
SOME VIEWS ABOUT THE RELATION BETWEEN THE RATE CONSTANTS OF RETARDED ELECTRODE REACTIONS REQUIRING REACTANT ADSORPTION AND THE CORRESPONDING INHIBITOR CONCENTRATIONS AT HIGH COVERAGES

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By the combination of some well known equations, an attempt is made to develop a relation between the logarithms of the rate constant, k , of inhibited reactions, requiring reactant adsorption and the corresponding inhibitor concentration c_i which can assign a definite physical meaning to the slope of any type of the $\ln k$ vs $\ln c_i$ plots.

It is known that, in the presence of strongly adsorbable surfactants, there is a significant influence of the adsorption film on the kinetics of reactions which require reactant adsorption.

Nowadays it became a common practice¹⁻¹⁰ that the correlation between the presence of the film and the reaction kinetics is preferably expressed by the dependence of the logarithm of the rate constants, $\ln k$, on the film pressure, π_i or equivalently on the logarithm of the corresponding bulk inhibitor concentrations, $\ln c_i$, at full coverage, $\theta \approx 1$. Experiments have shown^{2,4,5,9,11-14} that between $\ln k$ and π_i or $\ln c_i$, there is always a linear dependence with negative, zero and sometimes positive slope. This linearity seems to be a general rule, almost independent of the kind of reactant and as far as we know, also independent of the kind of inhibitor. At $\theta \approx 1$, the theories of Lipkowski, Guidelli and their coworkers^{3,4,15}, predominantly appreciating steric factors and regarding interactions and double layer effects as constant, usually offer a sound interpretation for any type of the $\ln k$ vs $\ln c_i$ dependence, except when k increases with increasing c_i (positive slope).

In the present paper we attempt by combining of some well known relations^{3,4} to show that when equivalently accounting for interactions and steric factors, for $\theta \approx 1$, it is possible to assign a physical meaning to the slope of any type of the $\ln k$ vs $\ln c_i$ plots.

DISCUSSION

Experimental results have shown that in the case of reactions requiring reactant adsorption the rate constant, k , of the retarded reactions is usually decreasing with increasing bulk adsorbate concentration, c_i , in such a way that the corresponding $\ln k$ vs $\ln c_i$ plots are linear with negative slopes^{1,2,4,9}. Not rarely¹¹⁻¹⁵, a region of negative slopes is followed, for increasing c_i , by a region where k is independent of c_i i.e. the $\ln k$ vs $\ln c_i$ plots present a zero slope. More rarely¹¹⁻¹⁴, it is observed that in systems which represent a combination of negative and zero slopes, further increase of c_i leads to a reincrease of k , so that fairly linear $\ln k$ vs $\ln c_i$ plots with positive slopes are obtained.

According to the theories of Lipkowski, Guidelli and their coworkers^{4,15}, the region of negative slopes corresponds to the formation of the activated complex after reactant adsorption at the reaction site, followed by the incorporation of the already adsorbed species, viz. the solvent molecule at low θ and the surfactant at $\theta \approx 1$. Under these conditions the following well known equation¹ is valid:

$$\ln k = \text{constant} - (r_{\neq}/r_i) \ln c_i, \quad (1)$$

where r_{\neq} and r_i are the number of solvent molecules having a cross sectional area equal to that of the activated complex and the inhibitor, respectively. On the other hand, the region of zero slopes corresponds¹⁵ to the formation of an activated complex after a surface reaction between the reactant and the surfactant. Obviously this case cannot be interpreted in terms of Eq. (1).

Plots of $\ln k$ vs $\ln c_i$ with positive slopes are reported for the following reactant-surfactant couples: $(C_3H_7)_2C_6H_5PO-Bi(III)$, $(C_4H_9)_2C_6H_5PO-Bi(III)$,

$C_6H_{13}(C_2H_5)_2PO-Bi(III)$, $C_7H_{15}(C_2H_5)_2PO-Bi(III)$, $C_8H_{17}(C_2H_5)_2-Bi(III)$ (ref.¹¹), $C_8H_{17}(CH_3)_2PO-Cu^{2+}$, $C_9H_{19}(CH_3)_2PO-Cu^{2+}$ (ref.¹²), (sodium dodecyl sulfate + dodecyl alcohol)- Cd^{2+} (ref.¹³, Fig. 1), and $[CH_3(C_6H_5)_3As]^+-Cd^{2+}$ (ref.¹⁴, Fig. 2).

These systems cannot be interpreted by Eq. (1) either. The interpretations given are usually of a qualitative character and they concern either a "passive" effect of increasing permeability of the adsorbed film due to micellization¹¹⁻¹³, or an "active" effect of reaction reacceleration¹⁶ due to catalytic effects.

However, the linearity of these diagrams is obvious and the question is whether this linearity is an artefact or whether it has a definite physical meaning. Before answering this question we will recall that in an early publication¹⁷ Parsons has pointed out that the parameter b (ref.¹⁸) of relation:

$$\ln k = \text{constant} + b \ln(1 - \theta) \quad (2)$$

includes the contribution from both the terms of the right hand side of the relation:

$$\ln(k/k_{\Gamma_i=0}) = -2B_{*,i}\Gamma_i + r_i \ln[r_i(1 - \Gamma_i/\Gamma_s)], \quad (3)$$

i.e. the interaction $B_{*,i}$ and the stereochemical factor r_i . In Eq. (3) Γ_s is the saturation value of the surface concentration Γ_i , related through $\Gamma_i/\Gamma_s = \Theta$ and

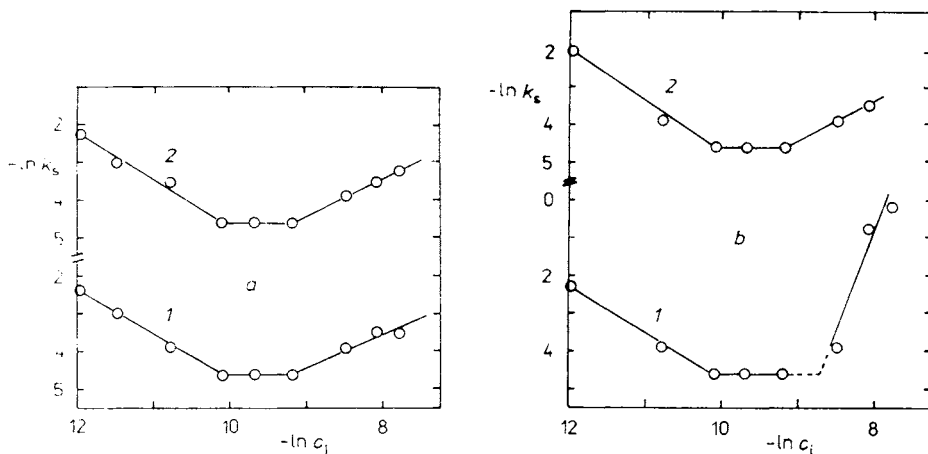


FIG. 1

Dependence of $\ln k_s$ on $\ln c_i$ (i stands for sodium dodecyl sulfate) for Cd^{2+} reduction in the presence of a mixture of: *a* 99.5% sodium dodecyl sulfate + 0.5% dodecyl alcohol; *b* 98.6% sodium dodecyl sulfate + 1.4% dodecyl alcohol, at 20 cs^{-1} 1 and 500 cs^{-1} 2 a.c. measuring signal. Base solution aqueous 0.5M-NaCl. Taken from ref.¹³

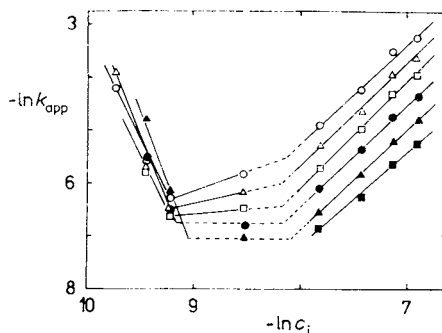


FIG. 2

Dependence of $\ln k_{\text{app}}$ on $\ln c_i$ for Cd^{2+} reduction in the presence of $\text{CH}_3(\text{C}_6\text{H}_5)_3\text{As}$, at the following electrode potentials in V (SCE): \circ -0.9; \triangle -1.0; \square -1.1; \bullet -1.2; \blacktriangle -1.3; \blacksquare -1.4. Base solution aqueous 0.2M- KNO_3 . Taken from ref.¹⁴

$$2 B_{\neq,i} \Gamma_i - r_i \ln [r_i(1 - \Gamma_i/\Gamma_s)] = \ln \gamma_{\neq} \quad (4)$$

is the activity coefficient of the activated complex. Evidently, $\ln \gamma_{\neq}$ operates as a measure of the relative retardation of the electrode reaction due to the presence of the adsorbed film.

After the above work of Parsons the theory and practice, up to now, was based on some sort of "neutralization" of the interactions on behalf of the steric factors. Although for $\Theta \approx 1$ double layer effects can be regarded as constant, it is only for a few categories of substances that this condition can guarantee that steric factors predominate while interactions remain constant, leading to a linear $\ln k$ vs $\ln c_i$ relation in the frames of Eq. (1). As such substances we mention aliphatic alcohols and acids, i.e. substances with completely asymmetrical molecules presenting weak particle-particle interactions. On the other hand in the presence of phosphororganic, arsenicorganic and other similar compounds, i.e. substances with nearly symmetrical molecules but with very strong interactions, for $\Theta \approx 1$ steric factors seem to play a less important role compared to that played by the lateral interactions, also leading to fairly linear $\ln k$ vs $\ln c_i$ plots^{11-15,19,20}.

Below, by a simple manipulation of some well known equations, equivalently accounting for both interactions and steric factors, a more general relation than Eq. (1) is derived. Henceforth by k_{Θ} we will denote the rate constant which corresponds to a non zero degree of coverage. We combine the relations^{3,4}:

$$\ln(k_{\Theta}/k_{\Theta=0}) = a_{\neq,i} \Theta + r_{\neq} \ln(1 - \Theta) \quad (5)$$

and

$$\beta_i c_i = \frac{\Theta}{r_i(1 - \Theta)^{r_i}} \exp(-2a_i \Theta), \quad (6)$$

where a and r denote the interaction parameter and the number of the displaced solvent molecules. The symbols i and \neq correspond to the activated complex and the inhibitor, respectively.

From Eq. (6) we obtain:

$$\Theta = -(1/2a_i) \left[\ln \beta_i c_i - \ln \frac{\Theta}{r_i(1 - \Theta)^{r_i}} \right]. \quad (7)$$

Therefore, from Eqs (5) and (7) we obtain:

$$\ln(k_{\Theta}/k_{\Theta=0}) = -(a_{\neq,i}/2a_i) \left[\ln \beta_i c_i - \ln \frac{\Theta}{r_i(1 - \Theta)^{r_i}} \right] + r_{\neq} \ln(1 - \Theta). \quad (8)$$

If the constant terms are included in the factor A , then Eq. (8) becomes:

$$\ln k_{\Theta} = A - (a_{\neq,i}/2a_i) \ln c_i + (a_{\neq,i}/2a_i) \ln \Theta + [r_{\neq} - (a_{\neq,i}/2a_i) r_i] \ln (1 - \Theta). \quad (9)$$

Equation (9) is a general relation between $\ln k_{\Theta}$ and $\ln c_i$, in terms of interactions and steric factors, for $0 < \Theta < 1$.

If we assume that $\Theta \approx 1$ but $\Theta \neq$ constant, then Eq. (9) becomes:

$$\ln k_{\Theta} = A - (a_{\neq,i}/2a_i) \ln c_i + [r_{\neq} - (a_{\neq,i}/2a_i) r_i] \ln (1 - \Theta). \quad (10)$$

Relation (10) is of the general form:

$$\ln k_{\Theta} = f[\ln c_i, \ln (1 - \Theta)]. \quad (11)$$

It is known²¹, that this relation represents a 3-D system in which the functions:

$$\ln k_{\Theta} = f(\ln c_i) \quad (12a)$$

and

$$\ln k_{\Theta} = f[\ln (1 - \Theta)] \quad (12b)$$

are orthogonal projections of the corresponding 3-D curves.

If one of the Eqs (12a) or (12b) and also the relation:

$$\ln (1 - \Theta) = f(\ln c_i) \quad (13)$$

are linear, then the remaining one is linear as well. At the plateau of the adsorption isotherm the experimental results, known from the literature, support the linearity of relation (12b).

On the other hand, for $\Theta \approx 1$ Eq. (6) can be written as:

$$\ln (1 - \Theta) = \text{constant} - (1/r_i) \ln c_i \quad (14)$$

which is obviously a linear dependence. Thus for $\Theta \approx 1$ and $\Theta \neq$ constant, (Eq. 12a) is linear and consequently the relation between $\ln k$ and $\ln c_i$, within Eq. (10), is also linear.

If we assume that $\Theta \approx 1$ and $\Theta =$ constant, then $1 - \Theta$ is also constant and Eq. (10) is written as:

$$\ln k_{\Theta} = A - (a_{\neq,i}/2a_i) \ln c_i. \quad (15)$$

Equation (15) evidently represents a linear relation between $\ln k_{\Theta}$ and $\ln c_i$, at any constant value of the electrode coverage.

According to Afanasiev and Damaskin²², the term $a_{\neq,i}/2a_i$ accounts for "the relative decrease in the attractive interaction between the adsorbed molecules, when incorporated in the adsorption layer of depolarizer particles". This interpretation has been criticized by Guidelli *et al.*⁴ as being of qualitative character. Nevertheless the term $a_{\neq,i}/2a_i$ can be reasonably regarded as (i) a measure of the balance of the various lateral interactions and (ii) in analogy to the term $B_{\neq,i}$ of (3), as a measure of the contribution of these interactions to the relative retardation of the reaction, which is expressed by $\ln(k_{\Theta}/k_{\Theta=0})$. An inspection of Eqs (3) and (10) reveals a reasonable similarity between their right hand sides which is rendered more clear when Frumkin isotherm is obeyed, i.e. when $r_i \approx 1$. Then (10) becomes:

$$\ln k_{\Theta} = A - (a_{\neq,i}/2a_i) \ln [c_i(1 - \Theta)] + r_{\neq} \ln (1 - \Theta). \quad (16)$$

The analogy between (3) and (16) is clear and accounting for (4) we can set:

$$\ln \gamma_{\text{TOTAL}} = (a_{\neq,i}/2a_i) \ln [c_i(1 - \Theta)] - r_{\neq} \ln (1 - \Theta), \quad (17)$$

where

$$\ln \gamma_{\text{TOTAL}} = \ln \gamma_{\text{INT}} + \ln \gamma_{\text{SF}} \quad (18)$$

and γ_{TOTAL} is the overall activity coefficient of the interfacial solution, which incorporates the effect of the lateral interactions, γ_{INT} and the steric factors, γ_{SF} , respectively.

If the effect of the steric factors can be considered as constant, which is more likely to happen for symmetrical surfactants and $\Theta = \text{constant}$, then Eq. (17) becomes:

$$\ln \gamma_{\text{TOTAL}} = \text{constant} + (a_{\neq,i}/2a_i) \ln c_i. \quad (19)$$

Therefore the ratio $a_{\neq,i}/2a_i$ is related to $\ln \gamma_{\text{INT}}$ and in this case its values give information about the deviations of the interfacial mixture of surfactant (A), reactant (R) and solvent (S) from Raoult's law, in analogy to the views of Mohilner²³ and Trasatti^{24,25}.

When the slope of the $\ln k_{\Theta}$ vs $\ln c_i$ plots is positive, then the interfacial mixture exhibits negative deviations from Raoult's law. The miscibility of the R, A and S compounds is very limited. This happens when, for example, the surfactant aggregates in the bulk, due to micelle formation. In this case the permeability of the adsorption film is increasing and subsequently the rate constant increases. Very limited miscibility and negative deviations must be also exhibited when aggregation takes place at the interface. This is the case of film association, which results in the formation of

“holes”^{26,27} in the adsorption film. However, so far no systematic experimental verification of positive $\ln k_{\theta}$ vs $\ln c_i$ slope has been reported.

When the slope of the $\ln k_{\theta}$ vs $\ln c_i$ plots is negative, the system presents positive deviations from the law of Raoult. In this case the miscibility of the R, A, S compounds at the interface is significant. According to the degree of coverage, at high θ the formation of R-A complexes is favoured, while at low θ , R-S complexes are formed. For the case that the ratio $a_{\neq,i}/2a_i$ tends to zero and $\theta \approx 1$, $\theta = \text{constant}$, then Eq. (10) gives:

$$\ln k_{\theta} = A + r_{\neq} \ln(1 - \theta) \quad (20)$$

easily leading¹ to Eq. (1), which enables the calculation of the area per activated complex particle from the values of the ratio r_{\neq}/r_i .

Finally when the slope of the $\ln k_{\theta}$ vs $\ln c_i$ plots is zero, this implies that $\ln k_{\theta}$ is independent of the bulk surfactant concentration. In analogy to the views of Trasatti^{24,25}, zero slope may also be regarded as a case of positive deviations from the law of Raoult. In this sense zero slope, according either to Eq. (10) or Eq. (15) implies that $a_{\neq,i} \ll 2a_i$ or that R-A interactions are much weaker than the A-A ones. The case that neither the A-A interactions are strong enough, then represents a random arrangement of the interfacial mixture. On the other hand negative slopes may correspond to a more organized structure of the surface layer.

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