

FACTORS INFLUENCING THE LIMITING CURRENT IN PULSE POLAROGRAPHY

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The variation of the limiting current as a function of h , the corrected height of the mercury column, and t , the time delay plus pulse width, are studied and compared with the similar relationships of DC polarography. Diffusion, adsorption, kinetic and catalytic processes are examined. Though pulse polarography is in almost every respect a much more powerful technique than DC polarography, it is shown that while the latter allows a distinction to be drawn between the different processes, by using the above mentioned relationships, the former is not suitable for the same purpose.

The variation of the limiting current as a function of h , the corrected height of the mercury column, is well known in DC polarography. The value of h fixes automatically those of m , the flux of mercury, and of t , the drop time. On combining these two factors, in the case of a diffusion process, we have the relationships¹:

$$i_d = kh^{1/2} = k't^{1/6} . \quad (1)$$

In the case of an adsorption process, we have²:

$$i_a = kh = k't^{-1/3} . \quad (2)$$

When the process is a kinetic one, i_k is independent of h , but still depends on t (ref.³):

$$i_k = kt^{2/3} . \quad (3)$$

Finally, catalytic currents may show various dependencies on h and t , according to the mechanism of the process^{4,5}.

In principle the i - h - t relationships should not be the same in pulse polarography, since here the drop life does not depend entirely on h , but can be independently fixed as an instrumental parameter. Furthermore, while in DC polarography the polarization time is the same as the drop life, in pulse polarography both terms are *per se* different. So, divergent criteria are to be expected to rule these relationships in the latter technique.

EXPERIMENTAL

The i_d vs h relationship for a diffusion process was studied with solutions of $1 \cdot 10^{-4}$ mol dm^{-3} K_2CrO_4 in 0.1 mol dm^{-3} NaOH . The adsorption process was studied with solutions of $1 \cdot 10^{-4}$ mol dm^{-3} $\text{Pb}(\text{NO}_3)_2$, $4 \cdot 10^{-5}$ mol dm^{-3} H_2SO_4 in a supporting electrolyte of 0.01 mol $\cdot \text{dm}^{-3}$ NaNO_3 and $5 \cdot 10^{-4}$ mol dm^{-3} KBr . For the kinetic current, solutions of $1 \cdot 10^{-4}$ mol $\cdot \text{dm}^{-3}$ formaldehyde in 0.1 mol dm^{-3} LiOH plus 0.01 mol dm^{-3} LiCl were employed. Catalytic currents were examined in solutions of $1 \cdot 10^{-5}$ mol dm^{-3} NaNO_3 and $2 \cdot 10^{-5}$ mol dm^{-3} $\text{UO}_2(\text{CH}_3\text{COO})_2$, in a supporting electrolyte of 0.01 mol dm^{-3} HCl and 0.1 mol dm^{-3} KCl , and in solutions of 0.5 mol dm^{-3} NaNO_3 , 0.1 mol dm^{-3} H_2SO_4 , and $1 \cdot 10^{-4}$ mol dm^{-3} $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4 \text{H}_2\text{O}$. Catalytic hydrogen currents were studied in solutions of 0.0129 mol $\cdot \text{dm}^{-3}$ pyridine in 0.1 mol dm^{-3} LiCl . Polarograms were recorded on a Southern Analytical model A3100 pulse polarograph, operating in the normal mode. The delay time was, nominally, 0.5 , 1 , 2 , 3 , 4 , and 5 s, and the pulse width was 40 ms, the current being averaged and measured only in the last 20 ms. The true values of these factors were calibrated to 0.1% with a Tektronix oscilloscope, in its turn calibrated in the time axis with a high-precision quartz oscillator. Chemicals were of AR grade; water was tridistilled and mercury was washed with nitric acid and distilled *in vacuo*. The heights of the mercury column were measured with a cathetometer. The effective heights were 74.25 , 61.10 , and 41.25 cm, after correction for the back-pressure. Temperature was $25 \pm 0.02^\circ\text{C}$, controlled with a Bühler thermostat.

DISCUSSION

For diffusion processes in pulse polarography the following relationship has been found⁶:

$$i_d = kt^{0.691} \quad (4)$$

The exponent 0.691 is the product $2/3$ times 1.036 , the latter being a factor calculated by Smith⁷. The relationship between i_d and h follows from the equation of Fonds, Brinkman and Los⁸, through m , the flux of mercury, and comes to be:

$$i_d = k'h^{2/3} \quad (5)$$

Kinetic currents have been studied by Brinkman and Los⁹ by pulse polarography. They, and also Galvez and Serna¹⁰ in a similar way, deduced the theoretical equations which give the following relationship:

$$i_k = km^{2/3}t^{2/3} \quad (6)$$

Though the value of t does not depend on h in pulse polarography, m still does, so:

$$i_k = k'h^{2/3}, \quad t = \text{const.} \quad (7)$$

$$i_k = k''t^{2/3}, \quad h = \text{const.} \quad (8)$$

The true power of t is always 0.691, this being valid also in the following equations. The same authors^{11,12} studied the catalytic current for the case of an electroactive species reduced at the electrode and regenerated by a chemical reaction. From these equations we have:

$$i_c = km^{2/3}t^{2/3}. \quad (9)$$

As a result,

$$i_c = k'h^{2/3}, \quad t = \text{const.} \quad (10)$$

$$i_c = k''t^{2/3}, \quad h = \text{const.} \quad (11)$$

Adsorption phenomena have been studied by Anson and coworkers^{13,14}. From their equation we have:

$$i_a = km^{2/3}t^{2/3}. \quad (12)$$

And as a corollary, it follows that:

$$i_a = k'h^{2/3}, \quad t = \text{const.} \quad (13)$$

$$i_a = k''t^{2/3}, \quad h = \text{const.} \quad (14)$$

Summing up, theoretically, in every case, the limiting current in pulse polarography obeys the same relationship with h and t , the technique not being useful for distinguishing the different processes. In this respect pulse polarography is at a clear disadvantage as compared with DC polarography.

Experimental results confirm these theoretical considerations. For a diffusion process, the case of the chromate solutions in alkaline medium, the power of t was found to be 0.691 ± 0.010 , while the power of h was 0.667 ± 0.003 . The reduction of formaldehyde in LiCl + LiOH supporting electrolyte is a classical example of a kinetic process¹⁵. Formaldehyde exists in aqueous solutions as the hydrated form, methyleneglycol, which does not reduce at the mercury electrode if it is not previously converted into the anhydrous form. In this case, experimental values for the exponent of h were 0.667 ± 0.020 , while those for the power of t were 0.691 ± 0.005 . For the case of an electroactive species regenerated by a chemical reaction two examples already studied by Kolthoff and coworkers by DC polarography were chosen, namely, the nitrate reduction catalysed by the uranyl ion¹⁶ and by the molybdate ion¹⁷. Results agree with the expected values. The power of h is 0.667 ± 0.020 and the power of t is 0.691 ± 0.020 . Further, pyridine in LiCl is an example of the catalytic hydrogen evolution process¹⁸. Results were largely disappointing but it is noteworthy that the same occurs when the system is studied by DC polarography. In our case the power of h comes to be 0.5, at variance with the expected 0.667 value.

TABLE I
Values of the powers of h and t

	DC polarography		Normal pulse polarography	
	h	t	h	t
i_d	1/2	1/6	0.667	0.691
i_a	1	-1/3	0.667	0.691
i_k	0	2/3	0.667	0.691
i_c^a	?	?	0.667	0.691
i_c^b	?	?	?	0.691

^a Electroactive species regenerated by a chemical reaction; ^b catalytic evolution of hydrogen.

The power of t is the expected 0.691 ± 0.014 . Lead ions in the presence of bromides yield adsorption waves when studied by pulse polarography¹⁹. In this case, experimental values for the power of t are 0.691 ± 0.010 , while the power of h is 0.667 ± 0.013 . All these relationships and those of DC polarography are assembled in Table I for comparative purposes.

In conclusion, though in most cases pulse polarography is a technique with ample advantages over DC polarography for analytical or basic electrochemical research, the fact that the drop life is monitored independently of h renders the distinction between diffusion, kinetic, catalytic and adsorption processes impossible by the study of the relationships of $i-h-t$, which are, on the other side, useful in DC polarography.

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