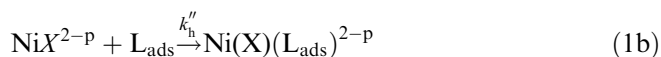


Yakov I. Tur'yan · Fernando Mata · Jorge Moyano  
Pavel Gorenbein · Ron Kohen

## Mechanism of the electroreduction of Ni (II) ions on mercury electrodes catalyzed by pyridine and its derivatives: nicotinamide, *N,N*-diethylnicotinamide and nicotine: concept of parallel heterogeneous catalytic reactions

Received: 6 December 2004 / Revised: 20 December 2004 / Accepted: 13 May 2005 / Published online: 17 November 2005  
© Springer-Verlag 2005

**Abstract** The theory of the polarographic catalytic currents (mechanism CE) has been developed for the system:  $\text{Ni}^{2+}$ -L- $\text{X}^{\text{p-}}$  where L: pyridine (Py), nicotinamide (NA), *N,N*-diethylnicotinamide (DEN), nicotine (NC) and  $\text{X}^{\text{p-}}$ :  $\text{NO}_3^-$ ,  $\text{AcO}^-$ ,  $\text{HPO}_4^{2-}$ . The theory is based on the kinetic parallel heterogeneous catalytic reactions:



with the use of Langmuir's adsorbed isotherm. The kinetic equations obtained for average and instantaneous currents allowed to determine the Langmuir's parameters ( $\text{NA} < \text{DEN} < \text{NC}$ ), kinetic parameters and the contribution of reactions 1a and b to the summary catalytic currents. The  $k''_h$  value rises with the increase of the  $\text{NiX}^{2-\text{p}}$  stability constant. The correlation  $k''_h \gg k'_h$  was explained by the additional effect of the field electrode through  $\text{X}^{\text{p-}}$ . These effects base the reaction 1b instead of accepted early alternative reaction of the ligand exchange. In spite of the fact that  $k''_h \gg k'_h$ , the contribution of the reaction 1a in the summary catalytic current attained more than 60% (Py, DEN) due to the influence of the  $\psi_0$  potential.

**Keywords** Polarographic catalytic currents · Nickel (II) catalytic systems · Catalysis by pyridine and its derivatives · Parallel heterogeneous catalytic reactions · Kinetic and adsorbed parameters

### Introduction

Catalytic current at the dropping mercury electrode corresponding to the polarographic prewave of a metal ion's electroreduction catalyzed by a ligand represents a great interest for electrochemistry, analytical and coordinate chemistry [1–4].

Catalytic systems Ni (II)-pyridine (Py) and its derivatives: nicotinamide (NA), *N,N*-diethylnicotinamide (DEN) and nicotine (NC) may be considered as a model. However, the kinetics and mechanism of electrocatalytic process in these systems were developed insufficiently, especially for NA, DEN and NC. This work develops the theory of the catalytic currents, analyzes and compares data on the kinetics and mechanism of electrocatalytic processes in the Ni (II)-Py (NA, DEN, NC) systems on the basis of the concept of parallel heterogeneous catalytic reactions with participation of the adsorbed ligand-catalyst [5], using the Langmuir's adsorbed isotherm [6, 7].

### Theoretical part

The mechanism of the considered prewaves has been discovered by Mark and Reilly [8, 9] as the catalytic process which takes place with participation of the adsorbed at electrode ligand-catalyst (heterogeneous reaction). Further development of this mechanism was continued by Tur'yan et al. [2, 5, 10, 11]. The authors [10, 11] proposed the concept of parallel heterogeneous catalytic reaction. The volume-hydrated metal ions and its complexes with ligand-catalyst and anions of the

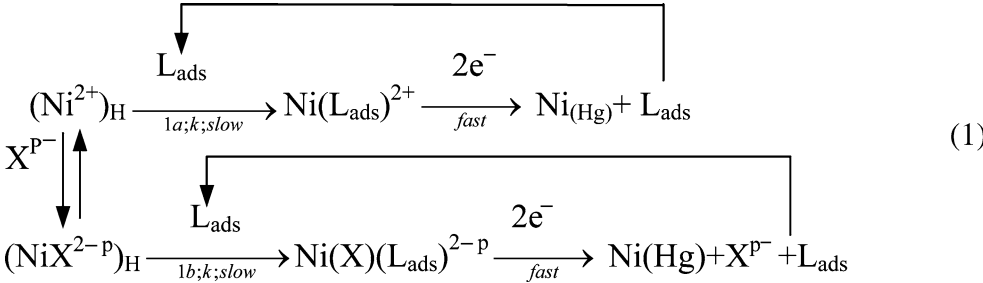
Dedicated to Professor Zbigniew Galus on the occasion of his 70th birthday and in recognition of his many contributions to electrochemistry

Y. I. Tur'yan · P. Gorenbein (✉) · R. Kohen  
Department of Pharmacy, The Hebrew University of Jerusalem,  
POB 12065, Jerusalem 91120, Israel  
E-mail: gor\_n\_bein@yahoo.co.uk

F. Mata · J. Moyano  
Departamento de Química Física, Facultad de Ciencias,  
Universidad de Valladolid, 47 005, Valladolid, Spain

supporting electrolyte from one side and adsorbed ligand-catalyst from the other side participated in this heterogeneous process. Equilibrium between hydrated metal ions and complexes in the bulk solution including reaction plane near electrode surface (the outer Helmholtz plane) was accepted [10, 11]. This equilibrium and also adsorbed equilibrium including the low ligand-catalyst concentration ( $\geq 5.0 \times 10^{-5}$  M) have been proved by the determination of the stability constants of the complexes on the basis of the catalytic current [12]. Precipitation of the complex in the considered heterogeneous catalytic reaction has also been analyzed by Mark et al. [13] but without taking into account of the equilibrium of  $\text{NiX}^{2-p}$  formation also near the electrode surface that did not allow to obtain kinetic parameters of the process.

Further we consider the concept of parallel heterogeneous catalytic reactions [5] in abridged form when the participation of the complexes  $\text{NiL}^{2+}$  and  $\text{NiLX}^{(2-p)}$  in the heterogeneous catalytic reactions may be neglected;  $L_s$  is the ligand-catalyst;  $X^{p-}$  is the anion of the supporting electrolyte. Hence we obtain the scheme (1) of the catalytic process for limiting catalytic current. Note that Mark et al. [13] paid attention to the existence of two alternative reactions 1b (scheme 1): reaction of the ligand exchange and reaction of the mixed complex formation. As it will be shown in ‘‘Discussion’’, it is necessary to prefer the latter reaction, as it was made in scheme (1), unlike Ref. [5].



In Scheme 1: index ‘‘H’’ is the outer Helmholtz plane,  $k'_h$  and  $k_h$  are the heterogeneous rate constants;  $\text{Ni}(L_{\text{ads}})^{2+}$  and  $\text{Ni(X)}(L_{\text{ads}})^{2-p}$  are the electroactive complexes adsorbed due to ligand-induced adsorption. At the same time, the direct adsorption of the analogous complexes from the bulk solution does not give rise to the electroactive species in the considered catalysis. These conclusions have been drawn from the kinetic, equilibrium and electrocapillary measurements [2, 3].

The low concentration range allows to use the Henry adsorption equation [10, 14]:

$$K_L = \frac{[L_{\text{ads}}]}{10^{-3}[L]_s} \quad (2)$$

where  $K_L$  is Henry constant (cm);  $[L]_s$  is the equilibrium concentration at the boundary between diffusion and double electric layer (more accurately,  $[L]_s$  should be

substituted with  $[L]_H$  here, but these values are practically equal for uncharged particles).

As it was shown by Mata et al. [6, 7], it is necessary to use Langmuir’s adsorbed isotherm (Eq. 3) instead of Eq. 2 for wider interval of  $C_L$  (Py and NC).

$$[L'_{\text{ads}}] = \frac{10^{-3}K_L[L]_s}{1 + \omega[L]_s} \quad (3)$$

where  $\omega$  is Langmuir’s parameter.

Knobloch [15] has also observed the applying of Langmuir’s isotherm for the process of the hydrogen catalytic evolution under influence of the product NA electroreduction.

Taking into account that heterogeneous chemical reactions of type (1) correspond to the limiting current of prewave and at pseudo-first order ( $[L_{\text{ads}}] = \text{const}$ ), Koutecky’s equation [16] was used in works [10, 14] that is analogous to the equation for the description of electron irreversible transport kinetics. For average current this equation accepts form:

$$\chi_1 = \left(\frac{12t_1}{7D}\right)^{0.5} k_{\text{ef}} \quad (4)$$

and for instantaneous currents

$$\chi = \left(\frac{12t}{7D}\right)^{0.5} k_{\text{ef}} \quad (5)$$

where  $\chi_1(\chi)$  is the Koutecky’s parameter;  $t_1$  is drop lifetime;  $t$  is the time elapsed after the beginning of the drop growth;  $D$  is the common diffusion coefficient;  $k_{\text{ef}}$  is the effective summary heterogeneous rate constant of the parallel formation of  $\text{Ni}(L_{\text{ads}})^{2+}$  and  $\text{Ni(X)}(L_{\text{ads}})^{2-p}$  at the conditions of the limiting catalytic current when the opposite heterogeneous reaction may be neglected; it is also being related to the effective heterogeneous rate constant for individual parallel reactions (see below);  $\chi_1(\chi)$  is determined from  $\bar{F}(\chi_1)$  and  $F(\chi)$  values, respectively, using Koutecky’s tables [16, 17]. The  $\bar{F}(\chi_1)$  and  $F(\chi)$  values are calculated from the equations:

$$\bar{F}(\chi_1) = \frac{\sum \bar{I}_{\text{lim}}^c}{\bar{I}_{\text{lim}}^d} \quad (6)$$

$$F(\chi) = \frac{\sum I_{\text{lim}}^c}{I_{\text{lim}}^d}, \quad (7)$$

where  $\sum \bar{I}_{\text{lim}}^c$ ,  $\sum I_{\text{lim}}^c$  being the average and instantaneous limiting catalytic currents, respectively (as the summary current for parallel catalytic reactions in Scheme (1));  $\bar{I}_{\text{lim}}^d$ ,  $I_{\text{lim}}^d$  are the average and instantaneous limiting diffusion currents, respectively.

For average currents, Weber and Koutecky [17] have obtained very accurate analytical solution corresponding to Koutecky's table [16, 17]:

$$\frac{\sum \bar{I}_{\text{lim}}^c}{\bar{I}_{\text{lim}}^d - \sum \bar{I}_{\text{lim}}^c} = 0.677\chi_1 \quad (8)$$

Besides the simplicity of the kinetic calculations another important advantage of the analytical solutions is the inclusion of  $\bar{I}_{\text{lim}}^d(I_{\text{lim}}^d)$  in the kinetic equation and hence of the concentration of nickel(II) species,  $C_{\text{Ni}}$ .

$$k_{\text{ef}} = \frac{[\text{L}_{\text{ads}}] \{ k'_h \exp(-\psi_0(2F/RT)) + k''_h(\beta_1)_{\text{X}^{p-}} [\text{X}^{p-}]_s \exp(-\psi_0[(2-p)F/RT]) \}}{1 + (\beta_1)_{\text{L}} [\text{L}]_s + (\beta_1)_{\text{X}^{p-}} [\text{X}^{p-}]_s} \quad (16)$$

Some analytical solutions for instantaneous catalytic kinetic currents have been proposed [7, 13, 18, 19], which were more or less close to the accurate results obtained from Koutecky's table [16].

The solution [7, 13] was based on the plane static electrode and has the form:

$$\frac{\sum I_{\text{lim}}^c}{I_{\text{lim}}^d} = \left( \frac{7\pi}{12} \right)^{0.5} \chi \exp\left( \frac{7}{12} \chi^2 \right) \text{erfc} \left[ \left( \frac{7}{12} \right)^{0.5} \chi \right] \quad (9)$$

Our comparison with Koutecky's table has shown that Eq. 9 gave  $\chi$  values about 30% lower than the values from Koutecky's table. The principle reason is, most probably, neglect of plain electrode expanding (Eq. 9), which was taken into account by Koutecky [16].

Smithe et al. [18] approach gave the following equation:

$$\left( \frac{\sum I_{\text{lim}}^c}{I_{\text{lim}}^d - \sum I_{\text{lim}}^c} \right)^{0.917} = 1.030\chi \quad (10)$$

which at low  $F(\chi)$  ( $\leq 0.08$ ) has shown  $\chi$  values 7–21% higher than the values from Koutecky's table.

Jones and Aikens approach [19] (Eq. 11) gives good similarity of  $\chi$  values to Koutecky's table for wide range of  $F(\chi)$  values.

$$\left( \frac{\sum I_{\text{lim}}^c}{I_{\text{lim}}^d - \sum I_{\text{lim}}^c} \right)^{0.947} = 1.041\chi \quad (11)$$

Eq. 11 will be used by us below.

We applied the following equations for obtaining the  $k_{\text{ef}}$  (Eq. 4 or 5) dependence from the effective constants of the parallel heterogeneous catalytic reactions 1a and (b) (scheme 1):

$$k_{\text{ef}} C_{\text{Ni}}^s = k'_{\text{ef}} [\text{Ni}^{2+}]_s + k''_{\text{ef}} [\text{NiX}^{2-p}]_s \quad (12)$$

$$C_{\text{Ni}}^s = [\text{Ni}^{2+}]_s + [\text{NiL}^{2+}]_s + [\text{NiX}^{2-p}]_s \quad (13)$$

where  $k'_{\text{ef}}$  and  $k''_{\text{ef}}$  are the effective heterogeneous rate constants of the reactions 1a and b (scheme (1)), respectively.

Taking into account the equilibrium between  $\text{Ni}^{2+}$ ,  $\text{NiL}^{2+}$ ,  $\text{NiX}^{2-p}$  in any point of the solution and using Gierst's equation [20] for effective rate constants of the heterogeneous parallel catalytic reactions:

$$k'_{\text{ef}} = k'_h [\text{L}_{\text{ads}}] \exp\left(-\psi_0 \frac{2F}{RT}\right) \quad (14)$$

$$k''_{\text{ef}} = k''_h [\text{L}_{\text{ads}}] \exp\left(-\psi_0 \frac{(2-p)F}{RT}\right) \quad (15)$$

from Eqs. 12–15, we have obtained the following relationship:

where  $(\beta_1)_{\text{L}}$  and  $(\beta_1)_{\text{X}^{p-}}$  are the complex stability constants of  $\text{NiL}^{2+}$  and  $\text{NiX}^{2-p}$ , respectively (higher complexes can be neglected);  $\psi_0$  is the potential of the outer Helmholtz plane; the other symbols are generally accepted in electrochemistry.

For average limiting catalytic current (DC polarography) at the excess of  $\text{X}^{p-}$  ( $[\text{X}^{p-}]_s = C_{\text{X}^{p-}}$ ) from Eqs. 3, 4, 8 and 16 for scheme (1), we obtain kinetic equation (17):

$$\begin{aligned} Y_{\text{av}} &= \frac{\sum \bar{I}_{\text{lim}}^c \left\{ 1 + (\beta_1)_{\text{L}} [\text{L}]_s + (\beta_1)_{\text{X}^{p-}} C_{\text{X}^{p-}} \right\}}{(\bar{I}_{\text{lim}}^d - \sum \bar{I}_{\text{lim}}^c) [\text{L}]_s} \\ &= 0.886 \left( \frac{t_1}{D} \right)^{0.5} \frac{K_{\text{L}}}{1 + \omega [\text{L}]_s} \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) \right. \\ &\quad \left. + k''_h (\beta_1)_{\text{X}^{p-}} C_{\text{X}^{p-}} \exp\left(-\psi_0 \frac{(2-p)F}{RT}\right) \right\} \quad (17) \end{aligned}$$

For the limiting catalytic instantaneous current (DC fast polarography) from Eqs. 3, 5, 11 and 16 for scheme (1) we obtain kinetic equation (18).

$$\begin{aligned} Y_{\text{in}} &= \left( \frac{\sum I_{\text{lim}}^c}{I_{\text{lim}}^d - \sum I_{\text{lim}}^c} \right)^{0.947} \frac{\{ 1 + (\beta_1)_{\text{L}} [\text{L}]_s + (\beta_1)_{\text{X}^{p-}} C_{\text{X}^{p-}} \}}{[\text{L}]_s} \\ &= 1.363 \left( \frac{t}{D} \right)^{0.5} \frac{K_{\text{L}}}{1 + \omega [\text{L}]_s} \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) \right. \\ &\quad \left. + k''_h (\beta_1)_{\text{X}^{p-}} C_{\text{X}^{p-}} \exp\left(-\psi_0 \frac{(2-p)F}{RT}\right) \right\} \quad (18) \end{aligned}$$

The ligand-catalysts investigated here (Py, NA, DEN, NC) form with  $\text{Ni}^{2+}$  relatively weak complexes [ $(\beta_1)_{\text{L}} \leq 10^2$ ]. If protonation of nitrogen in pyridine ring can be neglected at small excess of  $\text{Ni}^{2+}$  and particularly

when  $C_L$  and  $C_{Ni}$  are close and also at a great excess of L ( $C_L \gg C_{Ni}$ ), the following correlation takes place:

$$[L]_s \cong C_L \quad (19)$$

When  $C_{Ni} \gg C_L$ ,  $[L]_s$  for average currents is calculated from Eq. 20 derived as in work [21], while also taking into account the  $NiX^{2-p}$  complex.

$$[L]_s = \frac{C_L \{1 + (\beta_1)_{X^{p-}} C_{X^{p-}}\} \bar{I}_{lim}^d}{\{1 + (\beta_1)_{X^{p-}} C_{X^{p-}}\} \bar{I}_{lim}^d + (\beta_1)_L (\bar{I}_{lim}^d - \sum \bar{I}_{lim}^c) C_{Ni}} \quad (20)$$

For instantaneous current the  $\sum \bar{I}_{lim}^c$  and  $\bar{I}_{lim}^d$  values in Eq. 20 must be substituted with  $\sum I_{lim}^c$  and  $I_{lim}^d$ , respectively.

If pH is decreased and the protonation of the nitrogen in the pyridine ring is substantial, taking into account catalytic inactivity of this protonated form [9, 10], the  $[L]_s$  value is calculated with Eq. 21 if  $C_L \gg C_{Ni}$  [21].

$$[L]_s = C_L \frac{K_a}{K_a + [H^+]} \quad (21)$$

$K_a$  is acid dissociation constant of the protonated nitrogen in the pyridine ring (Py, NA, DEN, NC). Generalization of these approaches has been given in work [22].

Equations 17 (average current) and 18 (instantaneous currents) allowed us to determine the Langmuir's parameter  $\omega$  investigating the linear dependences:

$$Y_{av}^{-1} \text{ vs. } [L]_s \quad (22)$$

or

$$Y_{in}^{-1} \text{ vs. } [L]_s \quad (23)$$

at constant  $C_{Ni}$ , potential ( $E$ ) of the  $\sum \bar{I}_{lim}^c$  ( $\sum I_{lim}^c$ ) measurement and  $t_1(t)$ , and also given the nature and concentration of the supporting electrolyte.

At the same condition and  $C_L = \text{const}$  but with changing of supporting electrolyte concentration Eqs. 17 and 18 can be transformed to the linear dependences:

$$\bar{Y}_{av} \text{ vs. } x \quad (24)$$

where  $\bar{Y}_{av} = Y_{av} \exp(\psi_0 \frac{2F}{RT})$  and  $x = C_{X^{p-}} \exp(\psi_0 \frac{pF}{RT})$  or

$$\bar{Y}_{in} \text{ vs. } x \quad (25)$$

where  $\bar{Y}_{in} = Y_{in} \exp(\psi_0 \frac{2F}{RT})$  and  $x = C_{X^{p-}} \exp(\psi_0 \frac{pF}{RT})$

Dependences (Eqs. 24, 25) allow to determine the kinetic parameters  $k'_h K_L$  and  $k''_h K_L$  using the parameter  $\omega$ .

For determination of  $k'_h K_L$  and  $k''_h K_L$  we can also use the dependences  $\sum \bar{I}_{lim}^c$  ( $\sum I_{lim}^c$ ) versus  $C_{Ni}$  at the condition 19 and  $C_L = \text{const}$  ( $\psi_0 = \text{const}$ ). Applying Ilkovic's equations [23]:

$$\bar{I}_{lim}^d = \bar{\kappa} C_{Ni} \quad (26)$$

or

$$I_{lim}^d = \kappa C_{Ni} \quad (27)$$

where  $\bar{\kappa}$  and  $\kappa$  are Ilkovic's constants for the average and instantaneous limiting diffusion current, respectively, from Eq. 17 we find the dependence  $\sum \bar{I}_{lim}^c$  vs.  $C_{Ni}$  for average current:

$$\sum \bar{I}_{lim}^c = \frac{A_{av} \bar{\kappa}}{1 + A_{av}} C_{Ni} \quad (28)$$

and from the Eq. 18 we obtain the dependence  $\sum I_{lim}^c$  versus  $C_{Ni}$  for instantaneous current:

$$\sum I_{lim}^c = \frac{A_{in} \kappa}{1 + A_{in}} C_{Ni} \quad (29)$$

The  $A_{av}$  and  $A_{in}$  are constants, which are described by the equations:

$$A_{av} = 0.886 \left(\frac{t_1}{D}\right)^{0.5} \frac{K_L C_L}{[1 + (\beta_1) C_L + (\beta_1)_{X^{p-}} C_{X^{p-}}] (1 + \omega C_L)} \times \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) + k''_h (\beta_1)_{X^{p-}} C_{X^{p-}} \exp\left[-\psi_0 \frac{(2-p)F}{RT}\right] \right\} \quad (30)$$

$$A_{in} = \left\{ 1.363 \left(\frac{t}{D}\right)^{0.5} \frac{K_L C_L}{[1 + (\beta_1) C_L + (\beta_1)_{X^{p-}} C_{X^{p-}}] (1 + \omega C_L)} \times \left( k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) + k''_h (\beta_1)_{X^{p-}} C_{X^{p-}} \times \exp\left[-\psi_0 \frac{(2-p)F}{RT}\right] \right) \right\}^{1.056} \quad (31)$$

From Eqs. 26–31 follows that the direct proportional dependence  $\sum \bar{I}_{lim}^c$  ( $\sum I_{lim}^c$ ) versus  $C_{Ni}$  should be observed at indicated conditions and  $[L]_s = \text{const}$  (pH = const).

Though most of the catalytic prewaves for metal ion-ligand (catalyst) systems connected with heterogeneous catalytic reactions of type (1), there are examples [2] of the homogeneous catalytic reactions caused, as above, by the CE mechanism. In the case of the assumed homogeneous catalytic reaction Bulmer et al. [24] used the kinetic equation that takes into account the superposition of the discharge of the complex-depolarizer from the solution bulk. Recently, more correct solution of the similar problem has been given by Tur'yan and Lovrić [25]. Bănică et al. [4, 26, 27] also assumed the homogeneous nature of the one of the catalytic reactions of the complex formation and used the kinetic equation for the irreversible redox reaction (mechanism EC). This approach is inaccurate for the following reasons: (1) unlike the redox catalytic reactions, in the kinetic calculations for the complex formation reaction it is necessary to take into account the reversibility of the homogeneous reaction independently from the complex stability constant value and independently from the

achievement of the limiting catalytic current, (2) unlike the redox catalytic reaction, in the general case it is necessary to take into account the presence of the complex-depolarizer in the solution bulk, especially accepted by Bănică et al. [26, 27] for high stability constant of the complex-depolarizer  $\text{Ni}(\text{NA})^{2+}$  (see below).

## Mechanism of the electrocatalytic processes and ligand-catalyst nature

### General conditions

The range of the supporting electrolyte ionic strength ( $I$ ) 0.05–0.5 has been chosen in order to provide the approximate constancy of the activity coefficients of ions [3] and hence, the constancy of  $(\beta_1)_L$  and  $(\beta_1)_{X^{p-}}$ .

The limiting catalytic current (the height of the prewave) should be measured at the given potential since the potential affects ligand–catalyst adsorption.

The  $\sum \bar{I}_{\text{lim}}^c$  includes a certain contribution of the non-catalytic discharge of  $\text{Ni}^{2+}$  ions ( $\bar{I}_0$ ) in the general case. If condition  $\bar{I}_{\text{lim}}^d \gg \bar{I}_0$  has not fulfilled the  $(\sum \bar{I}_{\text{lim}}^c)_{\text{corr}} \neq \sum \bar{I}_{\text{lim}} - \bar{I}_0$  and  $(\sum \bar{I}_{\text{lim}}^c)_{\text{corr}}$  is calculated by the equation [29]:

$$\left(\sum \bar{I}_{\text{lim}}^c\right)_{\text{corr}} = \bar{I}_{\text{lim}}^d \frac{\sum \bar{I}_{\text{lim}} - \bar{I}_0}{\bar{I}_{\text{lim}}^d - \bar{I}_0} \quad (32)$$

where  $\sum \bar{I}_{\text{lim}}$  is the total catalytic current;  $\bar{I}_0$  is the current of the non-catalytic discharge of  $\text{Ni}^{2+}$  at the same potential but at  $C_L=0$ . Equation 32 is given [29] for the average currents. The same equation is applied for instantaneous currents.

The limiting diffusion current should be obtained from the second (total) wave at the supporting electrolyte concentration  $\leq 0.2$  M, in order to eliminate the kinetic retardation [30].

The diffusion coefficient is assumed to be similar for all particles, including  $\text{Ni}^{2+}$ ; for  $\text{Ni}^{2+}$ , it is accepted to be equal to  $D=60 \times 10^{-6} \text{ cm}^2/\text{s}^{-1}$ , found by the radiochemical method for wide range of the supporting electrolyte concentrations [31].

The analysis of the double electric layer influence on the kinetics for all systems was carried out on the basis of  $\psi_0$ -potentials from Russell's table [32] after correction of the electrode potentials to NCE instead of SCE, as shown there. The  $\psi_0$ -potentials from the Russell's table are more accurate [3] than data presented by Yamaoka [33] for  $\text{NaClO}_4$  solutions probably because of some  $\text{Cl}^-_4$  adsorption, regardless of the negative charge of the electrode surface.

The influence of the L adsorption on the  $\psi_0$  potential was neglected because of the low L concentration. The  $\text{Ni}^{2+}$  influence on the  $\psi_0$  potential was neglected at substantial excess of supporting electrolyte only.

The supporting electrolytes for most investigated systems were  $\text{KNO}_3$  ( $\text{NaNO}_3$ ). It was caused by the

necessity to use the stability constant of the  $\text{Ni}(\text{NO}_3)^+$  complex  $(\beta_1)_{\text{NO}_3^-} = 0.4$  [34].

The temperature was 25°C unless indicated otherwise.

### Ligand–catalyst nature

#### Pyridine

The kinetic prewave in the  $\text{Ni}^{2+}$ -Py system was described by Tur'yan and Serova [35] but catalytic heterogeneous nature of this prewave was shown by Mark and Reiley [8, 9].

The parallel catalytic heterogeneous reactions (1) in the  $\text{Ni}^{2+}$ -Py system were investigated in Ref. [5] for the first time on the basis of the kinetic data [10] (DC polarography; average currents for summary prewave). In this data the influence of the parallel catalytic reaction with  $\text{Ni}(\text{Py})^{2+}$  participation was eliminated (extrapolation of the kinetic data to  $C_{\text{Py}}=0$  and obtaining an “ $\alpha$ ” parameter) and due to low  $C_{\text{Py}}$  the Henry's adsorbed isotherm has been used. At the same time, in this analysis [5] the stability constant of  $\text{Ni}(\text{NO}_3)^+$  complex was not taken into account and insufficiently accurate  $\psi_0$  values from Ref. [33] were used.

We repeated the kinetic analysis (Table 1) on the basis of Eq. 17 in form (Eq. 24) ( $\omega C_{\text{Py}} \ll 1$ ) using  $(\beta_1)_{\text{NO}_3^-} = 0.4$  [30] and  $\psi_0$  from Ref. [32]. Furthermore, in the initial data (kinetic parameter “ $\alpha$ ”) [10], more accurate condition was introduced:  $D_{\text{Ni}} \cong D_{\text{NiPy}^{2+}} = D$ . The data for verification of Eq. 17 in form Eq. 24 presented in Table 1, where kinetic parameter “ $\alpha$ ” was taken from Table 2 [10]. The  $(\beta_1)_{\text{Py}} = (99 \pm 5)$  value was obtained from Ref. [10]. The  $\sum \bar{I}_{\text{lim}}^c$  and the tabular  $\psi_0$  values at the  $E = -0.90$  V SCE;  $t_1 = 3.75$  s,  $D = 6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , pH = 6.5.

On the basis of Table 1, the linear equation was obtained:

$$\bar{Y}_{\text{av}} = 1.18 + 1.58 \times 10^2 x \quad R^2 = 0.999 \quad (33)$$

that confirms Eq. (17). Hence we have obtained ( $\omega[\text{Py}]_s \ll 1$ ):

$$1.18 = 0.886 k'_h K_{\text{Py}} \left(\frac{t_1}{D}\right)^{0.5} \quad (34)$$

**Table 1** Data for verification of Eq. 17 in the form of dependence (Eq. 24) for  $\text{Ni}^{2+}$ -Py system

$C_{\text{NaNO}_3}$ (M)	$-\psi_0$ , mV	$\alpha$ [10]	$\bar{Y}_{\text{av}}$ , M	$x$ (M)
0.05	93.0	21.1	1.35	$1.35 \times 10^{-3}$
0.07	85.8	13.3	1.51	$2.50 \times 10^{-3}$
0.1	78.0	8.7	1.82	$4.82 \times 10^{-3}$
0.2	83.8	6.0	3.92	$1.68 \times 10^{-2}$
0.5	47.5	5.3	13.67	$7.90 \times 10^{-2}$



**Table 2** Verification of Eq. 17 in form (22) in the acetate buffer (pH=5.3) for Ni<sup>2+</sup>-NA system

$C_{\text{NA}} \times 10^4$ (M)	2.50	5.00	10.0	15.0	20.0
$[\text{NA}]_s \times 10^4$ , M	2.45	4.90	9.80	14.7	19.6
$(Y_{\text{av}})^{-1} \times 10^4$ , M	1.77	2.02	2.44	2.88	3.42

$$1.58 \times 10^2 = 0.88 k_h'' K_{\text{Py}} (\beta_1)_{\text{NO}_3^-} \left(\frac{t_1}{D}\right)^{0.5} \quad (35)$$

and kinetic parameters were calculated:  $k_h' K_{\text{Py}} = 1.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$  and  $(k_h'')_{\text{NO}_3^-} K_{\text{Py}} = 0.56 \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$  for parallel heterogeneous catalytic reactions (1).

Though in number of works (for example, [24, 35]), the prewave in the Ni<sup>2+</sup>-Py system was associated by some authors with homogeneous reaction of the complex formation, at present there are no doubts that it is the heterogeneous process [3]. Complexity of the kinetic analysis consists in the participation (in general case) of the volume Ni(Py)<sup>2+</sup> complex in parallel heterogeneous catalytic reactions [10] and, hence, investigation of the conversion from Henry's isotherm to Langmuir's isotherm (see "Discussion") is difficult.

### Nicotinamide

The catalytic prewave in the Ni<sup>2+</sup>-NA system has been discovered by Ruvinsky et al. [36] and its heterogeneous nature was shown. This nature results from the effect of the maximum suppression of the main wave of Ni<sup>2+</sup> discharge due to NA adsorption. The NA adsorption has also been shown by Knobloch [15] electrocapillary measurements of the NA solution. However, from AC polarographic investigation, Elving et al. [37] have made a conclusion about slight surface activity of NA. This conclusion allowed Bănică et al. [26, 27] to accept the homogeneous nature of the catalytic reaction that results in the prewave in the Ni<sup>2+</sup>-NA system.

Taking into account the works of [15, 36] and especially the high sensitivity of electrocapillary measurements [15], we consider the catalytic parallel reactions (1) as heterogeneous also for Ni<sup>2+</sup>-NA system.

Besides the consideration of homogeneous catalytic reaction with the use of inaccurate kinetic equation (see Theoretical part), Bănică et al. [26, 27] applied an erroneous stability constant of the complex Ni(NA)<sup>2+</sup>:  $\lg(\beta_1)_{\text{NA}} = 3.40 - 3.54$ . The value  $\lg(\beta_1)_{\text{NA}} = 3.40$  was taken from work [38]. It is in fact pKa where Ka is the constant of acid dissociation of protonated nitrogen in the pyridine ring of NA. We estimated more correct  $(\beta_1)_{\text{NA}}$  value from the kinetic data [24, 38, 39] as ratio of the rate constant of the complex formation (close for Py and NA) to the rate constant of the complex dissociation. After recalculation to 25°C we have obtained  $(\beta_1)_{\text{NA}} = 31 (I = 1.0)$ . Similar  $(\beta_1)_{\text{NA}} = 30.9 (I = 0.03; \sim 0^\circ\text{C})$  has been found by Khakimov et al. [40] by cryoscopic method. The recalcu-

**Table 3** Verification of Eq. 17 in form (22) in the phosphate buffer (pH=7.2) for Ni<sup>2+</sup>-NA system

$(C_{\text{NA}} = [\text{NA}]_s) \times 10^4$ (M)	2.50	5.00	10.0	15.0	20.0
$(Y_{\text{av}})^{-1} \times 10^4$ , M	1.64	1.90	2.11	2.44	2.89

tion of this constant to 25°C using data from [24, 38, 39] gives  $(\beta_1)_{\text{NA}}$  approximately 30% smaller.

Thus, the correct  $(\beta_1)_{\text{NA}}$  constant (we use  $(\beta_1)_{\text{NA}} = 31$  below) is about two orders smaller than the one applied in works by Bănică et al. [26, 27].

pKa=3.40 ( $I=1$ , 24°C) [38] is close to pKa=3.35 ( $I=0$ ; 20°C) [41]. pKa=3.40 was used in the calculations below. Protonation of the nitrogen in the amide group at  $p \geq 2$  can be neglected because of pKa=0.67 ( $I=0$ ; 20°C) for this nitrogen [41].

Since our kinetic calculations have been carried out for data obtained from acetate and phosphate buffers [27], we have used the following stability constants of Ni<sup>2+</sup> complexes: Ni(OAc)<sup>+</sup>:  $(\beta_1)_{\text{AcO}^-} = 10 (I = 0.1)$  [42],  $(\beta_1)_{\text{AcO}^-} = 6.5 (I = 0.2)$  [43],  $(\beta_1)_{\text{AcO}^-} = 7.4 (I = 0.16; \text{our calculations})$  and NiHPO<sub>4</sub>:  $(\beta_1)_{\text{HPO}_4^{2-}} = 120 (I = 0.1)$  [44],  $(\beta_1)_{\text{HPO}_4} = 104 (I = 0.2; \text{our calculations for investigated condition, using activity coefficients [28]})$ , others such as Ni<sup>2+</sup> phosphate complexes were not observed [44].

For the description of the ionic strength and HPO<sub>4</sub><sup>2-</sup> concentration in the phosphate buffer (pH=7.2) [27], we used the acid dissociation constant of H<sub>2</sub>PO<sub>4</sub><sup>2-</sup>: pKa=6.70 ( $I=0.1$ ) [44] and pKa=6.67 ( $I=0.2; \text{our calculations}$ ).

We have used the following experimental data [27] for verification of the concept of the parallel heterogeneous catalytic reaction. Our Table 2 corresponds to Fig. 2 [27]: acetate buffer, pH=5.3, [NaOAc]=0.164 M, [HOAc]=0.036 M,  $I=0.16$ . Our Table 3 corresponds to Fig. 2: phosphate buffer, pH=7.2,  $[\text{HPO}_4^{2-}] = 5.76 \cdot 10^{-2} \text{ M}$ ,  $[\text{H}_2\text{PO}_4^-] = 2.12 \cdot 10^{-2} \text{ M}$ ,  $[\text{Cl}^-] = 2.12 \cdot 10^{-2} \text{ M}$ ,  $[\text{K}^+] = 0.16 \text{ M}$ ,  $I = 0.22$ . In both cases:  $C_{\text{Ni}} = 5.0 \times 10^{-4} \text{ M}$ ;  $t_1 = 3.44 \text{ s}$ ; average currents.

Tables 2 and 3 were calculated for verification of Eq. 17 in form (Eq. 22) for the determination of Langmuir's parameter  $\omega$  and for further kinetic calculations. The  $[\text{NA}]_s$  in acetate buffer (pH=5.3) was calculated by Eq. 21 (Table 2). For phosphate buffer (pH=7.2) the correlation 19 has been used.

Linear dependences in form (Eq. 22) obtained from Tables 2 and 3 confirm Eq. 17, for acetate buffer:

$$(Y_{\text{av}})^{-1} = 1.54 \times 10^{-4} + 0.094[\text{NA}]_s \quad R^2 = 0.998 \quad (36)$$

and for phosphate buffer:

$$(Y_{\text{av}})^{-1} = 1.49 \times 10^{-4} + 0.067[\text{NA}]_s \quad R^2 = 0.984 \quad (37)$$

Hence Langmuir's parameters for acetate buffer (Eq. 36)  $\omega = (0.084/1.54 \times 10^{-4}) = 6.1 \times 10^2 \text{ M}^{-1}$  and for phosphate

buffer (Eq. 37)  $\omega = (0.067/1.49 \times 10^{-4}) = 4.5 \times 10^2 \text{ M}^{-1}$  have been calculated.

On the basis of Eqs. 17 and 36, we have obtained the following equation (acetate buffer):

$$\frac{1}{1.54 \cdot 10^{-4}} = 0.886 \left(\frac{t_1}{D}\right)^{0.5} K_{\text{NA}} \times \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) + (k''_h)_{\text{AcO}^-} (\beta_1)_{\text{AcO}^-} C_{\text{AcO}^-} \exp\left(-\psi_0 \frac{F}{RT}\right) \right\} \quad (38)$$

and on the basis of Eqs. 17 and 37 for phosphate buffer:

$$\frac{1}{1.49 \cdot 10^{-4}} = 0.886 \left(\frac{t_1}{D}\right)^{0.5} K_{\text{NA}} \times \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) + (k''_h)_{\text{HPO}_4^{2-}} (\beta_1)_{\text{HPO}_4^{2-}} C_{\text{HPO}_4^{2-}} \right\} \quad (39)$$

For further calculations Eqs. 38 and 39 were used for acetate buffer (pH=5.3):  $t_1 = 3.44 \text{ s}$ ,  $D = 6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $\psi_0 = -72.0 \text{ mV}$  at  $E (\sum \bar{I}_{\text{lim}}^c) = -0.90 \text{ V(SCE)}$  and  $C_{\text{NaOAc}} = 0.164 \text{ M}$ ,  $(\beta_1)_{\text{AcO}^-} = 7.4$ ,  $C_{\text{AcO}^-} = 0.164 \text{ M}$ , and for phosphate buffer, (pH=7.2):  $t_1 = 3.44 \text{ s}$ ,  $D = 6.0 \cdot 10^{-6} \text{ M}$ ,  $\psi_0 = -72.0 \text{ mV}$  at  $E (\sum \bar{I}_{\text{lim}}^c) = -0.90 \text{ V}$  and  $[\text{K}^+] = 0.16 \text{ M}$ ,  $(\beta_1)_{\text{HPO}_4^{2-}} = 104$ ,  $C_{\text{HPO}_4^{2-}} = 5.76 \cdot 10^{-2} \text{ M}$ .

In addition, we used the dependence  $\sum \bar{I}_{\text{lim}}^c$  versus  $C_{\text{Ni}}$  at  $C_{\text{NA}} = 2.0 \times 10^{-4} \text{ M}$  in the acetate buffer (pH=4.6) (Fig. 4) [27]. Linear dependence  $\sum \bar{I}_{\text{lim}}^c$  versus  $C_{\text{Ni}}$  according to Eq. 28 is confirmed at low  $C_{\text{Ni}}$  ( $\leq 1.0 \times 10^{-4} \text{ M}$ ) that was shown [27] more exactly by the differential pulse polarography only. The reason of the linear dependence violation is the inhibition process with the  $C_{\text{Ni}}$  increase at relatively low pH (pH=4.6). Probably, it is associated with the adsorption of the protonated complexes, including mixed complexes [45].

For more accurate determination of the  $A_{\text{av}}$  by Eq. 28, we have used the tangent in the  $C_{\text{Ni}} = 0$  point (Fig. 4) [27]. This tangent coincided with the curve  $\sum \bar{I}_{\text{lim}}^c$  versus  $C_{\text{Ni}}$  at  $C_{\text{Ni}} \leq 1.0 \times 10^{-4}$ . Hence from the slope of the tangent  $2.50 \times 10^3 \mu\text{A M}^{-1}$  and  $\bar{\kappa} = 6.14 \times 10^3 \mu\text{A M}^{-1}$  and by means of Eq. 28 parameter  $A_{\text{AV}} = 0.687$  was obtained. Using this parameter for acetate buffer (pH=4.6) from Eq. 30 it was found:

$$0.687 = 0.886 \left(\frac{t_1}{D}\right)^{0.5} \times \frac{K_{\text{NA}} [\text{NA}]_s}{\{1 + (\beta_1)_{\text{NA}} [\text{NA}]_s + (\beta_1)_{\text{AcO}^-} C_{\text{AcO}^-}\} (1 + \omega [\text{L}]_s)} \times \left\{ k'_h \exp\left(-\psi_0 \frac{2F}{RT}\right) + (k''_h)_{\text{AcO}^-} (\beta_1)_{\text{AcO}^-} \times C_{\text{AcO}^-} \exp\left(-\psi_0 \frac{F}{RT}\right) \right\} \quad (40)$$

For calculation on the basis of Eq. 40 it is necessary to use:  $t_1 = 3.44 \text{ s}$ ,  $D = 6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $[\text{NA}]_s = 1.85 \times 10^{-4} \text{ M}$  (from  $C_{\text{NA}} = 2.0 \times 10^{-4} \text{ M}$  and by means of

Eq. 21 at pH=4.6 and  $I=0.10$ ),  $(\beta_1)_{\text{NA}} = 31$ ,  $(\beta_1)_{\text{AcO}^-} = 10$ ,  $C_{\text{AcO}^-} = 0.098 \text{ M}$ ,  $\omega = 6.1 \times 10^2 \text{ M}^{-1}$ ,  $\psi_0 = -81.5 \text{ mV}$  at  $E (\sum \bar{I}_{\text{lim}}^c) = -0.90 \text{ V(SCE)}$  and  $C_{\text{AcO}^-} = 0.1 \text{ M}$ .

Joint solution of Eqs. 38 and 40 gives  $k'_h K_{\text{NA}} = 3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$  and  $(k''_h)_{\text{AcO}^-} K_{\text{NA}} = 0.43 \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$ . Using Eq. 39 and  $k'_h K_{\text{NA}} = 3.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$ , we have obtained the value  $(k''_h)_{\text{HPO}_4^{2-}} K_{\text{NA}} = 1.5 \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$ .

#### *N,N*-diethylnicotinamide

Catalytic prewave in the system  $\text{Ni}^{2+}$ -DEN was discovered by Shavgulidze et al. [46–48] and it was characterized by these authors as the result of the catalytic heterogeneous process.

The stability constant of  $\text{Ni}(\text{DEN})^{2+}$  complex  $(\beta_1)_{\text{DEN}} = 43$  was determined [48] from catalytic current [2]. The constant acid dissociation of the protonated nitrogen in pyridine ring  $\text{pK}_a = 3.48$  was obtained by us through potentiometric titration. Similar to NA behavior (see Nicotinamide) at pH $\geq 5$ , the protonation of nitrogen in amide group can be neglected.

We investigated (Tables 4, 5)  $\text{Ni}^{2+}$ -DEN system with DC tast polarography (instantaneous currents) for verification of the concept of parallel heterogeneous catalytic reactions.

The conditions of the experiment are the same as in Ref. [7]. The drop time  $t$  was maintained mechanically at 3.5 s. The  $\sum \bar{I}_{\text{lim}}^c$  for the prewave was measured at the potential  $E = -0.95 \text{ V(SCE)}$ .

Data in Table 4 correspond to the following conditions: supporting electrolyte 0.1 M  $\text{KNO}_3$  pH=7.0 that was adjusted by adding few drops of very diluted solution of  $\text{HNO}_3$  and  $\text{KOH}$ ,  $C_{\text{Ni}} = 7.5 \times 10^{-5} \text{ M}$ ,  $I^d = 0.2 \mu\text{A}$ . Data in Table 5 correspond to conditions:  $C_{\text{Ni}} = 7.5 \times 10^{-5} \text{ M}$ ,  $C_{\text{DEN}} = 5.0 \times 10^{-5} \text{ M}$ . Equation 19 is observed in the case of both tables.

The obtained linear dependences from Table 4 are as follows:

**Table 4** Verification of Eq. 18 in the form of dependence (23) for  $\text{Ni}^{2+}$ -DEN system

$(C_{\text{DEN}} = [\text{DEN}]_s) \times 10^4 \text{ (M)}$	0.5	1.0	2.0	4.0	8.0
$\frac{\sum \bar{I}_{\text{lim}}^c}{(I_{\text{lim}}^d - \sum \bar{I}_{\text{lim}}^c)}$	0.212	0.394	0.706	1.128	1.500
$(Y_{\text{in}})^{-1} \times 10^4, \text{ M}$	2.08	2.31	2.65	3.38	5.07

**Table 5** Verification of Eq. 18 in the form of dependence (25) for  $\text{Ni}^{2+}$ -DEN system

$C_{\text{KNO}_3}, \text{ M}$	0.075	0.10	0.15	0.20
$\frac{\sum \bar{I}_{\text{lim}}^c}{(I_{\text{lim}}^d - \sum \bar{I}_{\text{lim}}^c)}$	0.287	0.212	0.140	0.107
$\bar{Y}_{\text{in}}, \text{ M}^{-1}$	4.94	6.16	7.52	10.65
$x \times 10^3, \text{ M}$	2.10	3.58	7.17	12.78

$$(Y_{in})^{-1} = 1.87 \times 10^{-4} + 0.40[\text{DEN}]_s \quad R^2 = 0.999 \quad (41)$$

and from Table 5:

$$\bar{Y}_{in} = 4.02 + 5.15 \times 10^2 x \quad R^2 = 0.992 \quad (42)$$

shows the applicability of Eq. 18. From Eqs. 18 and 41, we have obtained the Langmuir's parameter  $\omega = (0.40/1.87 \times 10^{-4}) = 2.1 \times 10^3 \text{ M}^{-1}$ .

Utilizing Eqs. 18 and 42 we find:

$$4.02 = 1.363 \frac{(k'_h)K_{\text{DEN}}}{1 + \omega[\text{DEN}]_s} \left(\frac{t}{D}\right)^{0.5} \quad (43)$$

$$5.15 \cdot 10^2 = 1.363 \frac{(k''_h)_{\text{NO}_3^-} K_{\text{DEN}} (\beta_1)_{\text{NO}_3^-}}{1 + \omega[\text{DEN}]_s} \left(\frac{t}{D}\right)^{0.5} \quad (44)$$

From Eqs. 43 and 44 using  $\omega = 2.1 \times 10^3 \text{ M}^{-1}$ ,  $C_{\text{DEN}} = [\text{DEN}]_s = 5.0 \times 10^{-5} \text{ M}$ ,  $t = 3.5 \text{ s}$  and  $D = 6.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $(\beta_1)_{\text{NO}_3^-} = 0.4$ , we have determined  $(k'_h)K_{\text{DEN}} = 4.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$  and  $(k''_h)_{\text{NO}_3^-} K_{\text{DEN}} = 1.4 \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$ , respectively.

### Nicotine

The catalytic prewave with heterogeneous nature in the  $\text{Ni}^{2+}$ -NC system was discovered by Tur'yan et al. [12, 29, 49] at pH = 2.5–5.5 in the 0.5 M  $\text{NaClO}_4$  supporting electrolyte,  $E(\sum \bar{I}_{\text{lim}}^c) = -0.8 \text{ V}$ . The acid constant dissociation of NC  $\text{pK}_a = 3.37$  ( $I = 0.5$ ) was found by potentiometric titration [50] for protonated nitrogen in pyridine ring and  $\text{pK}_a = 8.07$  ( $I = 0.5$ ) for protonated nitrogen in pyrrolidine ring. Hence it follows that in the investigation of catalytic prewave pH range (pH = 2.5–5.5) [7, 12, 29, 49], NC is remained protonated on nitrogen in pyrrolidine ring ( $\text{NCH}^+$ ). At pH < 4, protonation of nitrogen in pyridine ring is observed ( $\text{NCH}_2^+$ ) and  $\sum \bar{I}_{\text{lim}}^c$  is decreased with the pH decrease [29].

The stability constant of the  $\text{Ni}(\text{NCH}^+)$  complex  $(\beta_1)_{\text{NCH}^+} = 50$  ( $I = 0.5$ ) was determined by potentiometric titration [50] and close value  $(\beta_1)_{\text{NCH}^+} = 51$  ( $I = 0.5$ ) was found from catalytic prewave [12]. We used  $(\beta_1)_{\text{NCH}^+} = 50$  in further calculations.

For the verification of Eq. 18, we have used the kinetic data from Fig. 1a [7] performing corresponding calculations (Table 6) for conditions: DC tast polarography (instantaneous currents),  $t = 3.5 \text{ s}$ , supporting

**Table 6** Verification of Eq. 18 in the form of dependence (23) for  $\text{Ni}^{2+}$ -NCH system

$C_{\text{NCH}}^+ \times 10^4, \text{ M}$	0.50	1.00	2.00	5.00	10.0
$[\text{NCH}^+]_s \times 10^4, \text{ M}$	0.36	0.70	1.43	3.63	7.28
$(Y_{in})^{-1} \times 10^4, \text{ M}$	1.52	2.34	3.56	7.70	14.60

electrolyte 0.1 M  $\text{KNO}_3$ , pH = 5.0,  $C_{\text{Ni}} = 1.0 \times 10^{-2} \text{ M}$ ,  $E(\sum \bar{I}_{\text{lim}}^c) = -0.9 \text{ V(SCE)}$ .

Since the condition  $C_{\text{Ni}} \gg C_{\text{NCH}}$  is fulfilled and some formation of  $\text{NCH}_2^+$  (pH = 5.0) takes place, Eqs. 20 and 21 were used for  $[\text{NCH}^+]_s$  calculation (Table 6).

Linear dependence  $(Y_{in})^{-1}$  versus  $[\text{NC}]_s$  ( $[\text{NCH}^+]_s$ ) corresponding to Table 6 is described by the following equation:

$$(Y_{in})^{-1} = 9.10 \times 10^{-5} + 1.88[\text{NCH}^+]_s \quad R^2 = 0.999 \quad (45)$$

this proves the Eq. 18. Hence Langmuir's parameter  $\omega = (1.88/9.10 \times 10^{-5}) = 2.1 \times 10^4 \text{ M}^{-1}$  was found.

In work [7], there are data about the influence of the double electric layer (changing of the supporting electrolyte concentration in the range 0.05–0.2 M  $\text{KNO}_3$ ) on the kinetics process. However, the correct use of Eq. 18 for analysis of this effect is complicated by the high  $\text{Ni}^{2+}$  concentration ( $1.0 \times 10^{-2} \text{ M}$ ) and, perhaps, its influence on  $\psi_0$  potential. In the case that was carried out by us  $\omega$  determination of  $C_{\text{Ni}}$  was also high, but the concentrations of  $C_{\text{Ni}}$  and of the supporting electrolyte were constant and  $\psi_0$  was kept constant also and these conditions made possible the correct  $\omega$  determination.

### Discussion

An idea of the Langmuir's isotherm use in the kinetic equation of the catalytic current ( $\text{Ni}^{2+}$ -Py and  $\text{Ni}^{2+}$ -NC systems) belongs to Mata et al. [6, 7].

This idea found the confirmation and evolution in this work (Table 7) for systems:  $\text{Ni}^{2+}$ -NA-AcO<sup>-</sup>,  $\text{Ni}^{2+}$ -NA-HPO<sup>2-</sup><sub>4</sub>,  $\text{Ni}^{2+}$ -DEN and  $\text{Ni}^{2+}$ -NC on the basis of more correct kinetic Eqs. (17, 18). System  $\text{Ni}^{2+}$ -Py was not analyzed because of  $\text{NiPy}^{2+}$  precipitation in the heterogeneous catalytic reactions [10] which complicates the kinetic equation:

$$Y_{\text{av}}(Y_{in}) = \frac{a + b[\text{Py}]_s}{1 + \omega[\text{Py}]_s} \quad (46)$$

**Table 7** Langmuir's parameters  $\omega$  determined from catalytic currents

L	Electrolyte	PH	I	$C_{\text{Ni}}$ mM	$C_1$ mM	$-E, \text{ V(SCE)}$	$\omega \text{ M}^{-1}$
NA <sup>a</sup>	0.164 M NaOAc + $3.6 \times 10^{-2}$ M HOAc	5.3	0.16	0.5	0.25-20	0.90	$6.1 \times 10^2$
NA <sup>a</sup>	$5.76 \times 10^{-2}$ M $\text{K}_2\text{HPO}_4$ + $2.12 \times 10^{-2}$ M $\text{KH}_2\text{PO}_4$ + $2.12 \times 10^{-2}$ M KCl	7.2	0.22	0.5	0.25–20	0.90	$4.5 \times 10^2$
DEN <sup>b</sup>	0.1 M $\text{KNO}_3$	7.0	0.1	0.075	0.5–8.0	0.95	$2.1 \times 10^3$
NCH <sup>+</sup> c	0.1 M $\text{KNO}_3$	5.0	0.1	10	0.05–1.0	0.90	$2.1 \times 10^4$

Catalytic currents: <sup>a</sup>from [27];

<sup>b</sup>in this work;

<sup>c</sup>from [7].



This complication was not taken into account in work [6].

We found that the Langmuir's parameter  $\omega$  (Table 7) increased in direction NA  $\rightarrow$  DEN  $\rightarrow$  NCH<sup>+</sup>. Probably, there is correlation with the increase of the adsorption in the same direction [51].

Knobloch [15] obtained  $\omega = 3.8 \times 10^2 \text{ M}^{-1}$  for dihydroamide of nicotinic acid also by the indirect method of hydrogen catalytic current. Dihydroamide of nicotinic acid is product of electroreduction of NA and the  $\omega$  value is close to  $\omega$  value for NA (Table 7).

Some difference in  $\omega$  for NCH<sup>+</sup> ( $\omega = 1.6 \times 10^4 \text{ M}^{-1}$  [7]) and in this work ( $\omega = 2.1 \times 10^4 \text{ M}^{-1}$ ; Table 7) were probably caused by more correct kinetic equation utilized in this work (see Theoretical part).

Though for NCH<sup>+</sup> Langmuir's isotherm had place even at very low  $C_{\text{NCH}^+}$  (Table 7), in work [51] applying of Henry's isotherm at  $C_{\text{NCH}^+} \leq 3.0 \times 10^{-3} \text{ M}$  in NaClO<sub>4</sub> supporting electrolyte has been shown. In the first case Ni<sup>2+</sup> presented in substantial excess (Table 7) but in work [51] Ni<sup>2+</sup> was absent.. The reason of Henry's isotherm to Langmuir's isotherm convert can be explained by the adsorption of Ni(NCH)<sup>3+</sup> complex. The influence of the adsorption of Ni<sup>2+</sup> complexes in Ni<sup>2+</sup>-NA-cO<sup>-</sup> system on the catalytic current has been noted in Nicotinamide section. We intend to the usual adsorption of electro-inactive complexes unlike ligand-induced complexes adsorption that was noted by Anson and Barclay [52]. Electro-catalytic current [2] is associated with the latter.

It is possible to note the difference in the adsorbed behavior of NCH<sup>+</sup> in KNO<sub>3</sub> (Table 7) and in NaClO<sub>4</sub> supporting electrolyte [51] caused by formation in NaClO<sub>4</sub> associated species NCH<sup>+</sup>·ClO<sub>4</sub><sup>-</sup> [53].

If NCH<sup>+</sup> species dominate in KNO<sub>3</sub> solution, the appreciable increase of  $\omega$  for NCH<sup>+</sup> (Table 7) may be explained by the  $\psi_0$  effect that is included in  $\omega$  parameter as multiplier for charged positive NCH<sup>+</sup> species:  $\exp(-\psi_0 \frac{F}{RT})$ .

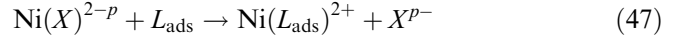
Kinetic parameters for parallel heterogeneous catalytic reactions 1a and b at  $\psi_0 = 0$ , found by us, are presented in Table 8.

The comparison of  $k''_h K_{NA}$  for: Ni<sup>2+</sup>-NA-AcO<sup>-</sup>, and Ni<sup>2+</sup>-NA-HPO<sup>2-</sup><sub>4</sub> systems (Table 8) allows us to make the conclusion that  $k''_h$  increase with the increase of complex (NiX<sup>2-p</sup>) stability constant  $(\beta_1)_{X^{p-}}$ . It is in relation the with kinetics of homogeneous reactions and was explained by Funahashe and Tanaka [54] by the

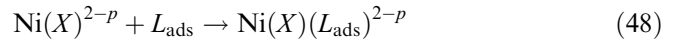
electrons' donation that increases with the increasing of complex Ni X<sup>2-p</sup> stability. This effect of X<sup>p-</sup> ligand facilitates the replacement of the remaining water molecules on the ligand-catalyst L<sub>ads</sub>. This influence is not substantial for both homogeneous [54] and heterogeneous (Table 8) processes. However, this influence of X<sup>p-</sup> and an additional effect of the field electrode (also through the X<sup>p-</sup>) causes considerable increase of  $k''_h$  as compared with  $k'_h$  ( $k''_h/k'_h = (1.1-3.9) \times 10^2$  (Table 8).

The analysis that was performed influence the X<sup>p-</sup> on the  $k''_h$  value ( $k''_h \gg k'_h$ ) bases as accepted above.

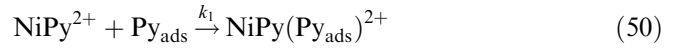
(Theoretical part) the choice from two alternative heterogeneous catalytic reactions [13]: the reaction of the ligand exchange:



and the reaction of the mixed complex formation:



on behalf of the reaction 48 (scheme 1). Note the proximity of the rate constants  $k_1$  and  $k_2$  obtained [10] for the heterogeneous catalytic reactions:



was caused by the high  $k_1$  value because of the parallel reaction with NiNO<sub>3</sub><sup>+</sup> participation which was not taken into account in the kinetic calculations [10].

For the appreciation of the contribution of the heterogeneous catalytic reactions 1a and b (scheme 1) in the summary catalytic current, for average catalytic currents from Eq. 17, we have found:

$$\frac{(\bar{I}_{\text{lim}}^c)_{1a}}{\sum \bar{I}_{\text{lim}}^c} 100 = \frac{100}{1 + (k''_h/k'_h)(\beta_1)_{X^{p-}} C_{X^{p-}} \exp(\psi_0 \frac{pF}{RT})} \% \quad (51)$$

and

$$(\bar{I}_{\text{lim}}^c)_{1b} \% = 100 - (\bar{I}_{\text{lim}}^c)_{1a} \% \quad (52)$$

For instantaneous current, the substitution in Eq. 18 of the 0.946 power for 1.0 allows (with some approximation) to use the same Eqs. 51 and 52. Results of  $(\bar{I}_{\text{lim}}^c)_{1a} (I_{\text{lim}}^c)_{1a}$  and  $(\bar{I}_{\text{lim}}^c)_{1b} (I_{\text{lim}}^c)_{1b}$  in % represented in Table 9

**Table 8** Kinetic parameters of catalytic parallel heterogeneous reduction in Ni<sup>2+</sup>-L-X<sup>p-</sup> systems determined from catalytic currents

L	X <sup>p-</sup>	pH	I	$(\beta_1)_L \text{ M}^{-1}$	$(\beta_1)_{X^{p-}} \text{ M}^{-1}$	$k'_h K_L \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$	$k''_h K_L \text{ M}^{-1} \text{ s}^{-1} \text{ cm}$	$\frac{k''_h}{k'_h} \times 10^{-2}$
Py	NO <sub>3</sub> <sup>-</sup>	6.5	0.05-0.5	99 ± 5	0.4	1.7	0.56	3.3
NA	AcO <sup>-</sup>	5.3	0.10-0.16	31	7.4-10	3.8	0.43	1.1
NA	HPO <sub>4</sub> <sup>2-</sup>	7.2	0.22	43	104	3.8	1.5	3.9
DEN	NO <sub>3</sub> <sup>-</sup>	7.0	0.075-0.2	50	0.4	4.3	1.4	3.2

For other details see Table 7

**Table 9** Contribution (%) of the heterogeneous catalytic reactions **1a** and **b** to the summary catalytic current

<i>L</i>	$X^{p-}$	$C_{X^{p-}M}$	$(\beta_1)_{X^{p-}}$	$C_{K+(C_{Na+})}$ (M)	$-E$ (V) (SCE)	$-\psi_0$ (mV)	$\left(\frac{k_h''}{k_h'}\right) \times 10^{-2}$	$(\bar{I}_{lim}^c)_{1a}$ (%)	$(\bar{I}_{lim}^c)_{1b}$ (%)
Py	$NO_3^-$	0.1	0.4	0.1	0.90	78.0	3.3	61	39
NA	$AcO^-$	0.164	7.4	0.164	0.90	72.0	1.1	11	89
NA	$HPO_4^{2-}$	$5.76 \times 10^{-2}$	104	0.16	0.90	72.0	3.9	10	90
DEN	$NO_3^-$	0.1	0.4	0.1	0.95	85.7	3.2	69 <sup>a</sup>	31 <sup>a</sup>

For other details see Tables 7 and 8

<sup>a</sup>The instantaneous currents

Table 9 shows that for indicated catalytic systems the contribution of both heterogeneous catalytic reactions **1a** and **b** (scheme 1) to the summary catalytic current is essential. In spite of  $k_h'' \gg k_h'$  the contribution of reaction **1a** achieves more than 60% (Py, DEN) due to the  $\psi_0$  potential influence.

At equal charge of  $NiNO_3^+$  and  $Ni(AcO)^+$ , the contribution of reaction **1b** increases with the increase of the complex stability constant (Py and NA or DEN and NA).

## Conclusions

1. The theory of the polarographic average and instantaneous catalytic currents that cause parallel heterogeneous catalytic reactions has been developed.
2. It was shown that catalytic currents considered in the literature for systems  $Ni^{2+}-L-X^{p-}$  where L: Py, NA, NC and  $X^{p-}$ :  $NO_3^-$ ,  $AcO^-$ ,  $HPO_4^{2-}$  and obtained in this work for L: DEN and  $X^{p-}$ :  $NO_3^-$  are described by the concept of the parallel heterogeneous catalytic reactions:  $Ni^{2+} + L_{ads} \rightarrow k_1' NiPy(Py_{ads})^{2+}$  and  $NiX^{2-p} + L_{ads} \rightarrow k_1'' Ni(X)(L_{ads})^{2-p}$ .
3. The obtained kinetic equations have confirmed the application of the Langmuir's adsorbed isotherm for the description of adsorbed equilibrium  $L \leftrightarrow L_{ads}$  and allowed us to determine the Langmuir's parameter  $\omega$  and kinetic parameters:  $k_h' K_L$  and  $k_h'' K_L$  where  $K_L$  is Henry's constant.
4. Langmuir's parameter  $\omega$  was determined increased to the direction  $NA \rightarrow DEN \rightarrow NC$ . The  $\omega$  value for NA is close to found in the literature on the basis of the hydrogen catalytic current in the presence of NA.
5. For NA  $k_h''(HPO_4^{2-}) > k_h''(AcO^-)$ , which correlates with the change of the complex stability constants  $(\beta_1)_{HPO_4^{2-}} > (\beta_1)_{AcO^-}$ . It corresponds to other homogeneous reactions considered in the literature.
6. We found that the correlation  $k_h'' \gg k_h'$ :  $(k_h''/k_h') = (1.1-3.9) \times 10^2$  can be explained by the influence of the field electrode through  $X^{p-}$  in addition to the usual influence of  $X^{p-}$  associated with the complex stability.
7. The effect of  $X^{p-}$  on the heterogeneous rate constant  $k_h''$  allowed us to choose from two alternative reactions: the ligand exchange reaction:  $Ni X^{2-p} + L_{ads} \rightarrow Ni(L)_{ads}^{2-p} + X^{p-}$  and reaction of the mixed complex formation:  $NiX^{2-p} + L_{ads} \rightarrow Ni(X)(L)_{ads}^{2-p}$ , the latter reaction is more probable.

8. The kinetic equations allowed to estimate the contribution of the every parallel heterogeneous catalytic reaction to the summary catalytic current. Despite the fact that  $k_h'' \gg k_h'$  the contribution of reaction **1a** achieves more than 60% (Py, DEN) due to the  $\psi_0$  potential influence.

## References

1. Mark HB Jr (1990) Analyst 115:667
2. Tur'yan YaI (1992) J Electroanal Chem 338:1
3. Tur'yan YaI, Ruvinsky OE, Zaitzev PM (1998) Polarographic Catalymetry. Khimiya, Moscow
4. Bănică FG, Ion A (2000) In Encyclopedia of Analytical Chemistry: Instrumentation and applications. Wiley, Chichester, p 11115
5. Tur'yan YaI (1990) Zh Obshchei Khim 60:1300
6. Mata F, Crespo MS (1979) Z Phys Chem (Leipzig) 260:1033
7. Crespo-Pinilla MS, Infante AB, Mata-Peréz F (2000) Can J Chem 78:521
8. Mark HB Jr, Reiley CN (1962) J Electroanal Chem 4:189
9. Mark HB Jr, Reiley CN (1963) Anal Chem 35:195
10. Tur'yan YaI, Malyavinskaya ON (1969) J Electroanal Chem 23:69
11. Tur'yan YaI, Ruvinsky OE (1970) J Electroanal Chem 28:381
12. Tur'yan YaI, Moskatov II (1981) Zh Obshchei Khim 51:1197
13. Čaja J, MacDonald HC Jr, Kirova-Eisner E, McCoy LR, Mark HB Jr (1972) J Phys Chem 76:1170
14. McCoy LR, Mark HB, Jr, Gierst L (1968) J Phys Chem 72:4637
15. Knobloch E (1947) Coll Czech Chem Commun 12:407
16. Koutecký J (1953) Coll Czech Chem Commun 18:597
17. Weber J, Koutecký J (1955) Coll Czech Chem Commun 20:980
18. Smithe DE, McCord TG, Hung HL (1967) Anal Chem 39:1149
19. Jones AR, Aikens DA (1983) Electrochim Acta 28:121
20. Gierst L (1959) Trans Symp Electrode Processes p109
21. Tur'yan YaI, Moskatov II (1983) Zh Obshchei Khim 53:29
22. Tur'yan YaI (1987) Zh Obshchei Khim 57:431
23. Heirovskiy J, Kůta J (1965) Principles of Polarography. Mir, Moscow, p 65
24. Bulmer RS, Coldin EF, Walton AW (1971) Trans Far Soc 67:3343
25. Tur'yan YaI, Lovrič M (2002) J Electroanal Chem 531:147
26. Bănică FG (1990) Rev Roum Chim 35:693
27. Bănică FG, Ion A (1994) Electroanalysis 6:1051
28. Lur'e YY (1989) Handbook of Analytic Chemistry. Khimiya, Moscow, p 87
29. Tur'yan YaI, Moskatov II (1982) Zh Obshchei Khim 52:1194
30. Dondoy J, Gierst L (1961) J Electroanal Chem 2:116
31. Sanborn RH, Orlemann EF (1955) J Am Chem Soc 77:3726
32. Russel CD (1963) J Electroanal Chem 6:486
33. Yamaoka H (1970) J Electroanal Chem 25:381
34. Bond AM (1971) J Phys Chem 75:2640
35. Tur'yan YaI, Serova GF (1957) Zh Fiz Khim 31:1976
36. Ruvinsky OE, Uspenskaya NM, Rodyazky VE (1979) Elektrokimiya 15:1579

37. Schmamel CO, Santhanam KSV, Elving PJ (1974) *J Electrochem Soc* 121:345
38. Moore P, Wilkins RG (1964) *J Chem Soc* 3454
39. Holyer RM, Hubbard CD, Kettle SFA, Wilkins RG (1965) *Inorgan Chem* 4:929
40. Khakimov KhKh, Azizov MA, Khakimova KS (1971) *Zh Neorgan Khim* 16:128
41. Jellinek HHG, Wayne MG (1951) *J Phys Colloid Chem* 55:173
42. Yasuda M, Yamasaki K, Ohtaki H (1960) *Bull Chem Soc Japan* 33:1067
43. Ohyoshi E (1973) *Bull Chem Soc Japan* 46:2758
44. Sigel H, Becker K, McCormick DB (1967) *Biochim Biophys Acta* 148:655
45. Fridman YaD, Dolgashova NV, Sargaev DS, Veresova RA (1973) *Zh Neorg Khim* 18:176
46. Shavgulidze VV, Getsadze ED, Bekauri NG (1979) *Proc Acad Sci Gruz SSR* 94:101
47. Shavgulidze VV, Getsadze ED (1980) *Elektrokhimiya* 16:308
48. Shavgulidze VV, Chagunava MR (1989) *Proc Acad Sci Gruz SSR* 135:373
49. Moskatov II, Tur'yan YaI, Sirko VN(1980) *Izv Vysch Uchebn Zaved Pisch Tekhnol* 5:137
50. Tur'yan YaI, Moskatov II (1980) *Zh Neorg Khim* 25:2742
51. Tur'yan YaI, Moskatov II (1982) *J Obshechi Khi* 52:115
52. Anson FC, Borclay PJ (1968) *Anal Chem* 40:1791
53. Gierst L, Tonder J, Gornelissen R, Lamy F (1965) In: *Topics of Modern Theoretical Electrochemistry*. Mir, Moscow, p 425
54. Funahashi S, Tanaka M (1969) *Inorg Chem* 8:2159