

# Double layer effects in the electroreduction of transition metal ions

W. Ronald Fawcett · Magdalena Hromadová

Received: 15 December 2006 / Revised: 15 May 2007 / Accepted: 4 June 2007 / Published online: 4 December 2007  
© Springer-Verlag 2007

**Abstract** Experimental data for the reduction of transition metal complex ions obtained recently at mercury and single-crystal gold electrodes are reviewed. It is shown that the effective charge on the reactant is generally not the same as the nominal charge, but that it may be found on a basis of an analysis of the kinetic data together with the appropriate double layer data. In addition, the effective charge on the product is usually smaller than the nominal value. As a result, the analysis of the double layer effect involves the construction of corrected Tafel plots, which differ significantly from those described in the early work of Frumkin.

## Introduction

Oleg Petrii is best known for his work on platinum electrochemistry and electrocatalysis. In fact, his early work with Frumkin involved the study of double-layer effects in electrode reactions at mercury [1, 2]. They examined in detail the effect of reactant location in the double layer and of ion pairing on the kinetics of electroreduction of anions. This work made use of extensive

double-layer data to construct corrected Tafel plots (cTps). Anion electroreduction is especially interesting at potentials negative of the point of zero charge (pzc) because the reactant is strongly repelled from the double layer and large double-layer effects are observed.

The electroreduction of transition metal ions is also a group of reactions in which double-layer effects are large and depend greatly on the position of the standard potential for the electrode process with respect to the pzc of the polarizable electrode. Extensive studies of these systems were made by Weaver and Anson [3–5]. Initially, the reduction of eight Cr(III) complexes of the general structure  $[\text{Cr}(\text{OH}_2)_5\text{X}]^{z+}$  were examined at a mercury electrode in concentrated perchlorate solutions at low pH (~2) [3]. The response of the system to iodide was determined in an experiment in which perchlorate ion was replaced by a small amount of iodide ion while keeping the ionic strength constant. This allowed Weaver and Anson to distinguish between inner sphere and outer sphere mechanisms for the reduction reaction.

In the inner sphere mechanism, the anion  $\text{X}^{\text{P}-}$  in the complex is adsorbed on the mercury electrode and interacts repulsively with adsorbed iodide ions when they are introduced. In the outer sphere mechanism, the anion  $\text{X}^{\text{P}-}$  does not specifically adsorb and remains in the diffuse layer. Under these circumstances, the addition of iodide accelerates the reaction because it makes the electrical field at the outer Helmholtz plane (oHp) more negative. Three systems followed the outer sphere pathway, namely,  $[\text{Cr}(\text{OH}_2)_6]^{3+}$ ,  $[\text{Cr}(\text{OH}_2)_5\text{F}]^{2+}$ , and  $[\text{Cr}(\text{OH}_2)_5\text{SO}_4]^+$ . These reactants have different charges and therefore different double-layer effects.

The initial study was extended later to Cr(III) ammine complexes [4] and Co(III) ammine complexes [5]. Thus, a rich variety of octahedral complex ions are available to study the outer sphere electron transfer mechanism. However, the

---

Dedicated to Professor Oleg A Petrii on the occasion of his 70th birthday and in honor of his significant contributions to the field of electrochemistry.

---

W. R. Fawcett (✉)  
Department of Chemistry, University of California,  
Davis, CA 95616, USA  
e-mail: wrfawcett@ucdavis.edu

M. Hromadová  
J. Heyrovsky Institute of Physical Chemistry,  
Dolejskova 3,  
Prague 8, Czech Republic

analysis of double-layer effects in the work by Weaver and Anson [3–5] was not complete because they did not have double-layer data to analyze their kinetic data in detail.

Hamelin and Weaver [6] extended the earlier work on mercury to single-crystal gold electrodes. They found that the rate constant for reduction of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  increased in the order  $\text{Au}(111) > \text{Au}(100) > \text{Au}(110)$  at a constant potential of +0.1 V against a saturated calomel electrode (SCE). The opposite trend was found for  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ . Double-layer effects for the first two systems were studied in greater detail by Hromadová and Fawcett [7, 8]. Analysis of the double-layer effect showed that the effective charge on  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is +2, and that on  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  +1.6.

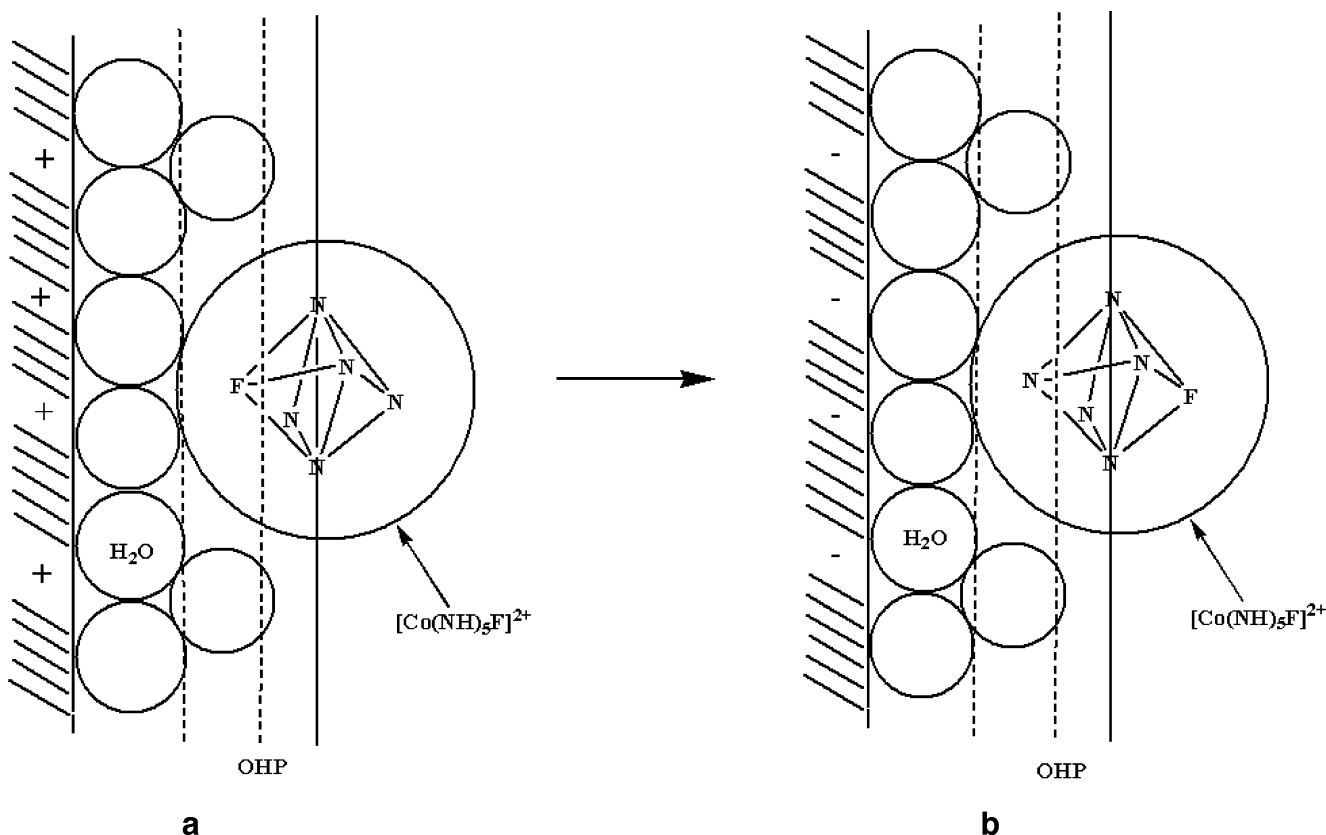
The observation that the effective charge is less than the nominal charge is attributed to the fact that the polyatomic reactant is in a position in the double layer where the individual atoms in the reactant can experience quite different electrostatic potentials. In other words, it is not valid to treat the reactant as a point charge in estimating the work done to bring it to its reaction site in the double layer. The ideas behind a more detailed analysis of double layer effects originated in the Petrii group in Moscow [9, 10].

By extending the kinetic study to single-crystal gold electrodes, one increases in a significant manner the number

of conditions under which the double-layer effect may be studied. At mercury one is limited to varying the ionic strength of the electrolyte solution. By extending the study to single-crystal gold electrodes, one increases the number of systems, which can be examined by at least a factor of four. This was shown clearly by the results of Hromadová and Fawcett [7, 8].

As pointed out by Fawcett and Gardner [11], reactants such as  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  possess a dipole moment as well as a charge. This means that the reactant will be oriented in the electrode's field in a direction that depends on the charge on the electrode (see Fig. 1). Furthermore, the reactant will reorient in the vicinity of the pzc. As a result, the effective charge on the reactant changes significantly as the electrode potential changes from positive values to negative. Another feature of double-layer effects especially in the presence of specifically adsorbed reactants or non-reacting ions is due to significant variation in the electrical potential in planes parallel to the interface, that is, to discreteness-of-charge effects.

This was considered by Fawcett and Solomon [12] with respect to the electroreduction of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  in the presence of adsorbed nitrate ions. Discreteness-of-charge effects are certainly important in the earlier work of Weaver and Anson [3–5] who studied the effects of adsorbed iodide anion on the electrode kinetics.



**Fig. 1** Position and orientation of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  at a positively charged polarizable electrode (a), and at a negatively charged polarizable electrode (b)

Another important aspect is the estimation of double-layer effects under conditions for which the Gouy–Chapman (GC) theory fails in a serious way. Weaver et al. [13] studied the electroreduction of  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  and  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  at high ionic strength and in a variety of 1:1, 2:1, and 3:1 electrolytes. On the basis of Monte Carlo (MC) simulations, the GC estimate of the potential drop across the diffuse layer is seriously in error when polyvalent ions are attracted into the diffuse layer [14, 15]. Furthermore, the extent of the departure from GC theory increases with ionic strength and with the charge on the ion. The double-layer effects observed in the Weaver study [13] should be reexamined on the basis of more recent models for the diffuse layer [20].

In the present paper, the magnitude of the double-layer effects expected for transition metal complexes is reconsidered. The construction of cTps for these systems [16] is also discussed. Emphasis is placed on cationic reactants with dipole moments.

### Theory

The treatment of double layer effects given here follows that outlined by Delahay [17]. Consider a simple one-electron reduction reaction



The potential dependence of the forward rate constant  $k_f$  is given by

$$\ln k_f = \ln k_{f0} - w_A/RT - \alpha(F\phi^m - w_A + w_B)/RT, \tag{2}$$

where  $k_{f0}$  is the forward rate constant when  $\phi^m$ ,  $w_A$ , and  $w_B$  are all zero,  $w_A$  and  $w_B$ , the work to bring the reactant and product, respectively, to their reaction sites in the double layer,  $\alpha$ , the true transfer coefficient, and  $\phi^m$ , the electrode potential on the rational scale. Recent discussion [7–10, 16, 18] has emphasized that the estimation of the work terms must be improved with respect to the point charge description given in earlier work [2, 17]. To do this, one needs a detailed description of the position of the polyatomic reactant in the double layer and of the partial charge on each atom [18]. The work done to bring  $i$  species to its reaction site is then

$$w_i = \sum_j z_j \phi^j, \tag{3}$$

where  $z_j$  is the partial charge on atom  $j$ , and  $\phi^j$ , the potential at this point. One then defines an effective charge on this species to be

$$z_{\text{ef}} = w_i/F\phi^d, \tag{4}$$

where  $\phi^d$  is the potential drop across the diffuse layer.

Replacing the work terms in Eq. 2 by their estimates in terms of effective charges, one obtains

$$\ln k_f = \ln k_{f0} - z_{\text{Ae}}f\phi^d - \alpha f\phi^m + \alpha(z_{\text{Ae}} - z_{\text{Be}})f\phi^d, \tag{5}$$

where  $z_{\text{Ae}}$  is the effective charge on reactant  $A$ , and  $z_{\text{Be}}$ , that on product  $B$ , and  $f = F/RT$ . In the classical Frumkin treatment, the effective charges are assumed to be equal to their nominal values,  $z_A$  and  $z_B$ , so that Eq. 5 reduces to the well-known result

$$\ln k_f = \ln k_{f0} - z_A f\phi^d - \alpha f(\phi^m - \phi^d) \tag{6}$$

However, in general,  $z_{\text{Ae}} - z_{\text{Be}}$  is not equal to unity so that the cTp takes the general form

$$\ln k_f + z_{\text{Ae}}f\phi^d = \ln k_{f0} - \alpha f(\phi^m - \delta\phi^d), \tag{7}$$

where

$$\delta = z_{\text{Ae}} - z_{\text{Be}} \tag{8}$$

Finally, the transfer coefficient obtained from the kinetic data without double-layer correction is

$$\alpha_{\text{ex}} = -\frac{RT}{F} \frac{d \ln k_f}{d\phi^m} = \alpha + (z_{\text{Ae}} - \alpha\delta) \frac{d\phi^d}{d\phi^m} \tag{9}$$

It is apparent that this quantity depends markedly on double-layer effects.

For 2:1 electrolytes, the potential drop across the diffuse layer estimated from MC simulations [14, 15] reaches a maximum for a charge density negative of the pzc. The potential at which this occurs depends on the ionic strength, but definitely is in the range for which kinetic data are often obtained. This phenomenon is attributed to the departure of the concentration profile from a relatively smooth character to a profile with oscillations [20]. On the basis of Eq. 9, when  $d\phi^d/d\phi^m$  is equal to zero,

$$\alpha_{\text{ex}} = \alpha \tag{10}$$

In other words, the true transfer coefficient may be obtained from the kinetic data without making a double-layer correction. This prediction of the MC results certainly merits further investigation.

### Results and discussion

Rusanova et al. [16] studied the reduction of  $[\text{Cr}(\text{OH}_2)_6]^{3+}$  at a mercury electrode in acidified solutions (pH=3.0) of  $\text{NaClO}_4$ . Examination of the kinetic data at 0.03 M and 0.3 M led to the conclusion that the effective charge on the reactant is 2.2. This result falls between values of  $z_{\text{Ae}}$  equal to 1.9 for an ionic strength of 0.3 M, and 2.6 for 0.03 M, which were estimated from the charge distribution in the reactant, and assuming that it is located entirely in the

diffuse layer. The corresponding estimates of  $\delta$  are 0.7 at 0.3 M, and 0.85 at 0.03 M. When cTps are constructed using these values of  $\delta$ , data at the two ionic strengths fall on one line with a slope corresponding to  $\alpha=0.5$ .  $\alpha_{\text{ex}}$  is greater than 0.5, its exact value depending on the ionic strength. For example, the value of  $\alpha_{\text{ex}}$  observed by Weaver and Anson [3] at Hg in 1 M NaClO<sub>4</sub> was 0.58.

The distribution of charge within the complex in the gas phase is especially interesting. In the case of [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup>, the net charge on the central Cr(III) ion is +2.12 e<sub>0</sub>, that is, considerably less than the nominal value of +3 e<sub>0</sub>. Thus, a charge of +0.146 e<sub>0</sub> is associated with each H<sub>2</sub>O molecule as ligand. Each H atom has a charge of +0.58 e<sub>0</sub> and the oxygen atom a charge of -1.02 e<sub>0</sub>. The water molecule, which is closest to the electrode, has the largest effect in determining the effective charge on the reactant. The atoms that are coplanar with the central Cr(III) are secondary in importance.

Finally, the water molecule furthest from the interface plays very little role in determining the effective charge. The net result ( $z_{\text{Ae}}=2.2$  e<sub>0</sub>) is easily rationalized on the basis of the quantum chemical data. In the case of [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>2+</sup>, the net charge on the central Cr(II) ion is +1.79 e<sub>0</sub>. Thus, the charge on each water molecule is much smaller (+0.035 e<sub>0</sub>). Estimation of the effective charge  $z_{\text{Be}}$  is more complicated for this species because of Jahn-Teller distortion of the octahedral complex.

The best way to obtain an estimate of the effective charge on the reactant is on the basis of the experimental data as shown by Hromadova and Fawcett [8]. Using the naïve form of the Frumkin equation (Eq. 6), one can write

$$-\frac{RT}{F} \frac{d \ln k_f}{d(\phi^m - \phi^d)} = z_A \frac{d\phi^d}{d(\phi^m - \phi^d)} + \alpha \quad (11)$$

A plot of the left-hand side against the derivative  $d\phi^d/d(\phi^m - \phi^d)$  should give a straight line with a slope equal to  $z_{\text{A}}$ . In fact, when applied to data for the reduction of [Co(NH<sub>3</sub>)<sub>5</sub>F]<sup>2+</sup> [8], the slope was approximately equal to  $z_{\text{Ae}}$ . The validity of this estimate was then confirmed on the basis of cTps.

Weaver and Satterberg [4] found that the value of  $\alpha_{\text{ex}}$  for [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> is significantly larger at Hg in acidified 1 M NaClO<sub>4</sub> (0.84) than that for [Cr(OH<sub>2</sub>)<sub>6</sub>]<sup>3+</sup> (0.58). They argued that the reaction site for the hexaamino complex is closer to the electrode than that for the hexaaquo complex on the basis of the point charge model for the reactant. However, it could also be due to a larger fraction of the charge being on the ammonia ligands, with a correspondingly smaller fraction on the central Cr(III). The necessary quantum chemical calculations for [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> have not yet been carried out.

Hromadová and Fawcett [7] studied the electroreduction of [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> as a function of potential at single-crystal

gold electrodes and concluded that  $z_{\text{Ae}}$  is equal to 2.0. At Au(210) in 0.01 M HClO<sub>4</sub>, the corresponding value of  $\alpha_{\text{ex}}$  is 1.74. This very large result is due to the fact that the coefficient  $d\phi^d/d\phi^m$  is very large (0.75) in the potential region where the kinetic data were obtained. On the basis of Eq. 9 and assuming that  $\alpha$  is 0.5, the estimate of  $\delta$  is 0.7. This is a reasonable result. The value of  $\alpha_{\text{ex}}$  depends both on ionic strength and on the nature of the Au substrate, a value of 1.24 being found for Au (111) in 0.093 M HClO<sub>4</sub>. Satterberg and Weaver [5] reported that  $\alpha_{\text{ex}}$  is equal to 0.88 for this system at Hg in 1.0 M KF.

Fawcett et al. [18] carried out extensive calculations of  $z_{\text{Ae}}$  and  $z_{\text{Be}}$  for the [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+/2+</sup> couple. They showed that the estimates of the effective charges depend greatly on the orientation of the reactant in the double layer as well as on the position of the oHp. For these reasons, it is quite difficult to predict the value of the effective charge from the quantum chemical calculations. Whenever possible, it should be found from an analysis of the electrochemical kinetic data together with the appropriate double-layer data.

Another reactant that has been studied in detail is [Co(NH<sub>3</sub>)<sub>5</sub>F]<sup>2+</sup> [5, 8, 12]. The value of  $\alpha_{\text{ex}}$  at Au(210) in 0.01 M HClO<sub>4</sub> is 1.33. The estimate of  $z_{\text{Ae}}$  from kinetic data at four different gold electrodes is 1.6. The estimate of  $\delta$  from Eq. 9 is 1.0, assuming that  $\alpha$  is 0.5. Experiments at Hg electrodes gave values of  $\alpha_{\text{ex}}$  equal to 0.75 [5] and 0.69 [12] in 0.2 M NaF.

This reaction occurs close to the pzc on Au(210). However, no significant change in the slope of the Tafel plot with potential could be seen. In general, one expects the orientation of a dipolar reactant such as [Co(NH<sub>3</sub>)<sub>5</sub>F]<sup>2+</sup> to change significantly in the vicinity of the pzc (see Fig. 1). This is an interesting question and certainly merits further investigation.

In all of the analysis presented here, it has been assumed that the true transfer coefficient is 0.5. This seems reasonable on the basis of the Marcus theory of electron transfer [19] and the simple nature of the reaction. If the reaction involves an inner sphere mechanism, such an assumption would not be valid. In general, the assumption could not be made for any reaction with an asymmetrical Gibbs energy barrier.

The effect of the parameter  $\delta$  not being unity was only considered in our most recent work [16]. As kinetic data are usually available over a very narrow potential range, assuming  $\delta$  is equal to one does not affect the linearity of the cTp. However, it does influence the value of the transfer coefficient obtained from the cTp. This is apparent from the results of our earlier analyses for the [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> [7] and [Co(NH<sub>3</sub>)<sub>5</sub>F]<sup>2+</sup> systems [8].

Almost all experimental data analyzed to date have made use of the GC theory to obtain estimates of  $\phi^d$ . However, improved models of the diffuse layer, which consider the

effects of ion size, are now available [20, 21]. According to the series approach, the potential drop across the diffuse layer for a symmetrical electrolyte, expressed in terms of the GC estimate, is given by

$$\phi^d = d_1 \phi^d(\text{GC}) + d_3 [\phi^d(\text{GC})^3], \quad (12)$$

where  $\phi^d(\text{GC})$  is the GC estimate of  $\phi^d$ . The parameters  $d_1$  and  $d_3$  depend of the size of the ions in the diffuse layer and on their charge. More details about the series model are given elsewhere [20, 21]. In the case when 1:1 electrolytes predominate in the diffuse layer, the difference between  $\phi^d$  and  $\phi^d(\text{GC})$  is not large, especially in the region near the pzc. Thus, it was shown by Rusanova et al. [16] that use of the improved estimates of  $\phi^d$  did not make a significant difference in the kinetic parameters obtained from cTps. As pointed out above, it is definitely necessary to use an improved model for the diffuse layer to analyze kinetic data obtained under circumstances where the predominant ions attracted into the diffuse layer are polyvalent.

## Conclusions

The recent developments in the theory of double-layer effects have significantly improved our understanding of the role of reactant location in the double layer. However, the number of systems for which detailed studies have been carried out is still limited. Work is currently going on in one of our laboratories to study a wider variety of transition metal ion couples, especially those that have dipole moments. In addition, studies of these systems are being extended to 2:1 electrolytes such as  $\text{Ca}(\text{ClO}_4)_2$  and Ba

$(\text{ClO}_4)_2$  so that the effect of the maximum in the diffuse layer potential drop may be investigated more thoroughly.

**Acknowledgements** Financial support to WRF from the National Science Foundation, Washington (grant CHE04-51103), and to MH from the Czech Academy of Sciences (grants GAAV A400400605, KJB 400400603 and MSMT LC510) are gratefully acknowledged.

## References

- Petrii OA, Frumkin AN (1962) Doklady Akad Nauk SSSR 146:1121
- Frumkin AN, Petrii OA, Nikolaeva-Fedorovich NV (1963) Electrochim Acta 8:177
- Weaver MJ, Anson FC (1976) Inorg Chem 15:1871
- Weaver MJ, Satterberg TL (1977) J Phys Chem 81:1772
- Satterberg TL, Weaver MJ (1978) J Phys Chem 82:1784
- Hamelin A, Weaver MJ (1986) J Electroanal Chem 209:109
- Hromadová M, Fawcett WR (2000) J Phys Chem A 104:4356
- Hromadová M, Fawcett WR (2004) J Phys Chem B 108:3277
- Nazmutdinov RR, Tsirlina GA, Kharkats YI, Petrii OA, Probst M (1998) J Phys Chem B 102:677
- Tsirlina GA, Kharkats YI, Nazmutdinov RR, Petrii OA (1999) Elektrokhimiya 35:23
- Fawcett WR, Gardner CL (1977) J Electroanal Chem 82:303
- Fawcett WR, Solomon PH (1988) J Electroanal Chem 251:183
- Weaver MJ, Liu HY, Kim Y (1981) Can J Chem 59:1944
- Boda D, Fawcett WR, Henderson D, Sokolowski S (2002) J Chem Phys 116:7170
- Torrie GM, Valleau JP (1982) J Phys Chem 86:3251
- Rusanova MY, Tsirlina GA, Nazmutdinov RR, Fawcett WR (2005) J Phys Chem A 109:1348
- Delahay P (1965) Double layer and electrode kinetics, chap 7. Wiley- Interscience, New York
- Fawcett WR, Hromadová M, Tsirlina GA, Nazmutdinov RR (2001) J Electroanal Chem 498:93
- Marcus RA (1959) Can J Chem 37:155
- Smagala TG, Fawcett WR (2007) J Phys Chem B 111:1443
- Fawcett WR, Smagala TG (2006) Langmuir 22:10635