDA*)

(Received November 17, 1982)

The numerical values of the standard chemical free energies of solvation of monoatomic cations have recently been estimated for 70 ionic species in 14 non-aqueous solvents as well as in water[1] on the basis of the empirical rules reported previously[2]. On the other hand, the experimental values of the standard real free energies of hydration were reported by Randles[3] for a series of monoatomic cations. It may therefore be possible to estimate the surface potential of water χ_w from the comparison of these two quantities on the basis of eq. (1)

$$\overline{\alpha^{\circ}_{i,w}} = \alpha^{\circ}_{i,w} - z_i F \chi_w , \qquad (1)$$

where $\overline{\alpha^{\circ}_{i,w}}$ and $\alpha^{\circ}_{i,w}$ are the standard real and chemical free energies of hydration of ion i of valency z_i, and F the Faraday. The sign of χ_w is taken positive when the surface dipole turns its negative end towards the gas phase.

The relation between $\alpha^{\circ}_{i,w}/z_i$ and $\overline{\alpha^{\circ}_{i,w}}(R)/z_i$ is shown by the line (2) in the figure, where (R) means the Randles series. An excellent linearity between these two quantities is found which can be expressed by eq. (2)

$$\frac{\alpha^{\circ}_{i,w}}{z_i} = \frac{\overline{\alpha^{\circ}_{i,w}}(R)}{z_i} + 0.42, \text{ eV} . \qquad (2)$$

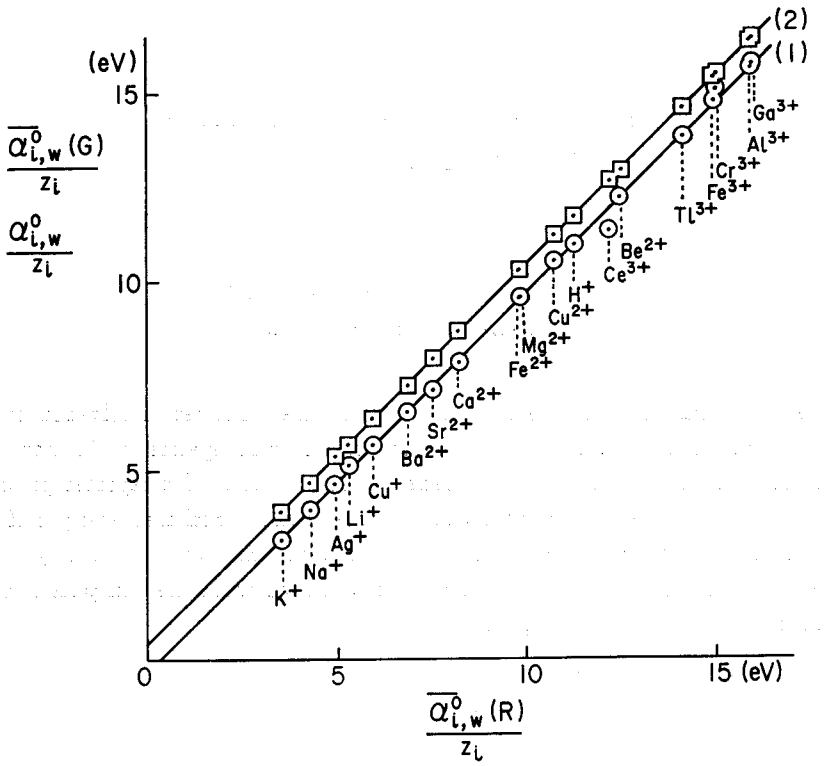
It follows from eqs. (1) and (2) that the value of χ_w can be estimated at 0.42 V.

On the other hand, Gomer and Tryson[4] have reported another series for $\overline{\alpha^{\circ}_{i,w}}$ which shows a systematic deviation from the Randles series given by eq. (3)

$$\frac{\overline{\alpha^{\circ}_{i,w}}(R)}{z_i} = \frac{\overline{\alpha^{\circ}_{i,w}}(G)}{z_i} + 0.31, \text{ eV} , \qquad (3)$$

as seen from the line (1) in the figure, where (G) means the series of Gomer and Tryson. If we use $\overline{\alpha^{\circ}_{i,w}}(G)$ in place of $\overline{\alpha^{\circ}_{i,w}}(R)$ in eq. (2), then we obtain $\chi_w = 0.73$ V. In this way we have at present alternative values $\chi_w = 0.42$ V or 0.73 V due to the discrepancy between the two series of the experimental values for $\overline{\alpha^{\circ}_{i,w}}$.

*) The Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.



The comparison of the two series of the real free energies of hydration $\overline{\alpha^0_{i,w}}(G)/z_i$ and $\overline{\alpha^0_{i,w}}(R)/z_i$—the straight line (1), and the relation between the chemical and real free energies of hydration $\alpha^0_{i,w}/z_i$ and $\overline{\alpha^0_{i,w}}(R)/z_i$—the straight line (2), for monoatomic cations at 25°C.

It should be noted, however, that the numerical values of $\alpha^0_{i,w}$ used in the present work includes the uncertainty of 0.3 eV[1], which results in the same uncertainty of the value of χ_w. It may therefore be concluded that the value of χ_w lies in the range $0.12<\chi_w<0.72$ V or $0.43<\chi_w<1.03$ V with the most probable value 0.42 V or 0.73 V according as the values of $\overline{\alpha^0_{i,w}}$ concerned.

On the other hand, Frumkin, Iofa and Gerovich[5] estimated the value of χ_w at 0.1~0.2 V from the change of the surface potential of aqueous solutions caused by the adsorption of surface active organic substances Kochurova and Rusanov[6] estimated the value of χ_w at 0.1 V in conformity with the result of Frumkin *et al.* from the difference $\Delta\chi_w$ in the values of χ_w between the initial and stationary states of water jets. They estimated the initial time of water jet stream using the time constant of the formation of the equilibrium surface of water, which was given at 0.44 m sec from the $\Delta\chi_w$ vs aging time curve. However, the time constant of the charging up of the electric double

layer at the metal-solution interface is less than a few microseconds, as reported previously for the platinum-hydrogen electrode in acidic solutions.[7] Therefore we cannot deny a possibility that the time constant of the orientation of water dipoles on the free surface is much less than that assumed by Kochurova and Rusanov, *i.e.*, $\chi_w =$ 0.1 V obtained by them seems to be a lower limit as expected also from the result obtained from the comparison of $\alpha^{\circ}_{1,w}$ and $\overline{\alpha^{\circ}_{1,w}}$ in the present work.

References

1) R. Notoya and A. Matsuda, J. Res. Inst. Catalysis, Hokkaido Univ., **30**, 61 (1982).
2) A. Matsuda, J. Res. Inst. Catalysis, Hokkaido Univ., **27**, 101 (1979); A. Matsuda and R. Notoya, J. Res. Inst. Catalysis, Hokkaido Univ., **28**, 67 (1980); **29**, 151 (1981); R. Notoya and A. Matsuda, J. Res. Inst. Catalysis, Hokkaido Univ., **30**, 1 (1982).
3) J. E. B. Randles, Trans. Faraday Soc., **52**, 1573 (1956).
4) R. Gomer and G. Tryson, J. Chem. Phys., **66**, 4413 (1977).
5) A. N. Frumkin, Z. A. Iofa and M. A. Gerovich, J. Phys. Chem., USSR, **30**, 1453 (1956).
6) N. N. Kochurova and A. I. Rusanov, J. Colloid and Interface Sci., **81**, 297 (1981).
7) R. Notoya and A. Matsuda, J. Res. Inst. Catalysis, Hokkaido Univ., **14**, 198 (1966).