946. *Dipole-moment Measurements of Coumarin Derivatives and their Orientation at a Dropping-mercury Electrode.*

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The dipole moments of coumarin and its 6-amino-, 6-acetamido-, 6-sulphamoyl-, and 6-chlorosulphonyl-derivatives have been determined. Coumarin derivatives are adsorbed with the dipole moment parallel to the mercury surface.

The polarography of nickel–coumarin solutions at the dropping-mercury electrode has been described in a previous paper.[1] In a variety of supporting electrolytes, nickel polarograms were found to be distorted by the presence of coumarin, and this distortion was attributed to its adsorption on the surface of the mercury droplet. In the work described here, the dipole moments of some coumarin derivatives have been measured, and their electrocapillary properties investigated, in order to gain additional information regarding the orientation of the molecules when adsorbed at the mercury surface. In addition to coumarin the following derivatives were used: 6-amino-, 6-acetamido-, 6-sulphamoyl-, and 6-chlorosulphonyl-coumarin.

Experimental

Materials.—Coumarin, crystallised from aqueous ethanol, had m. p. 68—69°. 6-Amino-courmarin was prepared from coumarin by Morgan and Micklethwait's method [2] and had m. p. 165—165·5°. 6-Acetamidocoumarin, m. p. 216—217°, was prepared by acetylating the amino-compound.[3] 6-Chlorosulphonylcoumarin, m. p. 119—120°, and 6-sulphamoylcoumarin, m. p 186—187°, were prepared by Rubtsov and Fedosova's method.[4]

The dioxan for the dipole-moment determinations was purified by Eigenberger's method,[5] and then had b. p. 101°, n_D^{25} 1·42006.

Dipole Moments.—Determinations were made in dioxan by a resonance method, with apparatus as described by Few, Smith, and Witten.[6] The crystal-controlled oscillator-frequency was 10^6 c./sec., and the capacitance was measured by a Sullivan precision calibrated air-condenser. The cell was of an all-glass type, similar to that described by Le Fèvre,[7] and had a capacitance of 80 $\mu\mu$F per dielectric constant unit.

Densities were determined with a modified Sprengel–Ostwald pyknometer of *ca.* 25 c.c. capacity, and refractive indices by using a Pulfrich refractometer.

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[1] Griffiths and Westmore, *J.*, 1962, 1704.
[2] Morgan and Micklethwait, *J.*, 1904, **85**, 1230.
[3] Gattermann, *Ber.*, 1894, **27**, 1937.
[4] Rubtsov and Fedosova, *J. Gen. Chem.* (*U.S.S.R.*), 1944, **14**, 848.
[5] Eigenberger, *J. prakt. Chem.*, 1931, **130** (ii), 75.
[6] Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.
[7] Le Fèvre, " Dipole Moments," Methuen, London, 1948.

TABLE 1.

Dielectric constants, refractive indices, and specific volumes of the solutions.

w	ε	n_D^{25}	v	w	ε	n_D^{25}	v
			Coumarin				
0·0	2·2052	1·42006	0·97276	0·023535	2·6524	1·42490	0·96891
0·006583	2·3274	1·42147	0·97147	0·030208	2·8057	1·42583	0·96773
0·011604	2·4216	1·42242	0·97087	0·035939	2·8909	1·42698	
0·015017	2·4922	1·42306	0·97023	0·057359	3·3261	1·43077	0·96292
			$\alpha_0 = 18\cdot62;\ \beta_0 = -0\cdot168;\ \gamma_0 = 0\cdot60.$				
			6-*Aminocoumarin*				
0·000244	2·2120	1·42012	0·97269	0·002601	2·2855	1·42064	0·97210
0·000658	2·2249	1·42022	0·97261	0·005337	2·3700	1·42127	0·97141
0·001348	2·2471	1·42037	0·97242				
			$\alpha_0 = 30\cdot90;\ \beta_0 = -0\cdot25;\ \gamma_0 = 0\cdot64.$				
			6-*Acetamidocoumarin*				
0·000092	2·2089	—	—	0·001517	2·2497	—	—
0·000237	2·2133	—	0·97271	0·001705	2·2576	1·42044	0·97223
0·000615	2·2266	—	0·97256	0·002067	2·2686	—	0·97211
0·000899	2·2348	—	0·97248				
			$\alpha_0 = 35\cdot0;\ \beta_0 = -0\cdot314;\ \gamma_0 = 0\cdot628.$				
			6-*Sulphamoylcoumarin*				
0·000291	2·2073	—	—	0·002554	—	1·42052	—
0·000681	2·2134	—	0·97258	0·002983	2·2425	—	0·97172
0·001081	—	1·42028	—	0·003945	—	1·42079	—
0·001146	2·2185	—	0·97244	0·004764	2·2598	—	0·97117
0·001758	—	1·42045	—	0·005276	2·2670	1·42104	—
0·001820	2·2294	—	0·97213				
			$\alpha_0 = 11\cdot86;\ \beta_0 = -0\cdot334;\ \gamma_0 = 0\cdot522.$				
			6-*Chlorosulphonylcoumarin*				
0·004341	2·2177	1·42075	—	0·012706	2·2419	1·42206	0·96817
0·008601	2·2271	1·42143	0·96973	0·021544	2·2669	1·42343	0·96510
			$\alpha_0 = 2\cdot87;\ \beta_0 = -0\cdot355;\ \gamma_0 = 0\cdot45.$				

Results.—Values of dielectric constant, ε, refractive index, n_D, and specific volume, v, of the solutions for various values of the weight-fraction, w, are given in Table 1. These values were used to evaluate the specific polarization and specific refraction of the solute by the method of Halverstadt and Kumler,[8] *viz.*,

$$p_2^\circ = \frac{3\alpha_0 v_1}{(\varepsilon_1 + 2)^2} + \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2}(v_1 + \beta_0) \text{ and } r_2^\circ = \frac{3\gamma_0 v_1}{(n_1^2 + 2)^2} + \frac{n_1^2 - 1}{n_1^2 + 2}(v_1 + \beta_0)$$

where v_1, ε_1, and n_1 are values for the pure solvent and α_0, β_0, and γ_0 are the values of $d\varepsilon/dw$, dv/dw, and dn_D/dw, respectively, at zero concentration, obtained by extrapolation. The total polarization, ${}_TP$, and molar refraction, R_D, were obtained by multiplying the specific quantities by the molecular weight, M, of the compound. Dipole moments were calculated from $\mu = 0\cdot01275\sqrt{({}_TP - {}_DP)T}$ where the distortion polarization, ${}_DP$, is given by ${}_DP = P_{\text{atom}} + P_{\text{electron}} = 1\cdot05R_D$. The results are summarized in Table 2.

TABLE 2.

Polarizations and dipole moments in dioxan.

Compound	M	p_2°	r_2°	${}_TP$	R_D	μ (D)
Coumarin	146·1	3·304	0·314	482·5	45·9	4·61
6-Aminocoumarin	161·1	5·307	0·299	854·7	48·1	6·27
6-Acetamidocoumarin	203·2	5·965	0·280	1212·0	56·9	7·51
6-Sulphamoylcoumarin.........	225·1	2·140	0·256	481·8	57·65	4·54
6-Chlorosulphonylcoumarin ...	244·6	0·651	0·238	159·2	58·2	2·19

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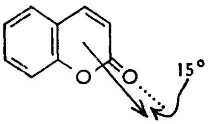
[8] Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

Electrocapillary Measurements.—The apparatus used and procedure employed were as described in a previous paper.[1]

DISCUSSION

Dipole Moments.—The value obtained for the dipole moment, μ, of coumarin in dioxan agrees well with those of Le Fèvre and Le Fèvre[9] (4·48 D in benzene at 25°) and Govinda Rau[10] (4·51 D in benzene at 20°), especially when it is recalled that in dioxan there is likely to be a higher contribution from the " solvent effect." The presence of a 6-amino-group in coumarin increases μ by 1·66 D. Few and Smith[11] showed that aniline has dipole moments of 1·53 and 1·77 D in benzene and dioxan, respectively, suggesting that the abnormally high value in dioxan is due to hydrogen bonding of the amino-hydrogen atoms to the oxygen atoms of the dioxan molecules. This hydrogen bonding is also possible for 6-aminocoumarin, so that the group moment of the amino-linkage should be approximately the same. Le Fèvre and Le Fèvre[9] calculated that, in coumarin, the line of action of the resultant dipole was inclined at an angle of 15° to the axis of the C=O bond, in a sense towards the oxygen atom, as shown. With this result for 6-aminocoumarin, vectorial addition gives a resultant dipole moment of 6·34 D, which is only slightly higher than the experimental result, and thus no abnormal effects are in operation.



Both aliphatic and aromatic amides have rather large dipole moments (about 3·4—3·6 D). The introduction of 6-acetamido-group into coumarin increases the dipole moment by 2·9 D, which indicates that although the dipoles act in approximately the same sense they are probably at an appreciable angle to one another (32° by vector addition, a value of 3·5 D being assumed for the amido-moment).

Little can be said about the remaining coumarin derivatives, owing to lack of information in the literature on the substituent groups.

Electrocapillary Properties.—The effect of coumarin on the mercury electrocapillary curve in 0·1M-potassium chloride has been described in a previous paper.[1] Polarographic results (drop-times) were used to construct curves resembling the electrocapillary curve, in the presence of coumarin and its 6-amino-, 6-acetamido-, and 6-sulphamoyl derivatives in 0·1M-potassium nitrate solution. The latter solution is capillary-inactive. The results are shown in Figs. 1—4. The 6-chlorosulphonyl derivative was not sufficiently soluble for measurements to be made. It was hoped to extend the positive branches of the curves beyond 0 V (*versus* the saturated calomel electrode) but in this region the results were non-reproducible.

It can be seen that, except for coumarin, which causes an apparently abnormal depression of the curve at −1·0 to −1·4 V, the curves are symmetrical about the electrocapillary maximum. For each compound, including coumarin, the electrocapillary maximum has not been shifted from its normal position. This suggests that when the derivatives are adsorbed at the mercury–solution interface there is no resultant dipole moment perpendicular to the mercury surface, *i.e.*, the molecules are adsorbed with the dipole moment parallel to the mercury surface. Since the lines of action of the dipoles in the molecules are parallel to the ring planes, the derivatives may be adsorbed either flat or edgewise. However, if the molecules were adsorbed with the ring-planes parallel to the mercury surface, some π-electron interaction with the mercury would be expected[12,13] and thus a shift of the electrocapillary maximum in a negative direction. Since there is no such shift, this form of adsorption appears not to occur.

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[9] Le Fèvre and Le Fèvre, *J.*, 1937, 1088.
[10] Govinda Rau, *Proc. Indian Acad. Sci.*, 1936, *A*, **4**, 687.
[11] Few and Smith, *J.*, 1949, 753.
[12] Blomgren and Bockris, *J. Phys. Chem.*, 1959, **63**, 1475.
[13] Blomgren, Bockris, and Jesch, *J. Phys. Chem.*, 1961, **65**, 2000.

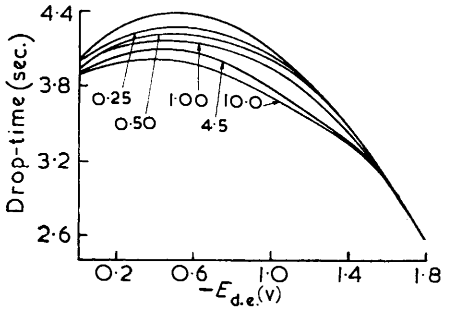

FIG. 1. Effect of coumarin (at concns. given on curves, in mmole/l.) on the electrocapillary curve.

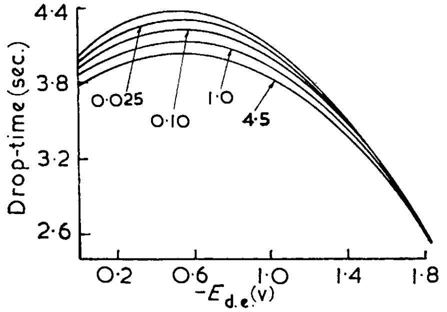

FIG. 2. Effect of 6-aminocoumarin (at concns. given on curves, in mmole/l.) on the electrocapillary curve.

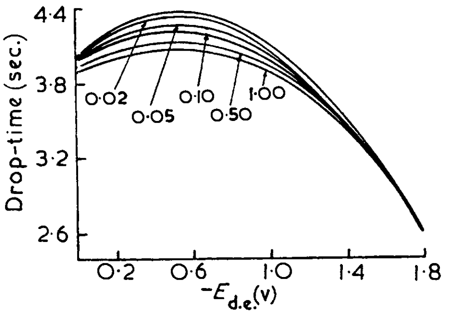

FIG. 3. Effect of 6-acetamidocoumarin (at concns. given on curves in mmole/l.) on the electrocapillary curve.

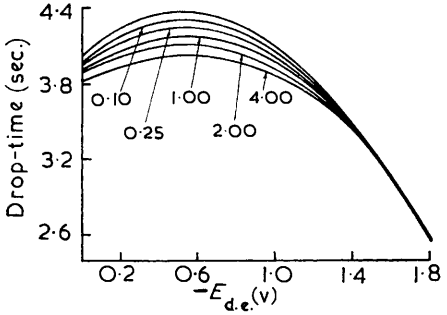

FIG. 4. Effect of 6-sulphamoylcoumarin (at concns. given on curves, in mmole/l.) on the electrocapillary curve.

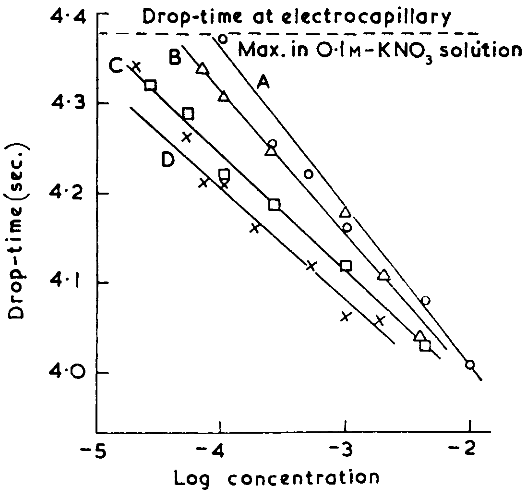

FIG. 5. Effect of coumarin derivatives on the mercury drop-time at the electrocapillary maximum.

A and ○, coumarin; B and △, 6-sulphamoylcoumarin; C and □, 6-aminocoumarin; D and ×, 6-acetamidocoumarin.

Recent kinetic studies have shown that the adsorption of organic molecules on mercury is a comparatively slow process, controlled in rate either by diffusion or by the reaction on the surface, or both.[14–17] The time required to reach adsorption equilibrium[12] is usually larger than the drop-period of a conventional polarograph. Since, in the present study, the drop-times were shorter than those usually employed in long-term equilibrium studies, the results are regarded as semi-quantitative.

It appears that the coumarin derivatives, except for coumarin itself, have a similar effect on the shape of the electrocapillary curve. To obtain a clearer picture of adsorption on mercury at the electrocapillary maximum, drop-times have been plotted against the logarithm of the concentration of the derivatives in question (Fig. 5). Straight lines have been drawn through the experimental points as this seems to be as satisfactory as any other procedure, especially as the reproducibility of the results is estimated to be only about ±0·02 sec. Gibbs's equation[18] predicts that the linear portions of such plots correspond to the maximum coverage at the potential studied; and the concentration at which the linear portion of the curve begins corresponds to the minimum concentration at which maximum coverage is achieved. The surface excess of each compound (Fig. 5) is proportional to the slope; for coumarin the surface excess and the minimum concentration at which it gives maximum coverage are the greatest.

The peculiar effect of coumarin on the electrocapillary curve at —1·0 to —1·4 v is in just that range of potential where the nickel polarograms are distorted, but the significance of this is not clear.

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[18] Parsons in " Modern Aspects of Electrochemistry," ed. Bockris, Butterworths, London, 1954.