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Polarographic Kinetic Currents of Formaldehyde and Kinetics of the Electrode Chemical Reactions*

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New approaches to the analysis of the polarographic (DCP) kinetic currents of formaldehyde have been developed. Anomalously high limiting kinetic current in strongly acidic media has been explained by catalytic hydrogen evolution upon CH_2OH^+ discharge after the protonation of CH_2O. On the other hand, the diffusion contribution of CH_2O from the bulk solution to the total limiting kinetic and diffusion currents should be taken into account for a correct determination of the rate constants of $CH_2(OH)_2$ dehydration reaction in the catalysis by H_2O molecules in neutral and weakly acidic media. At the same time, the electrode reaction of the direct formation of CH_2O from $CH_2(OH)O^-$ can be neglected in alkaline solutions. Thus, the two consecutive reactions, *i.e.* the formation of $CH_2(OH)_2$ from $CH_2(OH)O^-$ and H_2O and the dehydration reaction of $CH_2(OH)_2$ to CH_2O, proceed at the electrode in alkaline solutions. Detailed analyses of the diffusion coefficient and diffusion current of formaldehyde as well as equilibrium constants of the dimerization and acidic dissociation reactions of $CH_2(OH)_2$ and the hydration and protonation reactions of CH_2O allowed us to choose the most correct values for kinetic calculations.

Key words: polarographic kinetic currents, formaldehyde, electrode reactions.

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[*] Dedicated to my friend and colleague Professor Armin G. Stromberg on the occasion of his 90th birthday.

INTRODUCTION

Electrode reactions with coupled chemical reactions such as the reduction of formaldehyde (F) at mercury electrode remain the basis of the development of the theory of kinetic currents in direct current polarography (DCP),[1–16] pulse polarography (PP),[17,18] linear sweep voltammetry (LSV),[19–21] and other related methods.[22] In spite of extensive research that has been done in this field, some aspects of the kinetics and mechanism of the electrode chemical reactions have remained unsolved. These include the following: (i) the anomalously high limiting kinetic current observed in strongly acidic media,[10] (ii) too high rate constants of the dehydration reaction of $CH_2(OH)_2$ that have been already noted by Strehlow,[23] (iii) correct choice of the mechanism of CH_2O formation at the electrode in alkaline solutions.

These issues are addressed in this work. In addition, a revision of many physico-chemical parameters of the reactions in aqueous solutions containing formaldehyde has been done for kinetic calculations.

Since the general acid-base catalysis is needed for the dehydration reaction of $CH_2(OH)_2$, only buffer solutions or solutions with an excess of strong acid or alkali have been considered.

PHYSICO-CHEMICAL PARAMETERS

Diffusion Coefficient and Diffusion Current

Similarly to works,[1,3,6,7,17,18] we accepted that:

$$D_{CH_2O} \cong D_{CH_2(OH)_2} \cong D_{CH_2(OH)O^-} = D \qquad (1)$$

Only one correlation, $D_{CH_2(OH)_2} = D_{CH_2(OH)O^-}$, has been shown experimentally.[15] The D values that have been found experimentally[3a,7] refer to $D_{CH_2(OH)_2}$. These values are close (Table I).

The value of $D = D_{CH_3OH}$ (20 °C), which has been used in works,[1,6,14] is larger than $D_{CH_2(OH)_2}$ (Table I). However, the value of D_{CH_3OH} at 15 °C that has been used in Ref. 19 is close to the value of $D_{CH_2(OH)_2}$ determined at 20 °C (Table I).

Besides that the values of $D_{CH_2(OH)_2}$ and $D_{CH_2(OH)O^-}$ have been directly found,[3a,7] they can be calculated from the limiting diffusion current $\left(\sum \bar{i}_1^{\,d}\right)$ at high ionic strength[15] (Table I). These values are somehow lower than the value of $D_{CH_2(OH)_2}$[3a,7] (Table I). Lower values of $D_{CH_2(OH)_2}$ have been also obtained in Ref. 18 from the kinetic current in phosphate buffer. This was explained[18] by the formation of $CH_2(OH)HPO_4^{\,-}$ and $CH_2(OH)PO_4^{\,2-}$.

TABLE I

Diffusion coefficients of methanol and methylene glycol in aqueous solution

$\frac{t}{°C}$	$\frac{c_M(c_F)^a}{mol\ dm^{-3}}$	$\frac{D \times 10^5}{cm^2\ s^{-1}}$	Methods[b]	Refs.
		CH_3OH		
15	–	1.28	–	24
18	7.8×10^{-2}	1.37	–	25
20	0.91	1.35–1.64	–	25
		$CH_2(OH)_2$		
20	–	1.16	Och.	3a
20	0.25	1.22	EP	7
20	3.3×10^{-3} [c]	0.74	DCP [d]	15
25	0.25	1.36 [e]	EP	7, 17
25	0.38[f]	0.75	PP	18
25	3.3×10^{-3} [c]	0.83	DCP [d]	15

[a] c_M and c_F are the concentrations of methanol and methylene glycol, respectively.
[b] Och, Ochlom's method; EP, electrophoresis; DCP, direct current polarography; PP, pulse polarography.
[c] NaOH + NaCl = 1 mol dm^{-3}.
[d] From $\sum \bar{i}_1^d$ *vs.* 1/*T*.
[e] From *D* (20 °C)[7] and D_{CH_3OH} *vs.* *t* °C (Table I).
[f] 0.15 mol dm^{-3} NaH_2PO_4 + 0.15 mol dm^{-3} Na_2HPO_4.

To calculate $\sum \bar{i}_1^d$ (Ilkovic's equation),[26] we have used the value of $D = 1.22 \times 10^{-5}$ cm^2 s^{-1} (20 °C) analogously to Refs. 7, 12. The value of *D* (25 °C) (Table I) was estimated in Refs. 17, 18 from the dependence of D_{CH_3OH} on *t* °C.

Using[15] increased temperatures and alkaline solutions (pH = 12.3–14), the activation energy of $\Delta E = 2.0$ kcal mol^{-1} has been found from the straight line dependence of lg $\sum \bar{i}_1$ on 1/*T* in the range of temperatures between 65 and 85 °C. This ΔE value corresponds to the diffusion current[27] (ΔE value should be in the range of 1.7–2.7 kcal mol^{-1}), *i.e.* $\sum \bar{i}_1 = \sum \bar{i}_1^d$. Extrapolation of straight line dependence of lg $\sum \bar{i}_1^d$ on 1/T to low temperatures allowed to find the value of $\sum \bar{i}_1^d$ at low temperatures (Table I).

The dependences of lg $\sum \bar{i}_1$ on 1/*T* that have been found earlier [2,3a,4b] do not correspond to the diffusion current, since the value of ΔE / kcal mol^{-1} = 13 (0–65 °C),[2] 9.9 (20–60 °C),[3a] 3.5 (55–94 °C).[4b] The data[3a] (0.1 M NaOH) have been extrapolated by us in the range of temperatures 80–90 °C and the value of $\Delta E = 1.8$ kcal mol^{-1} has been derived. This allowed us to determine the $\sum \bar{i}_1^d$ (20 °C) for kinetic calculations (see below).

Equilibrium Constant of the Dimerization Reaction of $CH_2(OH)_2$

Similarly to Ref. 18 and on the basis of works,[27–30] we have used the equilibrium constant, K_D, of the dimerization reaction of $CH_2(OH)_2$ for the calculations. This value was determined by Eq. (2):

$$K_D = [\{(HOCH_2)_2\}O][H_2O]/[CH_2(OH)_2]^2 = 4.5 \text{ (20–25 °C)} \tag{2}$$

At $c_F \leq 0.05$ mol dm^{-3} (which usually takes place in DCP), the dimerization of $CH_2(OH)_2$ can be neglected.

Equilibrium Constant of the Hydration Reaction of CH_2O

The equilibrium constant of the hydration reaction, K_h, of CH_2O is expressed by Eq. (3).

$$K_h = [CH_2(OH)_2] \,/\, [CH_2O] \tag{3}$$

The equilibrium constant of the dehydration reaction is designated as K_d. These designations are the same as in Refs. 17, 18, 30 and 31 and are different from Refs. 1, 6, 7, 12 and 19.

To recalculate the K_h at different temperatures, we have used the enthalpy of the CH_2O hydration $\Delta_h H = -(8.4 \pm 0.5)$ kcal mol^{-1} from a more recent work.[32] This K_h value is close to average K_h values from the different works (Table II).

In addition to the indicated $\Delta_h H$ value, the effect of dimerization ($c_F \geq$ 0.1 mol dm^{-3}) and the effect of the nature and concentration of the supporting electrolyte[18] have been taken into account in recalculating K_h (Table III). Similarly to Ref. 18, the correction in a footnote in Ref. 20 of the data in Ref. 19 has not been used as it has not been introduced by the same author in Ref. 12.

The average values of $K_h = (2.2 \pm 0.1) \times 10^3$ (20 °C) and $K_h = (1.8 \pm 0.1) \times 10^3$ (25 °C) have been derived from most of the values of K_h compared in Table III (data without brackets) and used in further analysis.

TABLE II

Enthalpy of CH_2O hydration

$\frac{\Delta_h H}{\text{kcal mol}^{-1}}$	14.6	13.0	8.0	5.7	5.1	6.4	8.4 ± 0.5
Method[a]	S	DCP	VP	S	S	S	S
Ref.	33	2	34	35	30	36	32

[a] S, spectrophotometry; VP, vapour pressure; DCP, direct current polarography.

TABLE III

Equilibrium constants of the hydration reaction of CH_2O

t / °C	c_F/mol dm^{-3}	K_h	K_h recalc.	Method[a]	Ref.
20	$(1.4–2.6) \times 10^{-3}$	(1×10^4) [b]	2.4×10^3 [c]	S	33
20	0.525	2.3×10^3	2.2×10^3 [d]	LSV	19
20	0.9–4.2	(6.6×10^2)	–	S	30
20	$(0.8–4.0) \times 10^{-5}$	–	2.4×10^3 [c]	CS	37
20	0.217	2.3×10^3	2.2×10^3 [e]	LSV	12
20	0.38	–	2.0×10^3 [c]	PP	18
22	$(0.8–4.0) \times 10^{-5}$	2.2×10^3	–	CS	37
25	$(1.4–2.6) \times 10^{-3}$	–	1.9×10^3 [c]	S	33
25	0.525	–	1.7×10^3 [c]	LSV	19
25	0.217	–	1.7×10^3 [c]	LSV	12
25	$(0.8–4.0) \times 10^{-5}$	–	1.9×10^3 [c]	CS	37
25	3.4–13.3	(1.0×10^3)	–	S	35
25	0.9–4.2	(5.7×10^2)	–	S	30
25	–	(2.4×10^3)	–	S	36
25	0.38	–	1.6×10^3 [d]	PP	18
25	15.8–17.2	(2.6×10^3)	–	S	32
30	$c_F \longrightarrow 0$	(1.8×10^{-3})	–	VP	34

[a] LSV, linear sweep voltammetry; CS, chemical scavenger; for other see Tables I and II.
[b] Recalculation[33] to t °C with $\Delta_h H = -14.6$ kcal mol^{-1}.
[c] Recalculation to t °C with $\Delta_h H = -8.4$ kcal mol^{-1}.
[d] Correction taking into account the effect of phosphate and dimerization reaction.[18]
[e] Correction taking into account the dimerization effect.

Equilibrium Constant of the Acid Dissociation Reaction of $CH_2(OH)_2$

The equilibrium constant of the acid dissociation reaction of $CH_2(OH)_2$, K_a, is expressed by Eq. (4):

$$K_a = [H^+][CH_2(OH)O^-] / [CH_2(OH)_2] \quad (4)$$

Based on the data of Table IV, the correlation of pK_a *vs.* $1/T$ ($r^2 = 0.986$) has been obtained from the pK_a values (data without brackets). This correlation (Eq. (5)) is much better than that used earlier by Martin.[44]

$$pK_a = (3.95 \pm 0.07) + (2.76 \pm 0.16) \times 10^3/T \quad (5)$$

Thus, the values of pK_a = 13.37 (20 °C) and pK_a = 13.21 (25 °C) have been found from Eq. (5) and have been further used.

TABLE IV

Equlibrium constants of the acidic dissociation of $CH_2(OH)_2$

$t/°C$	c_F/mol dm^{-3}	pK_a	Method[a]	Ref.
0	0.50	14.0	FP	38
0	0.52	(13.7)	FP	39
15	–	(12.9)	K	40
20	3.75×10^{-4}	13.4	DCP	1
20	1×10^{-3}	(13.6)	DCP	7
20	4×10^{-3}	(13.6)	DCP	12
20	1×10^{-4}	(12.5)	S	13
23	0.08–0.89	(12.79)	P	41
25	$(0.06–191) \times 10^{-2}$	13.27	C	42
25	$(0.4–1.2) \times 10^{-2}$	13.28	PP	17
30	$c_F \longrightarrow 0$	(12.87)	P	43
40	$(9.5–72) \times 10^{-3}$	12.69	P	44
50	–	12.48	P	45

[a] FP, freezing-point; K, kinetic; C, conductometry; P, pH-metry; for other see Tables I and II.

Equilibrium Constant of the Protonation Reaction of CH_2O

This constant is expressed by Eq. (6):

$$K_{H^+} = [CH_2OH^+] / [CH_2O]\ h_o \tag{6}$$

where h_o is acidity.

The values of $pK_{H^+} = 4.2$ (25 °C) in Ref. 46 and $pK_{H^+} = 5.0$ (25 °C) in Ref. 30 have been found by the spectrophotometric method. After the constants have been recalculated to the same value of $K_h = 1.8 \times 10^3$ (see above), we have obtained the values of $pK_{H^+} = 4.5–4.9$ or $(pK_{H^+})_{av.} = 4.7 \pm 0.2$ for 20–25 °C.[30]

KINETICS OF THE ELECTRODE CHEMICAL REACTIONS

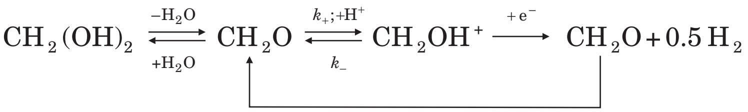
Acidic Solutions

From the data obtained by Epimakhov[10] (DCP method) in acidic solutions ($HClO_4$) it follows that the limiting kinetic current has increased and become considerably larger than the calculated limiting diffusion current ($CH_2(OH)_2 \longrightarrow CH_3OH$) at an increased concentration of $HClO_4$ at c_F = const. The possible polarographic maximum has been eliminated.[10]

On the other hand, when the limiting kinetic current was lower than the limiting diffusion current, the rate constant of the dehydration reaction of $CH_2(OH)_2$ under catalysis by H^+ ions calculated by us from Koutecky's equation[47,48] was by three orders larger than the one obtained by other methods (Table V).

Thus, it follows that the limiting kinetic current in strongly acidic solutions cannot be caused by the electroreduction of $CH_2(OH)_2$ or $CH_2O(CH_2OH^+)$ to CH_3OH, as it was accepted in Ref. 10.

To explain the anomalously high limiting kinetic current, the catalytic process of hydrogen evolution according to scheme (7) should be accepted instead of the electroreduction of CH_2OH^+ to CH_3OH:[10]



$$\begin{tikzcd} CH_2(OH)_2 \arrow[r, shift left, "-H_2O"] & CH_2O \arrow[l, shift left, "+H_2O"] \arrow[r, shift left, "k_+;+H^+"] & CH_2OH^+ \arrow[l, shift left, "k_-"] \arrow[r, "+e^-"] & CH_2O + 0.5\,H_2 \arrow[ll, bend left] \end{tikzcd} \tag{7}$$

Better agreement of scheme (7) with experimental data[10,11] can be obtained if we accept that the protonation reaction of CH_2O, as the rate deter-

TABLE V

Rate constants of the dehydration reaction of $CH_2(OH)_2$

$\frac{c_F}{\text{mol dm}^{-3}}$	I[a]	20 °C			25 °C			Method[b]	Ref.
		$\frac{k_d^{H}}{(\text{mol dm}^{-3})^{-1}\text{ s}^{-1}}$	$\frac{k_d^{H_2O} \times 10^3}{\text{s}^{-1}}$	$\frac{k_d^{OH} \times 10^{-3}}{(\text{mol dm}^{-3})^{-1}\text{ s}^{-1}}$	$\frac{k_d^{H}}{(\text{mol dm}^{-3})^{-1}\text{ s}^{-1}}$	$\frac{k_d^{H_2O} \times 10^3}{\text{s}^{-1}}$	$\frac{k_d^{OH} \times 10^{-3}}{(\text{mol dm}^{-3})^{-1}\text{ s}^{-1}}$		
4×10^{-3}	0.1	–	(34)	1.3	–	–	2.0 [c]	DCP	7, 26
$(1.2–2.5) \times 10^{-2}$	–	–	(17–19)	–	–	–	–	DCP	6
–	–	2.0	4.5	(0.77)	–	6.9 [d]	–	CS	49
–	–	–	3.3 [d]	1.1 [c]	2.7	5.1	1.6	CS	50
0.20–1.3	0.1	3.4	3.9	(24)	4.5	5.2	(33)	TJ	36
$(0.8–4.0) \times 10^{-5}$	–	–	3.7 [d]	–	–	5.7 [d]	–	CS	37
4×10^{-3}	0.1	–	(35)	(0.64)	–	–	–	DCP	12
$(0.4–1.2) \times 10^{-2}$	0.2	–	–	1.1 [c]	–	–	1.7	PP	17, 18
0.38	0.2	–	4.5 [d]	–	–	6.9	–	PP	18
–	1.0	–	2.7 [d]	1.4 [c]	2.84	4.2	2.1	CS	51
3.3×10^{-3}	1.0	–	–	1.4	–	–	2.1 [c]	DCP	16

[a] I, ionic strength.

[b] TJ, temperature jump; for other see Tables I and III.

[c] Recalculation to t °C with the activation energy[16] equal to 14.6 kcal mol^{-1}.

[d] Recalculation to t °C with the activation energy[49] equal to 14.8 kcal mol^{-1}.

mining step, proceeds in the reaction layer of minimum possible thickness, *i.e.*, it is close to the thickness of the double layer compact part.

For quantitative examination of scheme (7) the following initial equations (Eqs. (8) to (13)) have been used,[52] taking into account the conditions indicated above:

$$\bar{i}^{\mathrm{k}} = n_1 F \bar{q} k_{\mathrm{e}}^{\mathrm{o}} [\mathrm{CH_2OH^+}] \exp[(-\alpha F / RT)(E - E^{\mathrm{o}}_{\mathrm{CH_2OH^+}} - \psi_2)] \qquad (8)$$

$$\bar{i}^{\mathrm{k}} = 10^{-3} n_1 F \bar{q} \mu_{\mathrm{s}} \{k_+ (\,_{\mathrm{CH_2O}}\;\,_{\mathrm{H^+}} /\;^{\#}_{\mathrm{CH_2OH^+}}) [\mathrm{CH_2O}][\mathrm{H^+}] \cdot$$

$$\exp(-\psi_2 F / RT) - k_- [\mathrm{CH_2OH^+}]\} \qquad (9)$$

$$\bar{i}_1^{\mathrm{k}} = 10^{-3} n_1 F \bar{q} \mu_{\mathrm{s}} k_+ (\,_{\mathrm{CH_2O}}\;\,_{\mathrm{H^+}} /\;^{\#}_{\mathrm{CH_2OH^+}}) [\mathrm{CH_2O}][\mathrm{H^+}] \cdot$$

$$\exp(-\psi_2 F / RT) \qquad (10)$$

$$h_{\mathrm{o}} = f_{\mathrm{CH_2O}} f_{\mathrm{H^+}} [\mathrm{H^+}] / f^{\#}_{\mathrm{CH_2OH^+}} \qquad (11)$$

$$c_{\mathrm{F}} = [\mathrm{CH_2(OH)_2}] \qquad (12)$$

$$\bar{i}_1^{\mathrm{d}} = \bar{\chi} c_{\mathrm{F}} \qquad (13)$$

where: $\bar{i}^{\mathrm{k}}$ and $\bar{i}_1^{\mathrm{k}}$ are the average catalytic current at the E potential and average limiting current, respectively; n_1 is the number of electrons in the electroreduction of $\mathrm{CH_2OH^+}$ to 0.5 $\mathrm{H_2}$ ($n_1 = 1$); $\bar{q}$ is the average surface of the mercury drop; $k_{\mathrm{e}}^{\mathrm{o}}$ is the standard rate constant of the electron transfer; α is the transfer coefficient; $E^{\mathrm{o}}_{\mathrm{CH_2OH^+}}$ is the formal potential; ψ_2 is the potential at the outer Helmholtz plane; μ_{s} is the thickness of the reaction layer; f is the activity coefficient; $\bar{i}_1^{\mathrm{d}}$ is the average limiting diffusion current of the electroreduction of $\mathrm{CH_2(OH)_2}$ to $\mathrm{CH_3OH}$; $\bar{\chi}$ is Ilkovic's constant.

On the basis of Eqs. (3), (8) to (13), we have derived the following equations for the limiting catalytic current:

$$\bar{i}_1^{\mathrm{k}} = 10^{-3} n_1 F \bar{q} \mu_{\mathrm{s}} (k_+ / K_{\mathrm{h}}) c_{\mathrm{F}} h_{\mathrm{o}} \exp(-\psi_2 F / RT) \qquad (14)$$

$$\bar{i}_1^{\mathrm{k}} / \bar{i}_1^{\mathrm{d}} = 0.81 (n_1 / n_2)(t_1 / D)^{0.5} \mu_{\mathrm{s}} (k_+ / K_{\mathrm{h}}) h_{\mathrm{o}} \exp(-\psi_2 F / RT) \qquad (15)$$

and the catalytic wave equation:

$$E_{1/2} = E^{\circ}_{\mathrm{CH_2OH^+}} + \psi_2 + (RT/\alpha F)\ln(k_s^{\circ}/k_-) \tag{16}$$

where: n_2 is the number of electrons in the electroreduction of $CH_2(OH)$ to CH_3OH ($n_2 = 2$), t_1 is the drop time, $E_{1/2}$ is the half wave potential ($\bar{i}^{\,k} = \bar{i}_1^{\,k}/2$).

Directly proportional dependence of $\bar{i}_1^{\,k}$ on c_F at constant values of h_o, ψ_2, μ_s and $\bar{q}$ corresponds to Eq. (14) and is corroborated by experimental data.[11]

The shift of $E_{1/2}$ to the positive direction at an increased $c_{\mathrm{HClO_4}}$[10] is in agreement with Eq. (16) since ψ_2-potential is shifted in the same direction.[53–55] At $c_{\mathrm{HClO_4}} \geq 2.0$ mol dm^{-3} the shift of the ψ_2-potential becomes insignificant and leads $E_{1/2} \longrightarrow$ const to such conditions (Eq. 16). The value of $K_{\mathrm{H^+}}$ (see above) shows that the degree of CH_2O protonization is very low in such solutions (it is about 0.3% even for 5 mol dm^{-3} $HClO_4$). This means that the protonation of CH_2O cannot cause $E_{1/2} \longrightarrow$ const, as it was suggested by Epimakhov.[10]

To check Eq. (15), we have used the data[10] on the dependence of $\bar{i}_1^{\,k}$ *vs.* $c_{\mathrm{HClO_4}}$ at $c_F = 2.0 \times 10^{-5}$ mol dm^{-3} (Table VI) and $m^{2/3} t_1^{1/6} = 3.63$ mg$^{2/3}$ s$^{-1/2}$, t_1 was accepted = 3 s because t_1 in Ref. 10 is absent. The values of $D = 1.22 \times 10^{-5}$ cm^2 s^{-1} (Table I), $K_h = 2.2 \times 10^{-3}$ (Table III), h_o (Table VI) have been used from Ref. 25, ψ_2 values (Table VI) have been obtained from Refs. 53–55 for $NaClO_4$ at $E = -1.014$ V (S.C.E.). The change of $E_{1/2}$ in the $c_{\mathrm{HClO_4}}$ range (1.0–3.5 mol dm^{-3}) is insignificant. The calculated value of $\bar{i}_1^{\,d}$ equals 0.31 μA.

The values of $\mu_s k_+$ derived from Eq. (15) (Table VI) are almost independent of the acidity of the solution. This confirms Eq. (15). For $\mu_s \approx 10^{-8}$ cm the k_+ value equals $\approx 10^8$ mol dm^{-3} which is in agreement with the Bronsted dependence for the big group of acids[56] at $\mathrm{p}K_{\mathrm{H^+}} = 4.7$ (see above).

If the stage of the protonation reaction of CH_2O in scheme (7) should proceed in the adsorption layer, for the corroboration of Eqs. type (14) and (15), we should assume that the h_o values in the adsorption layer and solution are equal. However, this is improbable.

In conclusion, it should be noted that the catalytic hydrogen evolution proceeds at potentials more positive than the discharge of H_3O^+. The latter masks[10] the electroreduction of $CH_2(OH)_2$ to CH_3OH with the preceding stage of the $CH_2(OH)_2$ dehydration in strongly acidic solutions.

Neutral and Weakly Acidic Solutions

In such conditions the electroreduction of $CH_2(OH)_2$ to CH_3OH in DCP method takes place:[1,3,6,18]

$$\mathrm{CH_2(OH)_2} \underset{k_h;\,+\mathrm{H_2O}}{\overset{k_d;\,-\mathrm{H_2O}}{\rightleftarrows}} \mathrm{CH_2O} \xrightarrow{+2e^-;+2\mathrm{H^+}} \mathrm{CH_3OH} \tag{17}$$

TABLE VI

Checking the kinetic equation (15) on the basis of the dependence of i_l^k on c_{HClO_4} (from Ref. 10)

c_{HClO_4} / mol dm^{-3}	$\bar{i}_l^k$ / μA	h_o / mol dm^{-3}	$-\psi_2$ / mV	$\mu_s k_+$ / cm (mol dm^{-3})$^{-1}$ s^{-1}
1.0	0.14	1.66	45	0.50
1.5	0.26	3.39	37	0.63
2.0	0.51	6.03	33	0.81
2.5	0.77	10.23	29	0.84
3.0	1.08	16.98	26	0.80
3.5	1.36	29.51	24	0.63
				av. 0.70 ± 0.12

where: k_d and k_h are the rate constants of $CH_2(OH)_2$ dehydration and CH_2O hydration, respectively, which are dependent on the general acid base catalysis.[1,7,18,50]

Since at pH ≈ 7 the k_d value and, hence, the limiting kinetic current are low, high c_F is used[3c,6] to increase the limiting kinetic current. This means that it is impossible to neglect the diffusion contribution of CH_2O from the bulk solution as it is not taken into account using the usual Koutecky's equation.[47,48] Therefore, for similar processes, Koutecky's equation has been modified by us to Eq. 18 ($K_h >> 1$):[57]

$$\left\{\sum \bar{i}_l^k - \left(\sum \bar{i}_l^d / K_h\right)\right\} / \left(\sum \bar{i}_l^d - \sum \bar{i}_l^k\right) = 0.886\,(k_d t_1 / K_h)^{0.5} \qquad (18)$$

where: $\sum i_l^k$ and $\sum i_l^d$ are the sum of the average limiting kinetic and diffusion currents, respectively.

On condition that:

$$K_h \sum \bar{i}_l^k >> \bar{i}_l^d \qquad (19)$$

Eq. (18) becomes the usual Koutecky's equation.[47,48]

Landqvist[6] has investigated $\sum i_l^k$ in neutral solution (pH = 6.86) in detail. Use[6] of the erroneous K_h value from Ref. 33 caused the $k_d^{H_2O}$ value (upper index is the catalyst) to be higher than the data found by other methods (Table V). This was corrected by Bell and Evans[50] (K_h from Ref. 19). We have introduced an additional correction into these calculations, *i.e.* the use of the more correct Eq. (18) and the $\sum i_l^d$ value found with $D = 1.22 \times 10^{-5}$ cm^2 s^{-1}

instead of $D = 1.6 \times 10^{-5}$ cm^2 s^{-1} in Ref. 6. As a result, the value of $k_d^{H_2O} = 3.0 \times 10^{-3}$ s^{-1} (20 °C) has been obtained at $c_{HPO_4^{2-}} \longrightarrow 0$. This value is close to those found in Ref. 50 on the basis of data[6] $k_d^{H_2O} = 3.4 \times 10^{-3}$ s^{-1} because of the intercompensation of corrections. However, the more correct calculation is in principle significant. As it can be seen from Table V, the found $k_d^{H_2O}$ value is close to the data obtained by other methods.

Too high values of $k_d^{H_2O}$ (Table V) obtained by Brdicka[7,26] and Calusaru *et al.*[12] are probably due to higher pH (pH = 8–10) when the catalysis by $H_2BO_3^-$ and OH^- is dominant. In order to eliminate this effect, we have extrapolated the $\sum \bar{i}_l^k$ values, from Ref. 7 at $[H_3BO_3]$ = const (0.1 mol dm^{-3}) (Table 1 in Ref. 7) to pH = 7.0. As a result, the value of $k_d = (5.2 \pm 1.5) \times 10^{-3}$ s^{-1} at 20 °C has been obtained on the basic of Eq. (18). Then using the value of $k_d = k_d^{H_2O} + k_d^{H_2BO_3^-}[H_2BO_3^-]$, $K_{H_3BO_3} = 6.48 \times 10^{-10}$ (20 °C)[58] and $k_d^{H_2BO_3^-} = 3.0$ (mol dm^{-3})$^{-1}$ s^{-1} (20 °C) from Ref. 7, we have found the value of $k_d^{H_2O} = (3.3 \pm 15) \times 10^{-3}$ s^{-1} (20 °C). This value is in agreement with the above obtained one as well as with other data (Table V).

Bieber and Trumpler[3c] have studied $\sum \bar{i}_l^k$ (20 °C) at pH = 6.0. Using $t_1 = 3.5$ s (average value from those indicated in Ref. 3c) and $\sum \bar{i}_l^d$ found by us from the dependence[3a] of $\sum \bar{i}_l$ *vs.* $1/T$ (see above), the value of $k_d = 5.4 \times 10^{-3}$ s^{-1} (20 °C) has been calculated from Eq. (18). This value is probably somewhat higher than the value of $k_d^{H_2O}$ because of the buffer effect. The latter effect cannot be taken into account since the corresponding data about the concentration of the buffer is not given in Ref. 3c. Nevertheless, if we accept that $k_d^{H_2O} = k_d$, the obtained value of $k_d^{H_2O}$ is more correct than the one found earlier by the DCP method.

In the $k_d^{H_2O}$ determination, the correlation of $\sum \bar{i}_l^d >> \sum \bar{i}_l^k$ took place due to the high concentration of formaldehyde. Therefore, the condition of the stationariness of the diffusion and chemical reaction is unessential.[57a]

As indicated above, Strehlov[23] has paid attention to the too high rate constants obtained by the DCP method. He explained this by the effect of formaldehyde polymerization. Now we have seen that correct determination of $k_d^{H_2O}$ eliminates the problem of the too high rate constant ($k_d^{H_2O}$). On the other hand, at low c_F (≤ 0.05 mol dm^{-3}) the dimerization of $CH_2(OH)_2$ can be neglected (see above) in DCP.

Alkaline Solutions

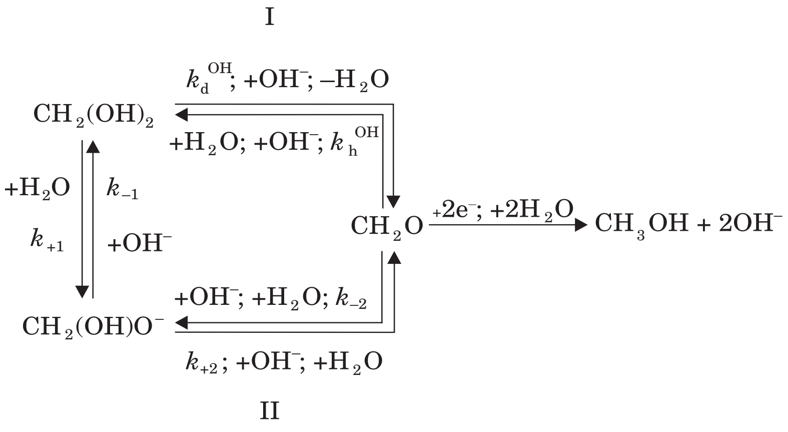
Eq. (12) is valid at pH ≤ 12 on the basis of K_h and K_a values (see above). Besides, correlation (19) is carried out for the DCP method at pH ≥ 8 because of the strong catalytic effect of OH^- ions. Hence, Eq. (18) should be substituted by the usual Koutecky's equation.[47,48]

From this equation, the value of k_d^{OH} in Ref. 16 at pH ≅ 12 has been found when practically only the OH^- ions participate in the catalysis. These k_d^{OH} values are almost the same or close to the PP data[17] at pH ≅ 12 and to the value of k_d^{OH} at pH < 7 determined by the scavenger method (Table V).[50,51] The last one is particularly important.

At pH > 12, Eq. (12) should be substituted by Eq. (20) taking into account K_h and K_a values (see above).

$$c_F = [CH_2(OH)_2] + [CH_2(OH)O^-] \tag{20}$$

Bell *et al.*[59,60] have noted that free aldehyde can be formed not only from its *gem*-diol molecule but also directly from a *gem*-diol anion. Hence, in alkaline solutions (pH > 12), two ways, I and II, of the CH_2O formation (basic catalysis) at the electrode are possible (scheme (21)):



(21)

Barnes and Zuman[13] (DCP) and Los *et al.* (PP)[17] have accepted that way II prevails whereas the dominant proceeding of way I has been considered in Refs. 14 and 16 (DCP). Thus, additional analysis including the possibility of parallel ways I and II is needed.

Los *et al.*[17] determined by PP the k_d^{OH} value at pH = 11.9–12.9, which was independent of pH and close to those[50,51] at pH < 7 when only way I was preferred (Table V). In Ref. 17 it was shown for the first time that the equilibrium (k_{+1} / k_{-1}) (scheme (21)) cannot be considered as a frozen equilibrium during the life time of each mercury drop, as it was accepted in Refs. 1, 7 and 12. To eliminate the influence of the equilibrium shift (k_{+1} / k_{-1}), the k_d^{OH} values were extrapolated to $t = 0$ (t is a pulse time) in Ref. 17.

The close values of k_d^{OH} at pH = 11.9–12.9 in Ref. 17 (when the $CH_2(OH)O^-$ concentration reaches up to 33% from c_F at 25 °C) to the ones at pH < 7 in

Refs. 50 and 51 (Table V) allow the conclusion that way I in scheme (21) is dominant and that the parallel way II could be neglected. Unfortunately, this conclusion has not been made in Ref. 17.

Other important proof that way I is dominant in scheme (21) is the consideration[16] of the kinetics of the successive reactions (k_{+1}) and ($k_\mathrm{d}^{\mathrm{OH}}$) at pH ≅ 14 when Eq. (20) should be substituted by Eq. (22).

$$c_\mathrm{F} \cong [\mathrm{CH_2(OH)O^-}] \qquad (22)$$

For these conditions, the correct kinetic equation (23) has been obtained ($[\mathrm{H}^+] << K_\mathrm{a}$) in Ref. 16, in contrast to the incorrect solution[61] for similar processes.

$$\left(\sum \bar{i}_1^{\,\mathrm{d}} - \sum \bar{i}_1^{\,\mathrm{k}}\right) [\mathrm{H}^+]^{0.5} / \sum \bar{i}_1^{\,\mathrm{k}} = 1.13\, K_\mathrm{a}\, (K_\mathrm{h} / K_\mathrm{w}\, k_\mathrm{d}^{\mathrm{OH}}\, t_1)^{0.5} +$$

$$1.13\, (K_\mathrm{a} / k_{+1}\, [\mathrm{H_2O}]\, t_1)^{0.5} \qquad (23)$$

where

$$K_\mathrm{w} = [\mathrm{H}^+]\ [\mathrm{OH}^-] \qquad (24)$$

Using the $k_\mathrm{d}^{\mathrm{OH}}$ at pH = 12 (see above), the value of $k_{+1} = (3.0 \pm 0.2) \times 10^{-2}$ (mol dm^{-3}) s^{-1} (20 °C) has been found[16] from Eq. (23). From the $k_\mathrm{d}^{\mathrm{OH}}$ and k_{+1} values it was concluded[16] that to use Eq. (23), the correlation $k_\mathrm{h} >> k_{-1}$ and the condition of stationariness of the diffusion and chemical reactions at pH ≅ 14 should be carried out.

The k_{+1} value was also corroborated by the analysis of the Bronsted equation.[16] Hence, this is a quantitative proof of the domination of way I in scheme (21).

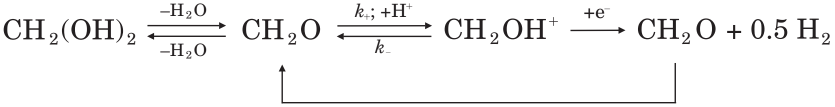
The conclusion that the reaction rate of way II should be negligible in comparison with that of way I has been also made by Hammett[62] on the basis of the analysis of the rate-determining transition states for ways I and II.

In conclusion, we should note that both ways in scheme (21) explain the maximum on the curve of $\bar{i}_1^{\,\mathrm{k}}$ *vs*. pH in the pH range between 12–14. At increased pH, $[\mathrm{CH_2(OH)_2}]$ and the thickness of the reaction layer decrease. However, the value of $\sum k_\mathrm{d}^{\mathrm{OH}} [\mathrm{OH}^-]$ increases (way I). At the same time, the value of $[\mathrm{CH_2(OH)O^-}]$ increases but the thickness of the reaction layer decreases (way II). The absence of the maximum in dependence on $\sum \bar{i}_1^{\,\mathrm{k}}$ *vs*. pH in the case of some carbonyl compounds[13] is explained by the fact that reaches $\sum \bar{i}_1^{\,\mathrm{d}}$ at increased pH.

CONCLUSIONS

For the kinetic calculations of the polarographic (DCP) catalytic and kinetic currents with participation of formaldehyde, the most reliable diffusion coefficient and diffusion currents of formaldehyde, equilibrium constants of the dimerization reaction and acidic dissociation of $CH_2(OH)_2$, and of hydration and protonization of CH_2O, have been applied.

The polarographic wave in strongly acidic solutions cannot be caused by electroreduction of CH_2OH^+ to CH_3OH, as it was accepted in Ref. 10. This wave was explained by the catalytic hydrogen evolution:

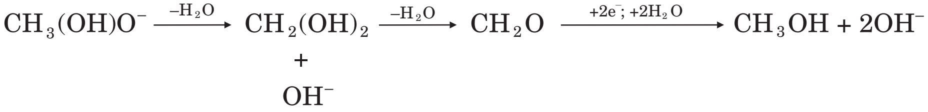


$$CH_2(OH)_2 \underset{-H_2O}{\overset{-H_2O}{\rightleftarrows}} CH_2O \underset{k_-}{\overset{k_+;\,+H^+}{\rightleftarrows}} CH_2OH^+ \xrightarrow{+e^-} CH_2O + 0.5\,H_2$$

The suggested mechanism of the catalytic process has been treated quantitatively.

For correct determination of the rate constant of the dehydration reaction of $CH_2(OH)_2$ in the catalysis by H_2O molecules in neutral and weakly acidic solutions, the diffusion contribution of CH_2O from the bulk solution to the polarographic diffusion and kinetic currents has been taken into account.

It was shown that in alkaline solutions (pH > 12) the direct formation of CH_2O at the electrode from $CH_2(OH)O^-$ can be neglected. The polarographic limiting kinetic current is controlled by this diffusion and by the two consecutive chemical reactions:



$$CH_3(OH)O^- \xrightarrow{-H_2O} \underset{\substack{+\\ OH^-}}{CH_2(OH)_2} \xrightarrow{-H_2O} CH_2O \xrightarrow{+2e^-;\,+2H_2O} CH_3OH + 2OH^-$$

REFERENCES

1. K. Vesely and R. Brdicka, *Collect. Czech. Chem. Commun.* **12** (1947) 313–332.
2. M. B. Neiman and M. I. Gerber, *Zh. Anal. Khim.* **2** (1947) 135–146.
3. R. Bieber and G. Trumpler, *Helv. Chim. Acta* **30** (1947) (a) 706–733; (b) 1109–1113; (c) 1286–1294.
4. G. A. Crowe Jr. and C. C. Lynch, *J. Am. Chem. Soc.* (a) **70** (1948) 3795–3797; (b) **71** (1949) 3731–3733.
5. M. A. Loshkarev and A. I. Chernikov, *Zh. Fiz. Khim.* **27** (1953) 1718–1724.

6. N. Landqvist, *Acta Chem. Scand.* **9** (1955) 867–892.
7. R. Brdicka, *Collect. Czech. Chem. Commun.* **20** (1955) 387–399.
8. J. Koutecky, *Collect. Czech. Chem. Commun.* **21** (1956) 652–661.
9. R. Brdicka and L. Nemec, *Rev. Polarogr. (Japan)* **11** (1963) 5–10.
10. V. N. Epimakhov, *Elektrokhimiya* **6** (1970) 322–324.
11. V. N. Epimakhov and A. N. Chuprova, *Zh. Anal. Khim.* (*USSR*) **27** (1972) 2271–2272.
12. A. Calusaru, I. Crisan, and J. Kuta, *J. Electroanal. Chem.* **46** (1973) 51–62.
13. D. Barnes and P. Zuman, *J. Electroanal. Chem.* **46** (1973) 323–342.
14. Ya. I. Tury'an, *Zh. Obshch. Khim.* **50** (1980) 1923–1931.
15. Ya. I. Tury'an and A. A. Kakos'yan, *Elektrokhimiya* **17** (1981) 1516–1518.
16. Ya. I. Tury'an, A. A. Kakos'yan, and S. A. Martem'yanov, *Elektrokhimiya* **19** (1983) 1482–1490.
17. J. M. Los, A. A. A. M. Brinkman, and B. J. C. Wetsema, *J. Electroanal. Chem.* **56** (1974) 187–197.
18. J. M. Los, L. F. Roeleveld, and B. J. C. Wetsema, *J. Electroanal. Chem.* **75** (1977) 819–837.
19. P. Valenta, *Collect. Czech. Chem. Commun.* **25** (1960) 853–861.
20. J. Kuta and P. Valenta, *Collect. Czech. Chem. Commun.* **28** (1963) 1593–1597.
21. S. Clarke and J. A. Harrison, *J. Electroanal. Chem.* **36** (1972) 109–115.
22. U. Nain and S. Kumbhat, *J. Electrochem. Soc. India* **43** (1994) 63–66.
23. H. Strehlow, in: G. G. Hammes (Ed.), *Investigation of Rates and Mechanisms of Reactions.* Mir, Moscow, 1977, pp. 317–376.
24. *International Critical Tables*, McGrow-Hill, N. Y., Vol. 5, 1929, p. 69.
25. *Reference-book of Chemist*, Khimiya, Moscow, Vol. III, 1964, pp. 925, 117.
26. J. Heyrovsky and J. Kuta, *Fundamentals of Polarography*, Mir, Moscow, 1965, pp. 72, 332.
27. M. Vadano, C. Trogus, and K. Hess, *Chem. Ber.* **67** (1934) 174–190.
28. A. Iliceto, *Gazz. Chim. Ital*. **81** (1951) 786–794.
29. P. Skell and H. Suhr, *Chem. Ber.* **94** (1961) 3317–3327.
30. M. I. Siling and B. Ya. Aksel'rod, *Zh. Fiz. Khim.* **42** (1968) 2780–2786.
31. R. P. Bell, in: V. Gold (Ed.), *Adv. Phys. Org. Chem*., Academic Press, London, Vol. 4, 1966, pp. 1–29.
32. A. A. Zavitsas, M. Coffiner, T. Wiseman, and L. R. Zavitsas, *J. Phys. Chem*. (a) **74** (1970) 2746–2750; (b) **97** (1993) 7792.
33. R. Bieber and G. Trumpler, *Helv. Chim*. Acta **30** (1947) 1860–1865.
34. A. Iliceto, *Gazz. Chim. Ital.* 84 (1954) 536–552.
35. L. C. Gruen and P. T. McTigue, *J. Chem. Soc.* (1963) 5217–5223.
36. H.-Gg. Schecker and G. Schulz, *Z. Phys. Chem.* N.F. **65** (1969) 221–224.
37. H. C. Sutton and T. M. Downes, *J. Chem. Soc., Chem. Commun*. (1972) 1–2.
38. H. Euler and A. Euler, *Ber. Dtsch. Chem. Ges*. **38** (1905) 2551–2560.
39. F. Auerbach, *Ber. Dtsch. Chem. Ges*. **38** (1905) 2833–2836.
40. R. Sauterey, *Ann. Chim*. **7** (1952) 5–74.
41. M. Wadano, *Chem. Ber.* **67** (1934) 191–197.
42. R. P. Bell and D. P. Onwood, *Trans. Faraday Soc*. **58** (1962) 1557–1561.
43. M. Levy, *J. Biol. Chem.* **105** (1934) 157–165.
44. R. J. L. Martin, *Aust. J. Chem*. **7** (1954) 400–405.
45. H. Euler and T. Lovgren, *Z. Anorg. Allg. Chem*. **147** (1925) 123–134.
46. P. T. Mc Tigue and J. M. Sime, *Aust. J. Chem.* **16** (1963) 592–595.

47. J. Koutecky, *Collect. Czech. Chem. Commun.* **18** (1953) 597–610.
48. J. Weber and J. Koutecky, *Collect. Czech. Chem. Commun.* **20** (1955) 980–983.
49. M. P. Le Henaff, *C. R. Acad. Sci., Paris* **256** (1963) 1752–1754.
50. R. P. Bell and P. G. Evans, *Proc. R. Soc. London, Ser. A* **291** (1966) 297–323.
51. L. H. Funderburk, L. Aldwin, and W. P. Jencks, *J. Am. Chem. Soc.* **100** (1978) 5444–5459.
52. Ya. I. Tur'yan, *Chemical Reactions in Polarography*, Khimiya, Moscow, 1980, pp. 53–55; 65–67.
53. N. S. Hush and J. W. Scarott, *J. Electroanal. Chem.* **7** (1964) 26–37.
54. H. Yamaoka, *J. Electroanal. Chem.* **25** (1970) 381–396.
55. Ya. I. Tur'yan, O. E. Ruvinskii, and P. M. Zaitsev, *Polarographic Katalymetry,* Khimiya, Moscow, 1998, pp. 34–35.
56. Ya. I. Tur'yan, *Collect. Czech. Chem. Commun.* **30** (1965) 4150–4167.
57. Ya. I. Tur'yan, *Croat. Chem. Acta* (a) **71** (1998) 727–743; (b) **72** (1999) 13–24.
58. G. G. Manov, N. J. Delollis, and S. F. Acree, *J. Res. Natl. Bur. Stand.* **33** (1944) 287–306.
59. R. P. Bell and W. C. E. Higginson, *Proc. R. Soc. London, Ser. A* **197** (1949) 141–159.
60. R. P. Bell and B. de B. Darwent, *Trans. Faraday Soc.* **46** (1950) 34–41.
61. J. Koutecky, *Collect. Czech. Chem. Commun.* **19** (1954) 1093–1098.
62. L. P. Hammett, *Physical Organic Chemistry. Reaction Rates, Equilibria and Mechanisms*, McGraw-Hill, New York, 1970, pp. 325–328.

SAŽETAK

Polarografske kinetičke struje formaldehida i kinetika kemijskih reakcija na elektrodi

Yakov I. Tur'yan

Razvijeni su novi pristupi analizi polarografskih kinetičkih struja formaldehida. Anomalno visoka granična kinetička struja u jakim kiselinama objašnjena je redukcijom vodikovih iona kataliziranom ionima CH_2OH^+ koji nastaju protonacijom molekula CH_2O. Za točno određivanje konstanti brzine dehidratacije molekula $CH_2(OH)_2$ u neutralnim i slabo kiselim medijima potrebno je uzeti u obzir doprinos difuzije CH_2O ukupnim graničnim kinetičkim i difuzijskim strujama. U baznim otopinama može se zanemariti reakcija direktnog raspada aniona $CH_2(OH)O^-$ na CH_2O i OH^-. Taj se proces sastoji od dviju uzastopnih reakcija: od stvaranja molekule $CH_2(OH)_2$ u kiselom mediju i hidratacije i protonacije CH_2O dehidratacijom molekule $CH_2(OH)_2$. Potanke analize difuzijskog koeficijenta i difuzijske struje formaldehida, kao i ravnotežnih konstanti dimerizacije, disocijacije $CH_2(OH)_2$ u kiselom mediju i hidratacije i protonacije CH_2O omogućuju izbor najtočnijih vrijednosti za kinetičke proračune.