POLAROGRAPHIC DETERMINATION OF 7-DIETHYLAMINO-4-METHYLCOUMARIN

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The polarographic behaviour of the title optical whitening agent was studied in aqueous-methanolic solutions. Conditions for its quantitation were found within the concentration regions of 10 to 100 μmol l^{-1} by tast polarography, 1 to 100 μmol l^{-1} by differential pulse polarography on the conventional dropping mercury electrode, and 0.1 to 10 μmol l^{-1} by differential pulse polarography on a static mercury drop electrode. The analytical procedures developed were applied to the determination of the compound in technical products.

7-Diethylamino-4-methylcoumarin ($C_{14}H_{17}NO_2$, formula *I* in Eq. (*A*); CAS name: 7-(diethylamino)-4-methyl-2*H*-1-benzopyran-2-one, CAS Registry Number: 91-44-1) is an optical whitening agent which is manufactured on an industrial scale to be added to washing powders or employed to whiten paper, cellulose acetate, and polyamides[1]. Since some coumarin derivatives cause photosensitization and exhibit mutagenic activity[2,3], it is desirable to have at disposal sensitive methods for the determination of trace amounts of this substance, which can get into the ecosystem with wastewaters from households, laundries, and from textile and paper industrial plants.

So far, 7-diethylamino-4-methylcoumarin was determined by absorption spectrophotometry following preconcentration by extraction or thin layer chromatography[4]. High performance liquid chromatography[5] and paper chromatography[6] have also been employed. An overview of the polarographic behaviour of coumarin-based optical whitening agents can be found in our previous paper[7]. Polarographic determination of 7-diethylamino-4-methylcoumarin, however, has not been reported. Therefore, the present work was devoted to the polarographic behaviour of this analyte, paying special attention to the determination of low concentrations of this coumarin derivative by differential pulse polarography (DPP) on a conventional dropping mercury electrode (DME) and on a static mercury drop electrode (SMDE).

EXPERIMENTAL

Reagents

7-Diethylamino-4-methylcoumarin was obtained from the technical product Tinopal SWN (Ciba-Geigy, Basel, Switzerland) by triple recrystallization from hot methanol. Its purity was checked by melting temperature measurement (67 °C, in agreement with the published value[2]), by measuring its UV spectrum in ethanol (observed band positions and absorbances were in agreement with published data[2]), and by thin layer chromatography[4,8], which gave a single spot using the following mobile phases: toluene–chloroform 2 : 3 (R_F = 0.20), toluene–chloroform–ethyl acetate 4 : 12 : 1 (R_F = 0.43) and 2 : 3 : 1 (R_F = 0.67), and toluene–chloroform–ethyl acetate–methanol 2 : 3 : 3 : 3 (R_F = 0.95).

Stock solution of the analyte in methanol ($c = 1 . 10^{-2}$ mol l^{-1}) was prepared by dissolving 2.3129 g of the substance in the solvent and diluting to a litre. More dilute solutions were prepared by dilution of this stock solution with methanol.

Britton–Robinson buffers and ammoniacal buffers were prepared conventionally. The other chemicals used were reagent grade products of Lachema, Brno, The Czech Republic. Water was recrystallized from a quartz still.

Another technical product containing the substance, Rylux VPA, was obtained from VCHZ Synthesia, Pardubice, The Czech Republic. Thin layer chromatography was conducted with a commercial set using Silufol UV 254 plates (Kavalier, Votice, The Czech Republic).

Apparatus

A PA 4 polarographic analyzer was used in combination with an XY-4105 recorder and an SMDE 1 static mercury drop electrode (all Laboratorni pristroje, Prague, The Czech Republic). The SMDE had a capillary diameter of 0.138 mm and its maximum drop size was governed by the valve opening period of 160 ms. A conventional dropping mercury electrode (DME) had a drop time (in 0.1 M NaCl at 0 V vs SCE) t = 7.04 s and flow rate m = 0.61 mg s^{-1} at a mercury reservoir height h = 36 cm. A saturated calomel reference electrode (SCE) was employed, and all potentials are reported relative to it. The auxiliary electrode was a platinum sheet. The potential sweep rate was 5 mV s^{-1}, electronically controlled drop time 1 s, pulse height –50 mV in DPP, and DME reservoir height 36 cm, unless stated otherwise. Oxygen was removed from the solutions by nitrogen purging; nitrogen for this was purified by passing it through a solution of chromium(II) ions in dilute hydrochloric acid (1 : 1) over a zinc amalgam. A bubbler containing a solution with the same methanol content as in the cell was inserted before it. All measurements were conducted at room temperature.

Acidity of solutions was measured with an OP-208/1 digital pH-meter (Radelkis, Hungary) using a combined glass–silver chloride electrode.

Spectrophotometric measurements were performed on a Pye Unicam PU 8800 UV/VIS instrument (Philips) using quartz cells 1 or 2 cm optical pathlength.

Varipipette 3000 micropipettes type A-20, A-200 and A-1000 (Plastomed, Poland) were employed to add small volumes of solutions.

Purification and separation procedures were implemented using an M 415 centrifuge (Chirana, The Czech Republic) and a rotary vacuum evaporator type 350 (Unipan, Poland).

Procedures

For the polarographic and voltammetric studies, 10 ml of the analyte solution in methanol at the desired concentration were added to a volumetric flask, diluted with methanol, and made up to volume with the Britton–Robinson buffer. This order of addition had to be adhered to because if a

methanolic solution of analyte is added to an aqueous solution of the buffer, the analyte may separate from the solution. The buffer solutions and methanol had to be stored in glass bottles rather than in polyethylene vessels because substances affecting unfavourably the determination of the lowest concentrations of 7-diethylamino-4-methylcoumarin can elute from polyethylene.

The solutions were nitrogen purged for 10 min prior to recording the polarographic or voltammetric curves. The calibration dependences were measured in triplicate and evaluated statistically. The limit of determination L_Q was calculated as the tenfold standard deviation from seven analyte determinations at concentrations corresponding to the lowest point of the calibration curve[9].

The following procedure was applied when quantitating 7-diethylamino-4-methylcoumarin in the technical products Tinopal SWN and Rylux VPA by DPP on a dropping mercury electrode. About 0.1 g of the product was weighed precisely, dissolved in a small volume of methanol, transferred to a 100 ml volumetric flask, and diluted to volume with methanol. A volume of 100 μl of this solution was injected into a 10 ml volumetric flask and diluted to volume with the Britton–Robinson buffer at pH 3.5. The differential pulse polarogram of this solution was recorded, and the analyte content was read from a calibration curve, obtained by measuring the pure substance.

When using UV spectrophotometry for determination of the analyte in the technical products, the procedure was as follows. A precisely weighed amount (about 0.1 g) of the product was dissolved in a small volume of methanol, transferred to a 100 ml volumetric flask, and diluted to volume with methanol. The spectrum was recorded, and analyte was determined by using a calibration curve, obtained by measuring the pure substance.

RESULTS AND DISCUSSION

Stability of Stock Solutions of 7-Diethylamino-4-methylcoumarin

The absorption spectrum of 7-diethylamino-4-methylcoumarin in methanol displays absorption maxima at 217, 243, and 377 nm (Fig. 1). The validity of Beer's law was confirmed for the concentration region of 2 – 100 μmol l^{-1}, and a molar absorptivity value of ε_{377} = 2.28 . 10^4 l mol^{-1} cm^{-1} was obtained from the absorbance vs

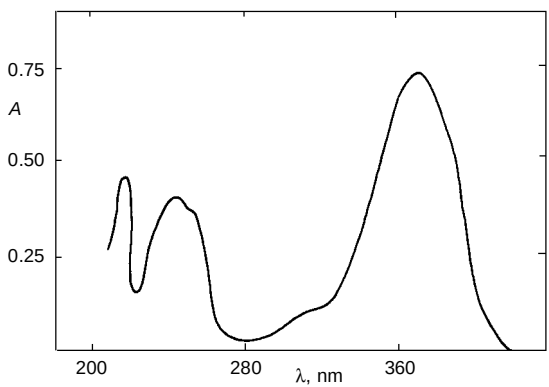


FIG. 1
Absorption spectrum of 7-diethylamino-4-methylcoumarin (c = 33 μmol l^{-1}) in methanol; optical pathlength 1 cm

concentration plot. The absorbance of stock solutions at concentrations of 10, 100, and 10 000 μmol l^{-1} stored in dark remained constant (within experimental error) for a week and did not decrease more than 1% and 2% in 2 and 4 weeks, respectively.

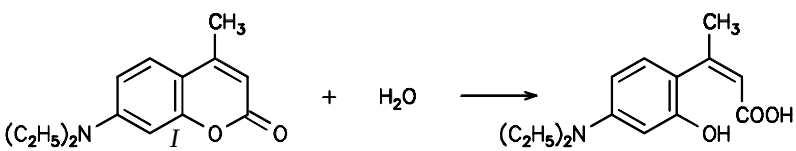
Tast Polarography and Differential Pulse Polarography of 7-Diethylamino-4-methylcoumarin on a Conventional Dropping Mercury Electrode

The effect of pH on the polarographic behaviour of 7-diethylamino-4-methyl- coumarin was examined in Britton–Robinson buffers at pH 2 – 12 in the presence of 1 vol.% methanol (because the stock solutions were in methanol). At pH < 8, both the half-wave potential $E_{1/2}$ and peak potential E_p shifted to more negative values with increasing pH; at pH > 8 the shift was minimal. The $E_{1/2}$ values of 7-diethylamino-4-methylcoumarin are more negative than those of unsubstituted coumarin, which is apparently due to the electron donor effect of the substituents, the methyl group in position 4 of the coumarin system in particular.

The limiting current I_{lim} and peak current I_p did not change appreciably with pH over the ranges of pH 3 – 5 and pH 7.5 – 10; the values obtained were basically only affected by the way and readiness of their reading from the polarogram (Figs 2 and 3). At pH < 3 the values were lower due to coincidence of the I_{lim} and I_p values with the base electrolyte decomposition current.

The slopes of the $E_{1/2}$ vs pH plot, determined by linear regression, were 115 mV per pH unit over the pH 3 – 5 range and 14 mV per pH unit over the pH 7.9 – 11 range. The slopes of the E_p vs pH plot were similar, viz. 100 and 9 mV per pH unit, respectively.

The wave or peak height decrease at pH > 10 can be explained in terms of basic hydrolysis of the substance following Eq. (*A*),

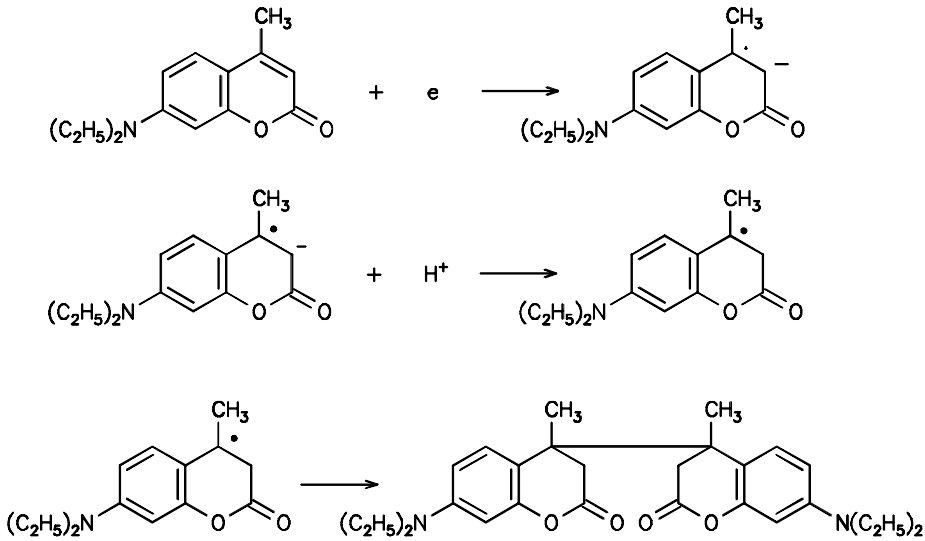


(*A*)

as in the case of coumarin[10,11] and its derivatives[7]. This hypothesis is borne out by the decrease of the wave of 7-diethylamino-4-methylcoumarin in time at pH 11.4.

The tast-polarographic wave height of 7-diethylamino-4-methylcoumarin at pH 3 – 5 and pH 7.5 – 10 is commensurate with that of unsubstituted coumarin. The dependence of the DC polarographic wave height on the square root of the mercury reservoir height is linear, giving evidence that the phenomenon is diffusion controlled. Cyclic voltammograms (Fig. 4) show that the phenomenon is irreversible at pH 3.5 and 9.1.

Based on the above facts it is suggested that, like coumarin[10], 7-diethylamino-4-methylcoumarin undergoes an irreversible one-electron reduction with subsequent dimerization of the formed radical-anion following Scheme 1. (It is not impossible,



SCHEME 1

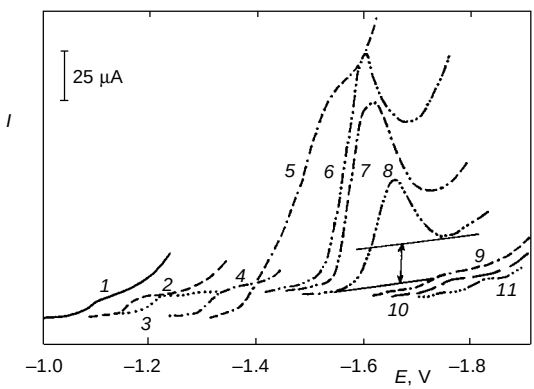


FIG. 2

Tast polarograms of 7-diethylamino-4-methylcoumarin (c = 100 μmol l^{-1}) in Britton–Robinson buffers containing 1 vol.% methanol at pH: *1* 2.2, *2* 2.7, *3* 3.5, *4* 4.3, *5* 5.0, *6* 6.0, *7* 6.5, *8* 6.9, *9* 7.9, *10* 9.1, *11* 11.4. Evaluation of polarograms with maxima is shown for curve *8*

TABLE I

Tast and DP polarographic parameters of 7-diethyl-4-methylcoumarin (c = 100 μmol l^{-1}) in Britton–Robinson buffers containing 1 vol.% methanol at various pH

pH[a]	$E_{1/2}$[b], V	I_{lim}[c], μA	E_p[d], V	I_p[e], μA
2.2	−1.12[f]	2.9[f]	−1.11	2.0
2.7	−1.18	3.8	−1.15	4.5
3.5	−1.28	5.3	−1.21	9.5
4.3	−1.36	6.3	−1.33	9.0
5.0	−1.46	65.1	−1.51	80.2
6.0	−1.53	73.0	−1.59	144.8
6.5	−1.56	39.9	−1.60	92.7
6.9	−1.60	23.2	−1.62	55.0
7.9	−1.73	6.3	−1.71	6.3
9.1	−1.74	6.0	−1.72	6.0
11.4	−1.77	2.5	−1.74	2.0

[a] pH value of solution containing 1 vol.% methanol; [b] half-wave potential; [c] limiting current; [d] peak potential; [e] peak current; [f] crude data only (polarogram was difficult to evaluate).

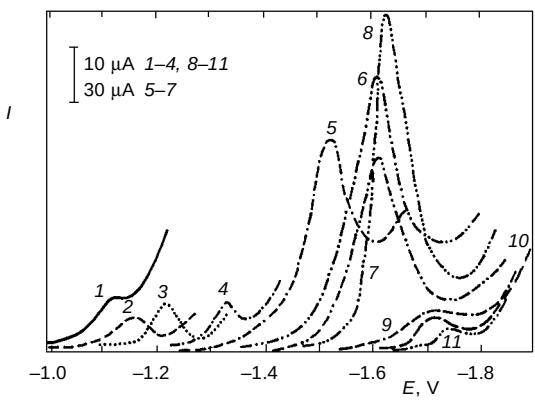


FIG. 3

DP polarograms of 7-diethylamino-4-methylcoumarin (c = 100 μmol l^{-1}) in Britton–Robinson buffers containing 1 vol.% methanol at pH: *1* 2.2, *2* 2.7, *3* 3.5, *4* 4.3, *5* 5.0, *6* 6.0, *7* 6.5, *8* 6.9, *9* 7.9, *10* 9.1, *11* 11.4

however, that the substituents in positions 4 and 7 affect the electron density distribution of the radical-anion and, hence, the localization of the free electron to the extent that linking will occur between positions other than as shown in Scheme 1).

Quite different is the polarographic behaviour of 7-diethylamino-4-methylcoumarin at pH 5 – 7.5. The tast polarograms display a maximum which is several times higher than the wave height (Fig. 2), and the DP polarograms are consistent with this (Fig. 3). The height and shape of this maximum, effect of pH and of the base electrolyte (whose increasing concentration brings about a decrease in the maximum), effect of the methanol content and of an addition of gelatin (Fig. 5) suggest that the phenomenon involves a catalytic decrease of the hydrogen overvoltage, which is related to the presence of a tertiary amino group in the analyte molecule. This is also borne out by the fact that at pH 6.5 the polarograms are virtually identical regardless of the mercury reservoir height. Figure 5 also demonstrates that the catalytic process is blocked efficiently by gelatin and methanol.

The cyclic voltammograms of 7-diethylamino-4-methylcoumarin at pH 6.5 (Fig. 3) document the occurrence of this catalytic effect as well, displaying a cathodic peak also during the reverse potential change at the working electrode. The fact that this cathodic peak during the reverse potential change is also higher at lower polarization rates is apparently due to the larger amount of the catalytically active substance diffusing towards the electrode surface during the slower reverse potential change.

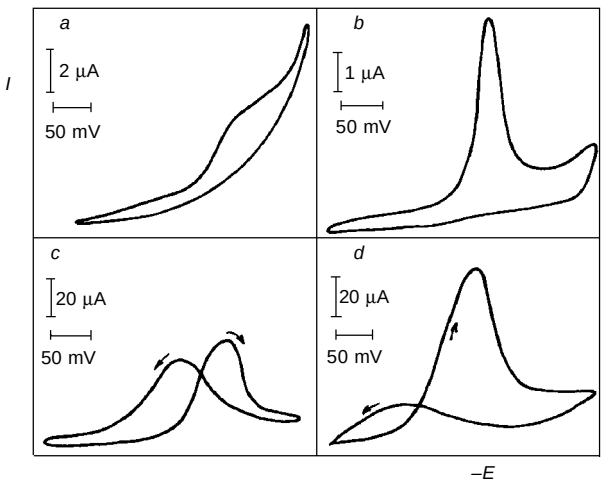


FIG. 4

Cyclic voltammograms of 7-diethylamino-4-methylcoumarin (c = 10 μmol l^{-1}) on a dropping mercury electrode in Britton–Robinson buffers containing 1 vol.% methanol at pH 3.5 (*a*), 9.1 (*b*), and 6.5 (*c*,*d*). Starting potential (V) and potential sweep rate (mV s^{-1}): *a* –1.20, 100; *b* –1.55, 100; *c* –1.45, 50; *d* –1.45, 200

The parameters of the wave or peak height dependences on the analyte concentration are given in Table II for selected pH values. This table shows that the analytical applicability of tast polarography is limited to the concentration region of 10 – 100 μmol l^{-1}. Another wave, apparently of catalytic origin, appears at pH 3.5 at higher concentrations, to coincide with the analytical wave. At pH 6.0, the wave height at analyte concentrations exceeding 300 μmol l^{-1} ceases to be concentration dependent, which is in accordance with its catalytic nature. Moreover, the wave height evaluation is aggravated by the atypical wave shape at this pH; in such case, the evaluating procedure shown in Fig. 2 appears to suit best. A pH about 9 is optimal for the evaluation of the tast polarographic waves. However, even in such solutions the limit of determination cannot be further reduced because of the high residual current which is apparently related to the very negative half-wave potential of the analytical wave. Reducing the base electrolyte concentration or increasing the methanol content does not help. On the other hand, the analyte cannot be quantitated at concentrations higher than 200 μmol l^{-1} because then the substance separates from the solution.

Furthermore, Table II and Fig. 3 demonstrate that the DPP technique is well suited to the determination of 7-diethyl-4-methylcoumarin both at pH 3.5 and pH 9.1 over the

TABLE II
Tast polarographic wave heights and DP polarographic peak heights of 7-diethylamino-4-methylcoumarin in dependence on its concentration in Britton–Robinson buffers containing 1 vol.% methanol

pH[a]	Method	c μmol l^{-1}	Slope mA mol^{-1} l	Intercept μA	r^b	L_Q[c] μmol l^{-1}
3.5	TAST	10 – 100	52	0.15	0.9890	22
	DPP	10 – 100	92	0.20	0.9989	–
	DPP[d]	1 – 10	226	0.12	0.9972	1.8
4.3	DPP/SMDE	1 – 10	0.285	0.04	0.9988	–
	DPP/SMDE	0.1 – 1	0.350	–0.008	0.9953	0.26
6.0	TAST[e]	10 – 100	640	0.12	0.9975	–
	TAST	1 – 10	350	–0.07	0.9901	4.6
	DPP	10 – 100	1 430	–5.22	0.9965	–
	DPP	1 – 10	–[f]	–[f]	–[f]	–
9.1	TAST	10 – 100	60	–0.13	0.9994	8.0
	DPP	10 – 100	61	–0.09	0.9989	
	DPP[d]	1 – 10	75	–0.02	0.9983	1.2

[a] pH of solution containing 1 vol.% methanol; [b] correlation coefficient; [c] limit of determination; [d] in tenfold dilute buffer; [e] polarogram evaluated as shown in Fig. 2; [f] a nonlinear dependence.

concentration region of 1 – 100 μmol l^{-1}; the limit of determination is slightly lower at pH about 9. Within the concentration region of 1 – 10 μmol l^{-1}, the tenfold dilute Britton–Robinson buffer suits well, giving a smoother base electrolyte curve. The DPP

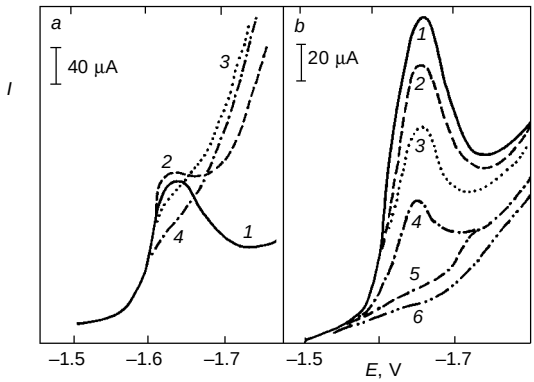


FIG. 5

Effect of gelatin (*a*) and methanol (*b*) on tast polarograms of 7-diethylamino-4-methylcoumarin (c = 100 μmol l^{-1}) in Britton–Robinson buffers at pH 6.2; *a* methanol content 1 vol.%, volume of 0.5% gelatin solution added to 10 ml of solution polarographed (ml): *1* 0, *2* 0.1, *3* 0.2, *4* 0.3; *b* methanol content (vol.%): *1* 0.2, *2* 2, *3* 5, *4* 10, *5* 20, *6* 50

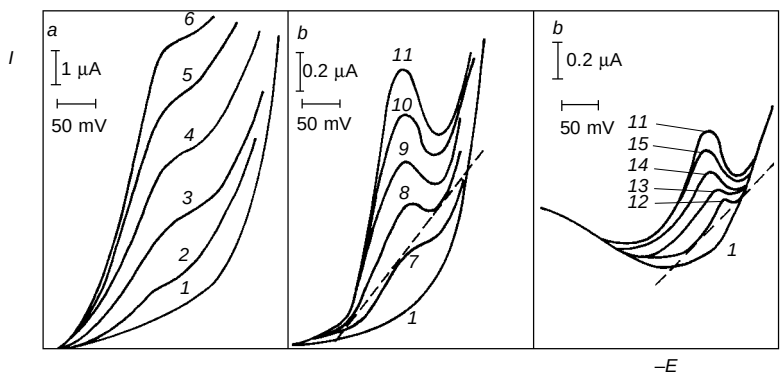


FIG. 6

Polarograms of 7-diethylamino-4-methylcoumarin in Britton–Robinson buffers containing 1 vol.% methanol; *a* tast and *b* DP polarograms on a DME at pH 9.1, starting potential –1.60 V; *c* DP polarograms on an SMDE at pH 4.3, starting potential –1.10 V. Analyte concentration (μmol l^{-1}): *1* 0, *2* 20, *3* 40, *4* 60, *5* 80, *6* 100, *7* 2, *8* 4, *9* 6, *10* 8, *11* 10, *12* 0.2, *13* 0.4, *14* 0.6, *15* 0.8, *16* 1.0. The dashed line is the baseline from which the peak height was evaluated

peaks obtained at pH 6.5 are high and well developed but fail to be linearly dependent on analyte concentration.

Tast and DP polarograms of 7-diethyl-4-methylcoumarin at the lowest applicable concentrations are shown in Fig. 6.

Differential Pulse Polarography of 7-Diethylamino-4-methylcoumarin on the Static Mercury Drop Electrode

Because of the very negative half-wave potential of the substance and high base electrolyte current, no suitable conditions could be found for its quantitation by differential pulse voltammetry on a hanging mercury drop electrode. In efforts to make the determination more sensitive, the application of differential pulse polarography on a static mercury drop electrode was examined.

Based on preliminary experiments, the Britton–Robinson buffer at pH 4.3 containing 1 vol.% methanol was used as the medium. The concentration dependence parameters are given in Table II, polarograms for the lowest attainable concentrations are shown in Fig. 6*c*.

The concentration dependence fails to be linear at concentrations higher than 20 μmol l^{-1}, apparently due to catalytic phenomena. The limit of determination is roughly one order of magnitude lower than by DPP on a dropping mercury electrode. No lower concentrations could be determined even if the buffer solution concentration was decreased or the methanol content increased.

Practical Applications

The DPP method on a DME was applied to the determination of 7-diethylamino-4-methylcoumarin in the technical products Tinopal SWN and Rylux VPA; the analyte contents in the two products were 55.2 and 71.9 wt.%, respectively, with standard deviation estimates of 0.71% and 0.80%, respectively (obtained from the range of 3 determinations). The spectrophotometric method gave contents of 54.0 and 71.05 wt.%, with standard deviation estimates of 0.48% and 0.53%, respectively (obtained as above). Moore's u-test confirmed that the results obtained by the two techniques did not differ at the 95% confidence level. If 7-diethylamino-4-methylcoumarin were to be determined in waste waters, it would have to be preconcentrated by a suitable method in dependence on the matrix, by extraction combined with thin layer chromatography for instance[4].

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