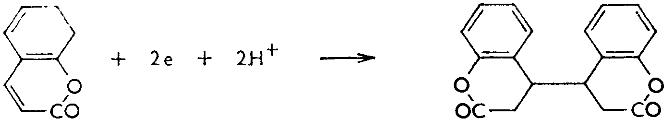
325. *Polarography of Nickel–Coumarin Solutions at a Dropping-mercury Electrode.*

By V. S. Griffiths and J. B. Westmore.

Nickel polarograms are distorted in the presence of coumarin. The distortion is attributed to the adsorption of coumarin on the surface of the dropping electrode, the extent of adsorption being a function of coumarin concentration and electrode potential. In the presence of an excess of nickel, in unbuffered solutions, the apparent height of the coumarin wave is reduced to one-half its value in nickel-free solutions. In buffered solution the height of the coumarin wave is normal.

In solutions of alkali nitrates or perchlorates nickel is reduced irreversibly at a dropping-mercury electrode. In presence of a maximum-suppressor, such as gelatin, it has a half-wave potential of approximately —1·1 v against the saturated calomel electrode (S.C.E.), and the slope of the wave is abnormally small.[1] In the presence of a large concentration of chloride the half-wave potential, $E_{\frac{1}{2}}$, is shifted to a more positive potential and the slope of the wave is increased.[2]

Reports on the polarography of coumarin in aqueous solutions with various supporting electrolytes are contradictory. On the one hand, Capka[3] states that the reduction of coumarin from Britton–Robinson buffers gives a wave for which $E_{\frac{1}{2}}$ varies with pH from $-1{\cdot}61$ to $-1{\cdot}68$ v at pH's 4·8 to 7·8; and it is $-1{\cdot}65$ v at pH's above 7·5; the height of the wave corresponds to a two-electron reduction. On the other hand, Harle and Lyons,[4] using a variety of buffered solutions, state that, for any pH at which reduction occurs, there is a single wave for which $E_{\frac{1}{2}}$ is independent of pH, being $-1{\cdot}53$ v against the standard calomel electrode. The wave-height corresponds to a one-electron reduction, leading to production of *meso*- and racemic forms of tetrahydro-4,4'-bicoumarinyl:



In view of this contradiction, the polarographic behaviour of coumarin was checked. In a 0·1M-potassium chloride as supporting electrolyte, $E_{\frac{1}{2}}$ was $-1{\cdot}54$ v and I (the " diffusion current constant ") was 1·86. The latter, in the Strehlow and von Stackelberg modification[5] of the Ilkovic equation, is obtained from the relation:

$$i_d = 607nD^{\frac{1}{2}}Cm^{\frac{2}{3}}t^{\frac{1}{6}}(1 + 17D^{\frac{1}{2}}m^{-\frac{1}{3}}t^{\frac{1}{6}}) = ICm^{\frac{2}{3}}t^{\frac{1}{6}}, \qquad (1)$$

where i_d is the diffusion current in microamperes, n is the number of electrons concerned in the reduction process, D is the diffusion coefficient in cm.^{2} sec.$^{-1}$, C is the concentration of the reducible compound in mmole/l., m is the rate of flow of mercury issuing from the capillary in mg./sec., t is the drop-time in seconds, and 607 is a term embodying mathematical and physical constants. In accord with Harle and Lyons, D was taken as $0{\cdot}8 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ (the value for quinaldic acid which structurally resembles coumarin). n was then found to be 1·04 and was thus taken to be 1. A similar result was obtained in a phosphate electrolyte buffered at pH 6·45. No evidence in favour of Capka's results was obtained.

Polarography of Nickel–Coumarin Solutions.—The first results were obtained with 0·1M-potassium chloride as a supporting electrolyte. Polarograms for a nickel concentration of 1·07 mmoles/l. and various coumarin concentrations are shown in Fig. 1. In Fig. 2 are shown nickel polarograms at varying concentrations in the presence of coumarin at a concentration of 0·69 mmole/l. (The curves shown are reproductions of curves automatically recorded by the polarograph after correction for the residual current, and the galvanometer oscillations have been omitted. Owing to the inertia of the galvanometer the curves are probably displaced from their true positions by about 0·02 v to more negative potentials.) Consideration of these two diagrams enables the following observations to be noted: (i) at small coumarin concentrations the nickel maximum, originally present, is suppressed; (ii) as the coumarin concentration increases, the character of the nickel wave alters and its position is rapidly shifted to more negative potentials; (iii) the height of the nickel wave is independent of coumarin concentration; (iv) the position of the nickel wave depends only on the coumarin concentration; (v) the position of the coumarin wave is independent of nickel concentration; (vi) the height of the coumarin

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[1] Kolthoff and Lingane, " Polarography," Interscience Publ. Inc., New York, 1st edn., 1946, p. 281; 2nd edn., 1952, p. 486.

[2] Pavlik, *Coll. Czech. Chem. Comm.*, 1931, **3**, 222.

[3] Capka, *Coll. Czech. Chem. Comm.*, 1950, **15**, 965.

[4] Harle and Lyons, *J.*, 1950, 1575.

[5] Strehlow and von Stackelberg, *Z. Elektrochem.*, 1950, **54**, 51.

wave decreases as the nickel concentration increases. Effect (ii) is well illustrated in Fig. 3 in which values of "$E_{\frac{1}{2}}$" for nickel are plotted against coumarin concentration (the term "$E_{\frac{1}{2}}$" is retained for reference purposes only, since it now has no theoretical significance). There is a sharp transition in the curve at a coumarin concentration of 0·95 mmole/l., which is also the point at which the characteristics of the nickel wave are changed.

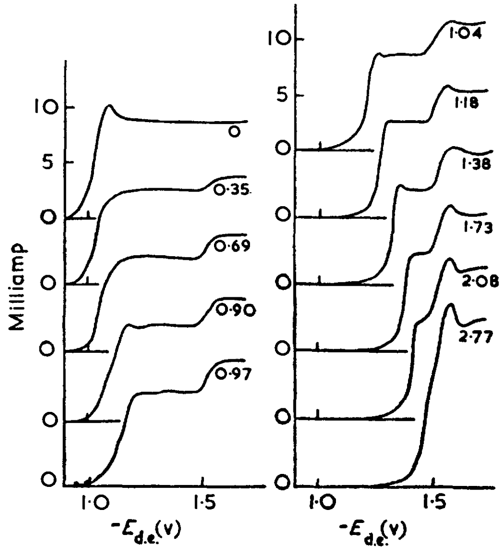


FIG. 1. Nickel polarograms 1·07 mmoles/l.) at coumarin concentrations given on the curves (in mmole/l.).

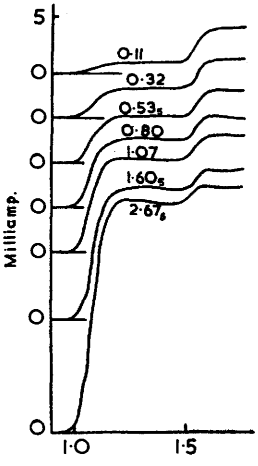


FIG. 2. Nickel polarograms (Ni concns. given on curves, in mmole/l.) at a coumarin concentration of 0·69 mmole/l.

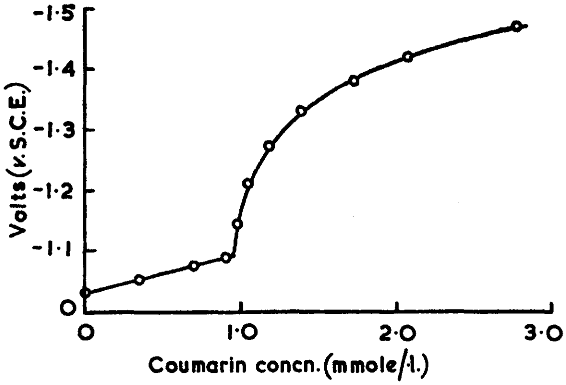


FIG. 3. "Half-wave potential" of nickel as a function of coumarin concentration.

An interpretation of these results is offered which requires two basic assumptions: (*a*) the product(s), or intermediate product, of the coumarin reduction reacts with nickel ions, in the diffusion layer, to give a product which is either insoluble or not capable of being reduced below —1·7 v; (*b*) coumarin is adsorbed at the mercury–solution interface on the surface of the mercury drop, thus hindering the nickel reduction, and the extent of the adsorption is a function of the cathode potential and the coumarin concentration in the bulk of the solution.

The evidence in favour of these assumptions is as follows.

(a) *Interpretation of the diffusion current phenomena at* —1·7 v. It has been seen that in the presence of nickel the height of the coumarin wave is decreased. This reduction in wave-height is not due to any decrease in the amount of coumarin being reduced, but rather to a decrease in the amount of nickel being reduced, as will now be shown.

The modified Ilkovic equation can be written in the form

$$i_d = 607nKCD^{\frac{1}{2}}m^{\frac{2}{3}}t^{\frac{1}{6}}; \qquad (2)$$

K is a correction term for the additional terms given in equation (1) and varies slightly with the capillary characteristics and the diffusion coefficient of the reducible species.

It is assumed that the product of the coumarin reduction may react with the incoming nickel ions, thus reducing the current due to the latter. From the modified Ilkovic equation the flux of coumarin molecules at the dropping electrode surface is directly proportional to the quantity $K_RC_RD_R^{\frac{1}{2}}$ where the subscript R represents coumarin. The flux of the nickel ion is proportional to $K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}}$. If the reaction occurs in the solution adjacent to the electrode, the rate at which the coumarin molecules are reduced is proportional to the rate at which they are brought in, and to $K_RC_RD_R^{\frac{1}{2}}$. If n coumarin reduction-product species react with one nickel ion, the amount of nickel available for reduction is decreased, and the net amount of nickel is proportional to $\left(K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}} - \frac{1}{n}K_RC_RD_R^{\frac{1}{2}}\right)$. The reduction of each nickel ion requires two electrons, so that the net contribution of nickel ion to the total current is given by

$$i_{Ni} = 607m^{\frac{2}{3}}t^{\frac{1}{6}}\left[2(K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}} - \frac{1}{n}K_RC_RD_R^{\frac{1}{2}})\right]. \qquad (3)$$

The reduction of each coumarin molecule requires one electron, so the contribution to the total current is given by

$$i_R = 607m^{\frac{2}{3}}t^{\frac{1}{6}}K_RC_RD_R^{\frac{1}{2}}. \qquad (4)$$

Thus, the total current at $-1\cdot7$ v is given by

$$i_T = 607m^{\frac{2}{3}}t^{\frac{1}{6}}\left[2(K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}} - \frac{1}{n}K_RC_RD_R^{\frac{1}{2}}) + K_RC_RD_R^{\frac{1}{2}}\right], \qquad (5)$$

which, in view of equation (1), can be simplified to

$$i_T/m^{\frac{2}{3}}t^{\frac{1}{6}} = I_{Ni}C_{Ni} + \left(1 - \frac{2}{n}\right)I_RC_R. \qquad (6)$$

Equation (5) is valid only when the proviso that the term $\left(K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}} - \frac{1}{n}K_RC_RD_R^{\frac{1}{2}}\right)$ cannot have a negative value holds. When $\frac{1}{n}K_RC_RD_R^{\frac{1}{2}}$ is greater than $K_{Ni}C_{Ni}D_{Ni}^{\frac{1}{2}}$ this term is taken as zero. In the latter case, for which coumarin is in excess, equation (6) simplifies to

$$i_T/m^{\frac{2}{3}}t^{\frac{1}{6}} = I_RC_R \qquad (7)$$

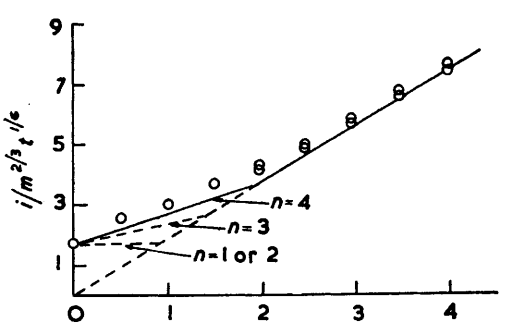
and is thus the same as the coumarin contribution in the absence of nickel. The apparent height of the coumarin wave in the presence of excess nickel is given by

$$i_{app}/m^{\frac{2}{3}}t^{\frac{1}{6}} = \left(1 - \frac{2}{n}\right)I_RC_R. \qquad (8)$$

Thus, the diffusion-current phenomena at $-1\cdot7$ v should be governed by expressions (6—8). In Figs. 4, 5, and 6 these equations are compared with experimental results for various values of n, with the experimentally determined values $I_{Ni} = 3\cdot30$, and $I_R = 1\cdot86$. The figures show that $n = 4$, the slight departure of the experimental points from the theoretical lines probably being due to imperfect interaction.

Such a treatment as just described is a gross simplification, and examples of similar, and simpler, diffusion problems are given by Koutceley and Kovyta.[6] *

(b) *Adsorption of coumarin at the dropping electrode.* Coumarin effectively suppresses the nickel maximum, which suggests that it is surface-active at the mercury–solution interface, since, in general, maxima are suppressed by small concentrations of surface-active compounds. The function of the maximum-suppressor is to form an adsorbed layer on the surface of the mercury drop. Such adsorption lowers the interfacial tension and may alter the shape of the electrocapillary curve.[7] The distortion of the nickel polarograms at the higher coumarin concentrations is also attributed to adsorption. Evidence in favour of this suggestion is next presented.



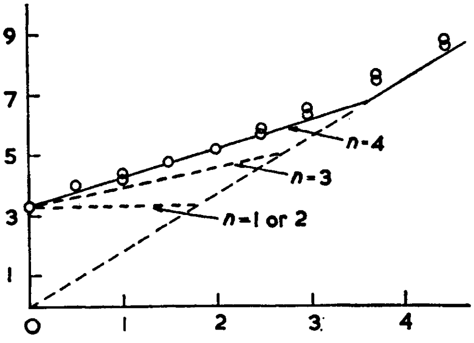


FIG. 4. FIG. 5.

FIG. 4. Total diffusion currents at —1·7 v. (Nickel sulphate 0·50 mmole/l.)

FIG. 5. Total diffusion currents at —1·7 v. (Nickel sulphate 1·00 mmole/l.)

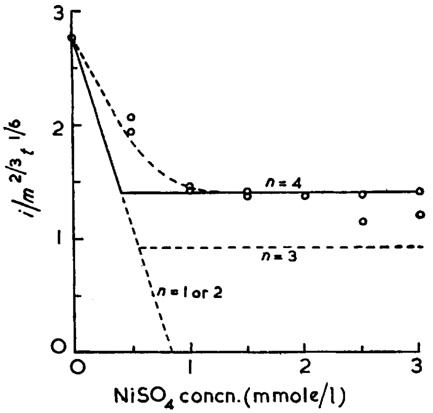


FIG. 6. Apparent height of the coumarin wave as a function of the nickel concentration. (Coumarin concn. 1·50 mmoles/l.)

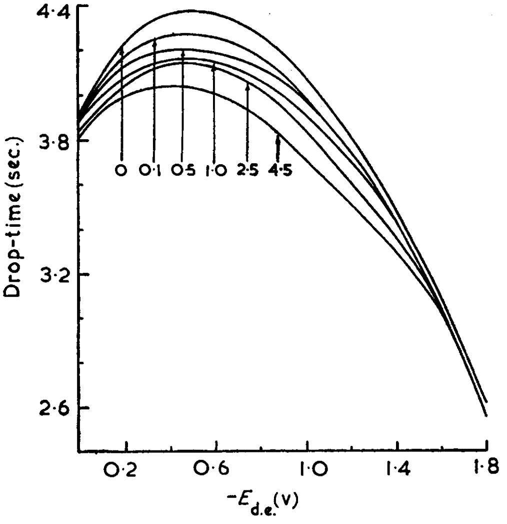


FIG. 7. Effect of coumarin (at concns. given on curves, in mmole/l.) on the electrocapillary curve.

Since the interfacial tension is directly proportional to the mercury drop-time a curve

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* We thank a Referee for drawing our attention to this paper.

[6] Koutceley and Kovyta, *Electrochim. Acta*, 1961, **3**, 318.

[7] Ref. 1, 1st edn., ch. VI; 2nd edn., ch. VIII.

very similar to the electrocapillary curve is obtained by plotting the mercury drop-time against various potentials of the dropping electrode.[7] Curves obtained for various coumarin concentrations in 0·1M-potassium chloride are shown in Fig. 7. It is seen that the interfacial tension is indeed lowered. The electrocapillary maximum is depressed rather than shifted to more positive or negative potentials, which indicates that since coumarin has a large dipole moment ($\mu = 4{\cdot}6$ D acting in the plane of the rings) it is adsorbed with its ring-plane parallel to the mercury surface. This deduction is supported by other work in which the relation between dipole moment and electrocapillary properties of some coumarin derivatives has been investigated. The potentials at which most of the coumarin is desorbed (complete desorption does not seem to occur within the observable potential range) are consistent with those at which the nickel ion is reduced in an equivalent coumarin concentration.

If the distortion of the nickel polarograms is a surface phenomenon, then (i) the effect of coumarin on the electrocapillary curve should be the same in any capillary-inactive supporting electrolyte, (ii) nickel polarograms should be similarly distorted by coumarin in any capillary-inactive, non-complexing supporting electrolyte, and (iii) similar distortions should be observed for other metal ions which reduce at similar potentials to nickel. Effect (i) was observed in chloride, nitrate, and phosphate electrolytes. Effect (ii) was observed in chloride, nitrate, sulphate, phosphate, and phthalate supporting electrolytes. Effect (iii) was observed for zinc and cobalt(II) ions. No contradictory evidence for any effect was obtained.

Polarography of Nickel–Coumarin Solutions in a Buffered Supporting Electrolyte.—Several polarographic reductions, especially of organic compounds, are sensitive to pH. Work similar to that just described was repeated with a supporting electrolyte of controlled pH. The work of Harle and Lyons indicates that the optimum operating pH is about 6·45 and at this pH nickel hydroxide is not precipitated. The supporting electrolyte was prepared from potassium dihydrogen phosphate and sodium hydroxide in such a way that the test samples had pH 6·45 and an alkali-ion concentration of 0·1 g.-ion/l.

In the presence of coumarin the nickel polarograms were distorted as before, but no decrease in the height of the coumarin wave occurred.

Controlled-potential Reductions on Nickel–Coumarin Solutions.—To gain additional information on the products of the reduction at −1·7 v the reduction was performed on an appreciable scale in a cell similar to that described by Lingane.[8] With the cathode potential maintained at −1·7 v in each case, the following solutions were reduced: (i) 0·6 g. of coumarin in 400 ml. of 0·1M-potassium chloride, (ii) 0·6 g. of coumarin and 0·25 g. of nickel sulphate (added as $NiSO_4,6H_2O$) in 400 ml. of 0·1M-potassium chloride, (iii) 0·6 g. of coumarin and 0·25 g. of nickel chloride in 400 ml. of phosphate buffer of pH 6·45 (the solution is saturated with coumarin and there are approximately four coumarin molecules for each nickel ion). In cases (i) and (iii) a white product was obtained. In case (ii) the product was pale green. Comparison of melting points, solubilities, and infrared spectra showed that the white products were identical. The same white product was extracted from the pale green one by use of dioxan. Treatment of the green product with hydrochloric acid gave a green solution in which nickel was present. Since its infrared spectrum showed no unexpected peaks the following conclusions are indicated. The white product, m. p. 240—242°, is a mixture of *meso-* and racemic tetrahydro-4,4′-bicoumarinyl, m. p. 280° and 247°,[4] and the green product is a mixture of this compound with nickel hydroxide.

The net reaction for the reduction of coumarin in buffered supporting electrolytes has been given previously. In buffered solutions the net reaction becomes

$$2R + 2e + 2H_2O = R_2H_2 + 2OH^-$$

where R represents coumarin. It is seen from this equation that the flux of hydroxide

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[8] Lingane, *J. Amer. Chem. Soc.*, 1943, **65**, 1348.

ions produced in the diffusion layer is the same as the flux of coumarin molecules diffusing into the diffusion layer. Thus, the following reaction might be expected to occur:

$$2R + 2e + 2H_2O + Ni^{2+} = R_2H_2 + Ni(OH)_2$$

This result requires that two coumarin molecules should be equivalent to each nickel ion, which is not in agreement with the experimental results. The experimental results are in agreement with a reaction such as

$$4R + 6e + 4H_2O + 2Ni^{2+} + Hg = 2R_2H_2 + Ni(OH)_2 + 2OH^- + Ni(Hg)$$

which can be explained by assuming that half the nickel ions can react with another reduction species to give a compound in which the nickel is still reducible. Alternatively, the reaction at the dropping electrode may follow a different course to that at a large quiet electrode. The issue thus remains in doubt. In any case, in the phosphate electrolyte the buffering action prevents formation of hydroxide ions and the normal polarographic additivity of diffusion currents is observed.

EXPERIMENTAL

The polarograph used was an Evershed and Vignoles, Tinley D.C. automatic recording polarograph, type 19/2, incorporating a derivative circuit. Its galvanometer was calibrated by substituting a standard variable resistance for the dropping electrode system, as described by Kolthoff and Lingane.[9] The polarographic cell used was of the H-type described by Lingane and Laitinen,[10] the anode being of mercury, covered with a layer of calomel and saturated potassium chloride solution. The cell was immersed in a water-bath maintained at 25° ± 0·5°. Hydrogen was used to remove dissolved oxygen. The characteristics of the capillary used for most of the work were (*a*) $m = 2{\cdot}132$ mg. sec.$^{-1}$, $t = 2{\cdot}92$ sec. (at $-1{\cdot}7$ v), ($m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}981$ mg.$^{\frac{2}{3}}$ sec.$^{-\frac{1}{2}}$); (*b*) $m = 1{\cdot}737$ mg. sec.$^{-1}$, $t = 3{\cdot}60$ sec. (at $-1{\cdot}7$ v), ($m^{\frac{2}{3}}t^{\frac{1}{6}} = 1{\cdot}788$ mg.$^{\frac{2}{3}}$sec.$^{-\frac{1}{2}}$).

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[9] Ref. 1, 1st edn., p. 228; 2nd edn., p. 320.

[10] Lingane and Laitinen, *Ind. Eng. Chem., Analyt.*, 1939, **11**, 504.