

Interrelation Between the Interaction Parameter and the Width of the Adsorption Voltammetric Peak

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It is known that the width of adsorption of a voltammetric peak is defined by lateral interactions in adsorption layer, so the peak width may be a key to intensity of these interactions. Correlation between the width of the peak and interaction parameter G has been examined in details. It is impossible to find the exact equation setting G as a direct function of peak width. Approximate equations are proposed to calculate G from the peak width with high accuracy in a wide range of G values. G value can be useful not only for characterization of lateral interactions in adsorbed layer (for finding adsorption isotherm parameters), but also for quick estimation of adsorption of electroactive substance.

Keywords: adsorption, voltammetry, voltammetric peak, lateral interactions

Introduction

Interpretation of a peak shape is a chemometrics problem common within the fields of chromatography, spectroscopy, and voltammetry.¹ In voltammetry of surface-confined species this problem is simplified, as the peak shape is controlled primarily by the interactions within adsorption layer, or within a thin layer of solid particles confined to the electrode. At these conditions, an adsorption voltammetric peak is observed, with its height proportional to potential scan rate, v . The shape of this peak is determined by the interaction parameter G , which is a quantitative measure of lateral interactions. Surely, other parameters such as total adsorption of electroactive substance could play its role. However, the role of G will be mostly outlined here, presuming formation of a monolayer of adsorbed substance in the most cases. This situation is familiar for anyone dealing with adsorption voltammetric techniques.

It is well known that an adsorption peak width at half of its height δ (hereafter width) is closely related to G .^{2,3} The simplest expression of this relation has been given in an excellent review by Honeychurch and Rechnitz:²

$$\delta = 90.5 - 55.51 \cdot G \quad (1)$$

Parameter G affects the electrochemical equilibrium of the adsorbed redox system, so the well known Nernst equation should be modified in this case:²

$$E = E_p + \frac{RT}{nF} \cdot \left[\ln \frac{x_O}{x_R} + G \cdot (x_R - x_O) \right] \quad (2)$$

where x is the molar fraction of redox forms in adsorption layer (indices O and R correspond to oxidized and reduced forms), E_p is the peak potential. Other notations have their usual meaning. This equation may be deduced from different models, and it is relevant not for adsorbed monolayers only, but also for modified electrodes, electroactive organic polymers, and inorganic insertion compounds.³⁻⁸ More elaborated models give almost similar relationships.⁹

Surely, the meaning of the interaction parameter is an important question. Actually, this is a kind of formal parameter that could help to simplify and unify the treatment of adsorption peaks of different origin. For some solid state electrochemical systems (such as Prussian Blue), G can be defined as:⁷

$$G = \frac{w}{RT} \quad (3)$$

where w is a coefficient in the equation of the enthalpy of mixing of oxidized and reduced forms (ΔG_m):⁷

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$$\Delta G_m = w \cdot x_O x_R + \ln(x_R \cdot \ln x_R + x_O \cdot \ln x_O) \quad (4)$$

It is much more difficult to explain the meaning of G in the case of adsorption monolayer or adsorption submonolayer, because there is a subtle interplay between the energies of adsorption interactions and the energies of lateral interactions within the monolayer. Any reader interested in this subject could be addressed to the excellent article written by Laviron.³

Since equation 1 is valid for $G < 1$ only,² it causes a definite error when used for very narrow peaks with $G > 1$. As it will be shown later, any linear equation does not fit exactly the G , δ relationship for high negative G as well. Therefore, it is of importance to set a new equation applicable for a wider range of the interaction parameter.

Methodology

Almost all the calculations were performed with MS Excel. G values were taken in the range of -10 - 1.975 with an increment of 0.025 . Dimensionless peak width was calculated from G as described later on in the article. Then different functions proposed for reverse calculation of G were examined, their parameters were fitted using Solver add-in.

Results and Discussion

Exact dependence of δ on G needs to be found for setting such an equation. The current-potential relationship for adsorbed redox system is given by the equation:^{2,3}

$$I = nFA \frac{d\Gamma_O}{dt} = nFA\Gamma_T \frac{dx_O}{dE} \cdot \frac{dE}{dt} = \frac{n^2 F^2}{RT} A\Gamma_T v \Psi \quad (5)$$

where A is the electrode area, Γ_O is adsorption of the oxidized form, Γ_T is the total adsorption of redox system (of both oxidized and reduced form), and Ψ is a dimensionless current:^{2,3}

$$\Psi = \frac{RT}{nF} \cdot \frac{dx_O}{dE} = \frac{dx_O}{d\phi} \quad (6)$$

The symbol ϕ denotes the dimensionless potential:²

$$\phi = \frac{nF}{RT} \cdot (E - E_p) \quad (7)$$

The derivative in equation 6 can be found from equation 2, so the dimensionless current can be finally expressed as:

$$\Psi = \frac{x_O x_R}{1 - 2G \cdot x_O x_R} \quad (8)$$

The dimensionless current reaches its maximal value Ψ_{\max} at $E = E_p$ and $x_O = x_R = 0.5$:

$$\Psi_{\max} = \frac{1}{4 - 2G} \quad (9)$$

Calculation of δ requires a ϕ value corresponding to $\Psi = 0.5\Psi_{\max}$. It may be found from modified Nernst equation 2 if relevant x_O is known. It is evident from equations 8 and 9 that a quadratic equation has to be solved to find x_O satisfying $\Psi = 0.5\Psi_{\max}$. Using equation 2 with the value obtained leads to the final expression:

$$\delta_\phi = 2 \ln(3 - G + \sqrt{4 - G} \cdot \sqrt{2 - G}) - 2G \sqrt{\frac{2 - G}{4 - G}} \quad (10)$$

where δ_ϕ is the dimensionless peak width:

$$\delta_\phi = \frac{nF}{RT} \delta \quad (11)$$

Equations 10 and 11 allow one to calculate the dependence of δ_ϕ on G . The highest possible limit of G is quite definite, and it is equal to 2; systems with larger G are thermodynamically unstable.^{2,3} However, none of the adsorption models implies a certain limit for high negative G values; the system with G as low as -9 has been reported.¹⁰ So all the calculations here are made for $1.975 > G > -10$, as the maximal range plausible in experiment.

Figure 1 shows a graphical representation of G as a function of δ_ϕ . For more profound analysis, a derivative of this dependence has been calculated numerically (Figure 2).

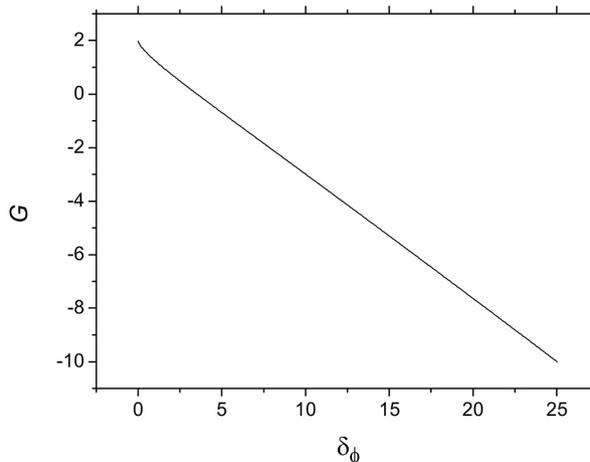


Figure 1. Interaction parameter as a function of the peak width in dimensionless potential scale (see the text for explanation).

The plot of G , δ_ϕ dependence looks perfectly linear for $G < 0$, but its derivative has a small but nearly constant slope, so it seems that a quadratic term should be added for perfect fitting at the highest negative G . The dependence for positive G is much more complex.

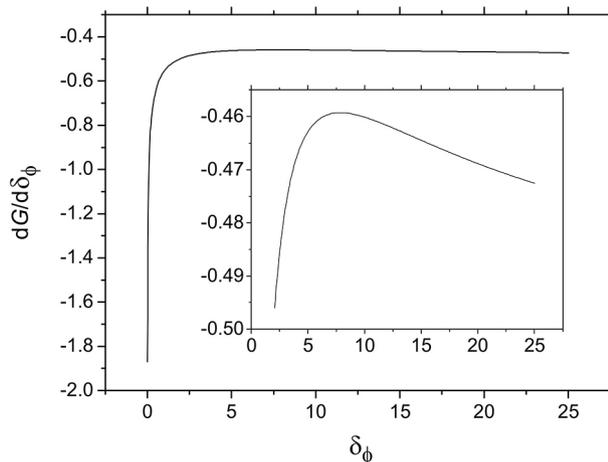


Figure 2. The first derivative of the dependence from Figure 1 calculated numerically. The inset: the same dependence for $-10 < G < 0.7$ only.

Let us build a function for reverse calculation of G from the peak width. It is impossible to find an exact solution, but an approximate equation with adjusted parameters can be chosen. The easiest way to set such a function is to make it linear. A practically linear dependence is observed for $-5 < G < 0$; linear fitting of this section gives an equation:

$$G = 1.62 - 0.461\delta_\phi \quad (12)$$

This dependence practically coincides with equation 1 when recalculated from dimensionless potential scale to millivolts and reversed (as δ_ϕ, G dependence). This linear dependence is really perfect; its parameters have been fitted as 1.617 ± 0.001 , and -0.4607 ± 0.001 (with a 95% confidence level). It means that equation 1 presented by Honeychurch and Rechnitz² has excellent accuracy in some range of G values. But how wide is this range? The usability criterion of a fitted function should be based on the error the function brings about; it must be less than an experimental error. For digital data recording, it is reasonable to accept that accuracy of δ determination ($\Delta\delta$) is 1 mV. So it is impossible to determine G value from δ with uncertainty (ΔG) less than:

$$\Delta G = \left| \frac{dG}{d\delta} \right| \cdot \Delta\delta \quad (13)$$

If the calculation error is less than ΔG , then the equation is suitable for a given G range; so ΔG value can be used as

a tolerance limit. The same can be applied to calculations with dimensionless peak width.

Figure 3 represents the calculation error (the deviation of the calculated value G_{calc} from the exact value) for equation 10 as a function of G . The tolerance limit ΔG is also given ($n = 1$ and 25°C assumed for calculation of $\Delta\delta$). It can be seen from Figure 3 that equation 10 is valid for $-6.7 < G < 0.4$ with high accuracy. The same G range may be assigned for equation 1. This is a great result, but possibly it is not suitable for all the situations that could be encountered in the experiment.

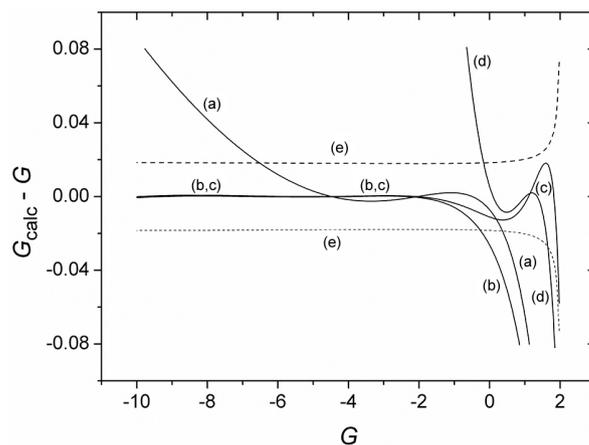


Figure 3. Calculation errors for the equations examined: (a) equation 12; (b) equation 14; (c) equation 15; (d) equation 16; (e) tolerance limit ΔG (dotted).

There is a simple way to make this equation even more precise. Figure 2 indicates a second order polynomial as a good choice for negative G region; fitting the data for $-10 < G < -2$ produces the equation:

$$G = 1.57 - 0.452\delta_\phi - 0.000431\delta_\phi^2 \quad (14)$$

It can be seen from Figure 3 that this equation is useful for any $G < -0.3$, and it is almost exact for $G < -2$. Values of $G < -10$ were regarded practically insignificant, and they were not tested. However, it seems that equation 14 is useful for much more negative G values as well.

Addition of an exponent to equation 14 is a suitable way to build an equation covering all the considered range of G . It allows one to keep a good fit obtained for negative G , and to achieve a reasonable correlation with the data for positive G . The resulting equation is:

$$G = 1.57 - 0.452\delta_\phi - 0.000431\delta_\phi^2 + 0.352 \cdot \exp(-0.891 \times \delta_\phi) \quad (15)$$

Figure 3 shows that this equation has a negligible error for any $G < -1.5$. For large positive G , the error rises rapidly,

but is still within the tolerance limit. It makes equation 15 acceptable for the whole G range under consideration, $-10 < G < 1.975$.

Equation 15 is more accurate compared with equation 12, and it is suitable for a wider range of interaction parameter, but it is much more complicated. It can be simplified for positive G because the quadratic term could be safely omitted for any $G > -1.5$. Equations 12 or 14 could be used instead of equation 15 in appropriate G domain, but none of them is precise for $G > 0.4$. An alternative to equation 15 for positive G can be found by fitting the dependence with a second order polynomial:

$$G = 1.83 - 0.593\delta_0 + 0.0214\delta_0^2 \quad (16)$$

This equation is useful for $-0.2 < G < 1.6$ (see Figure 3).

The proposed approach does not take into consideration some effects that are possible at high negative or positive values of G . If $G \ll 0$, the interaction energy of Ox and Red forms within the adsorbed layer may be so high that they can form the dimerised species.¹¹ An opposite situation may be at G tending to 2, with a trend to partial separation of the forms deviating from their stochastic distribution in the layer.¹²

Conclusions

It has been shown that interaction parameter G can be calculated with high precision from the width of adsorption voltammetric peak. However, are the G values obtained useful for anything behind an estimation of energy of lateral interaction? Yes, they are! Combining equations 3 and 9, one can easily estimate Γ_T value from the peak height (I_{\max}) if G is known:

$$\Gamma_T = \frac{RT}{n^2 F^2} \cdot \frac{4-2G}{Av} \cdot I_{\max} \quad (17)$$

Usual estimation of Γ_T requires peak integration:

$$\Gamma_T = \frac{\int_{-\infty}^{+\infty} IdE}{nFAv} \quad (18)$$

Γ_T is an important characteristic; this is a measure of electroactive substance quantity loaded on the electrode. It is very often of analytical value. Its estimation through measuring peak width and height is surely much easier than a peak integration.

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