STUDIES IN THE POLAROGRAPHIC BEHAVIOUR OF γ-BENZENE HEXACHLORIDE

BY U. SANJIVA, R. S. SUBRAHMANYA AND M. R. A. RAO

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SUMMARY

1. The quantitative estimation of the γ-isomer of benzene hexachloride by the polarographic method has been studied using dioxane, alcohol and acetone as the organic solvents and lithium chloride and sodium acetate as the base electrolyte. An optimum concentration of 50% dioxane and 0·5 M sodium acetate and 0·1 M lithium chloride in the base solution has been found to be suitable for the estimation of γ-benzene hexachloride in the range of $0{\cdot}2 \times 10^{-3}$ M to $2{\cdot}0 \times 10^{-3}$ M. This system does not require a maximum suppressor. Higher concentrations of sodium acetate with the use of gelatin as the maximum suppressor extends the applicability of the analytical method over a wider range of concentration of γ-benzene hexachloride. The sensitivity of the method was found to be higher in systems containing alcohol and acetone than in dioxane.

2. The concentration of γ-benzene hexachloride in commercial sample of ' Gammexane ' has been estimated, using alcohol as the solvent.

3. A diminution in the concentration of the organic solvent is always accompanied by an increase in the molar limiting current. This effect is attributed to a change in the diffusion coefficient of the reducible substance in the medium.

INTRODUCTION

The necessity for an accurate and easy method of estimation of the γ-isomer of benzene hexachloride has been a long-felt need. The biological, cryoscopic,[1, 2] partition chromatographic[3, 4] dehydrochlorination,[5] infra-red absorption[6, 7] and mass isotope dilution[8] methods employed for this purpose are often tedious and require specialized technique and skill. On account of these reasons newer and simpler methods are being developed for the analysis of the γ-isomer.

Keller *et al.*[9] showed in 1946 that benzene hexachloride gave rise to a polarographic wave, but they were not certain that the wave was only due to the γ-isomer. Ingram and Southern[10] reported that, of the four isomers, only the γ-isomer was reduced at the dropping mercury electrode. The wave obtained under their experimental conditions was not quite a normal one but appeared to involve the progressive reduction of the six chlorine atoms in the molecule. Hence, they concluded that the polarograms were not quite satisfactory. Grass and Spencer[11] extended this work and their results were in general agreement with those of Ingram and Southern.[10] Yoshikasu and Yasumori[12] estimated γ-benzene hexachloride by the polarographic method using alcohol as the solvent and ammonium chloride as the electrolyte. They reported that the wave height was proportional to the concentration of the γ-isomer. We were unable to confirm this finding because the polarograms obtained by us had kinks and involved considerable difficulty in the measurement of wave height. Kent Schwabe[13] and Makoto Suzuk and Minoru Nakajima[14] reported that the isomers of benzene hexachloride were reduced in presence of alkyl ammonium compounds, but they give no details regarding the range of concentrations over which the method yields accurate results. Gerrit Dragt[15] reported that the presence of heptachloride greatly interfered with the slope of the base line of the polarographic curve, necessitating an arbitrary measurement of the wave height.

The literature cited above indicates that there is diversity of opinion regarding the polarograms obtained during the estimation of γ-B.H.C. Our experience with these methods revealed that the polarograms were far from satisfactory. Further, the methods so far tried involve the use of complicated base-solutions or expensive supporting electrolytes. It was, therefore, desirable to develop more suitable methods for obtaining polarograms which would yield accurate results.

EXPERIMENTAL

Apparatus and Materials

The instrument used in these investigations was the automatically recording polarograph supplied by the Cambridge Instrument Co., Ltd. The electrolysis vessel used had two side tubes one for passing hydrogen and the other for connecting with the external calomel electrode. The dropping mercury electrode had a droptime of 3 sec./drop in 1 N potassium chloride with no applied potential and the value of m of the capillary was 1·95 mg. per sec.

The inorganic salts employed were of reagent quality. Dioxane was purified by the method of Weisberger and Proskauer.[16] The liquid was refluxed over sodium and distilled before use. Acetone was purified by the method suggested by Fieser.[17] It was dried over anhydrous potassium carbonate and distilled. Absolute ethyl alcohol was refluxed over silver nitrate to remove aldehydes and distilled before use. γ-Benzene hexachloride was obtained by the kind courtesy of Messrs. Imperial Chemical Industries, Ltd., and was further purified by crystallization from pure chloroform. Its melting point after purification was 112° C. as compared with the theoretical value of 112·5° C. reported by Slade.[18] Gold label gelatin was used as the maximum suppressor.

Solutions in the cell were kept free of air by bubbling electrolytic hydrogen which had been purified by passage over heated platinised asbestos. The hydrogen was equilibrated with the vapour of the test solution by bubbling the gas through a sample of the test solution kept in the thermostat.

Test solutions were made by dissolving known weights of the γ-benzene-hexachloride in the organic solvent, and adding a known volume of aqueous solution of the supporting electrolyte and finally making up with water to a suitable volume.

The following supporting electrolytes were tried: ammonium chloride, ammonium acetate, potassium chloride, potassium bromide, potassium iodide, sodium chloride and sodium acetate. A preliminary study indicated that sodium acetate was best suited to give well-defined polarographic waves. Methyl red, starch and gelatin were tried as maximum suppressors, but of these, only gelatin was found to be satisfactory.

All measurements were taken with the cell kept in a constant temperature bath maintained at 30° C. ± 0·1°.

The method employed in the present investigation for measuring the wave height is a modification of Taylor's[19] method developed by one of us (R. S. Subrahmanya), which consisted in the provision of a vernier along with the scale and T-square employed. The polarogram is wetted with water and mounted on a sheet of glass. The vertical height between the base line and the diffusion maximum is read out on the scale and indicated in Fig. 3. Suitable corrections are also applied for the residual current.

The effect of concentration of sodium acetate on the wave heights is given in Table I. In these experiments, the base solution had equal volumes of dioxane and water with 0·1 N lithium chloride and $0{\cdot}505 \times 10^{-3}$ M benzene hexachloride. No maximum suppressor was employed during these experiments. The results obtained are presented in Table I.

A close study of the polarograms (Figs. 1 *a* and *b*) revealed that when the concentration of sodium acetate was low (0·1 to 0·2 M), the polarograms exhibited a hump in the curve. As the concentration of the sodium acetate increased (0·3 to 0·7 M), the hump was suppressed and the maximum for

TABLE I

Effect of the Concentration of Sodium Acetate on the Wave Height in 50% Aqueous Dioxane

No.	Concentration of sodium acetate	Diffusion current i_d, microamp. corresponding to wave height
1	0·1 M	2·82
2	0·2 M	2·57
3	0·3 M	2·39
4	0·4 M	2·26
5	0·5 M	2·14
6	0·7 M	1·56
7	0·9 M	1·19

the diffusion current got spread out. Higher concentration of the supporting electrolyte indicated a rounded maximum. An optimum of 0·5 M sodium acetate was therefore used in all the subsequent experiments. From the table, it is also clear that the value of wave height decreases with an increase in concentration of the base electrolyte. It was noticed that the incorporation of lithium chloride in the base solution improved the nature of the polarograms by flattening the diffusion current plateau.

Concentration of dioxane in the base solution

Perrachio and Meloche[20] and Zanko and Manusova[21] have shown the non-aqueous solvents have profound influence on the nature of polarograms and their sensitivity. The optimum concentration of the dioxane in the base solution was therefore found out keeping the sodium acetate at 0·5 M. Fig. 2 indicates the results obtained. The polarograms were taken with solutions containing 1×10^{-3} M γ-benzenehexachloride, 0·1 M lithium chloride and 0·5 M sodium acetate and varying concentrations of dioxane. Curves 1, 2, 3 and 4 correspond to 30%, 40%, 50% and 60% dioxane respectively. It is evident that 50% dioxane is the optimum to obtain a good polarographic wave. At lower concentrations, the polarograms are highly irregular, while at too high a concentration (curve 4), a rounded maximum is obtained. The value of i_d/c obtained from the polarograms 2 and 3 are 8·42 and 4·36 respectively indicating thereby that a change of concentration of dioxane from 40% to 50% would diminish the wave height by nearly 50%.

A study of the relationship between the concentration of γ-benzene hexachloride and its diffusion current was carried out employing 50% dioxane. The results obtained are given in Table II. The polarograms of experiments 4, 5, 6 and 7 are presented in Fig. 3.

TABLE II

Effect of Concentration of γ-Benzene Hexachloride on the Diffusion Current

(0·1M lithium chloride, 0·5 M sodium acetate in 50% aqueous dioxane)

No.	Concentration of γ-Benzene hexachloride-Millimolar	i_d, microamp.	i_d/c
1	0·20	0·80	3·99
2	0·40	1·55	3·88
3	0·60	2·34	3·91
4	0·80	3·15	3·93
5	1·00	3·93	3·93
6	1·50	6·09	4·06
7	2·00	7·85	3·93

The values in Table II show that diffusion current (*id*) is proportional to the concentration of γ-benzene hexachloride in the region studied, *viz.*, $0 \cdot 2 \times 10^{-3}$ M to $2 \cdot 0 \times 10^{-3}$ M. The polarograms for higher concentrations, of γ-benzenehexachloride indicated that the values of the diffusion current could not be depended upon due to some vitiating factors.

Estimation of γ-benzene hexachloride in concentrations of $2 \cdot 00 \times 10^{-3}$ *M* and *above*

When the concentration of the base electrolyte, *viz.*, sodium acetate was increased from 0·5 M to 0·75 M, it was noticed that the polarograms obtained with $2 \cdot 0 \times 10^{-3}$ M to 8×10^{-3} M γ-benzene hexachloride gave rise to a rounded hump in the polarogram. Addition of gelatin was found to eliminate the hump, the optimum concentration of gelatin being 0·001%. Table III gives the relationship between the concentration of γ-benzene hexachloride and the wave height when gelatin is employed. The polarograms obtained are given in Fig. 4 for the experiments 4, 5, 6 and 7.

TABLE III

Effect of Concentration of γ-Benzene Hexachloride on the Diffusion Current

(0·1M lithium chloride, 0·75M sodium acetate, 0·001% gelatin in 50% aqueous dioxane)

No.	Concentration of γ-Benzene hexachloride–Millimolar	i_d, microamp.	i_d/c
1	0·2144	0·70	3·28
2	0·4085	1·32	3·23
3	0·6126	1·96	3·21
4	0·8164	2·62	3·21
5	1·021	3·26	3·20
6	1·532	4·95	3·23
7	2·042	6·53	3·23
8	3·970	12·98	3·27
9	5·955	18·09	3·04
10	7·940	22·79	2·87

From the above table, it can be seen that the wave height is proportional to the concentration in the range $0·2\times10^{-3}$ M to about $4·0\times10^{-3}$ M, but slightly falls off at higher concentrations of γ-benzene hexachloride. The effect of increasing sodium acetate concentration still further did not in any way improve the accuracy of the estimation.

Estimation of γ-benzene hexachloride in low concentrations

With a view to increase the accuracy of the estimations in low concentrations of γ-benzene hexachloride, trials were made with aqueous solutions containing 30% dioxane instead of 50%, employed for experiments given in Table II. The concentration of gelatin was increased to 0·002% while those of sodium acetate and lithium chloride were 0·5 M and 0·1 M respectively. The results obtained are given in Table IV. The polarograms obtained are reproduced in Fig. 5.

TABLE IV

Effect of Concentration of γ-Benzene Hexachloride on the Diffusion Current

(0·1M lithium chloride, 0·5M sodium acetate, 0·002% gelatin in 30% aqueous dioxane)

No.	Concentration of γ-Benzene hexachloride-Millimolar	i_d, microamp.	i_d/c
1	0·25	2·68	10·73
2	0·50	5·21	10·43
3	0·75	7·60	10·13
4	1·00	10·02	10·02

A comparison of the last column of Table IV with Table II shows that sensitiveness, *viz.*, i_d/c, is enhanced nearly three times. A further diminution of the dioxane content to 20% increased the value of i_d/c to 14·6, but the range over which the γ-benzene hexachloride could be estimated was very small, *viz.*, from $0{\cdot}03 \times 10^{-3}$ M to $0{\cdot}20 \times 10^{-3}$ M, and was not therefore considered to be of practical importance.

Use of alcohol and acetone as solvents

The effect of alcohol on the polarographic behaviour of γ-benzene hexachloride was next investigated. The base solution consisted of 50% alcohol, 0·5 M sodium acetate, 0·1 M lithium chloride, and 0·004% gelatin as maximum suppressor. Good polarograms were obtained in all the above cases. Table V gives the results obtained. A comparison of the results in Table V with those of Table II reveals that the accuracy of the method is greatly increased if alcoholic solutions are employed instead of solutions in dioxane.

When the concentration of ethyl alcohol was lowered to 25%, the sensitivity increased from 8·5 to 13·1. But, the concentration of γ-benzene hexachloride could be varied only from $0{\cdot}04 \times 10^{-3}$ M to $0{\cdot}2 \times 10^{-3}$ M only. The addition of ethyl alcohol enhances the sensitivity of the method as compared with dioxane (*cf.* Table II).

TABLE V

Effect of Concentration of γ-Benzene Hexachloride on the Diffusion Current in Presence of Alcohol

(0·1 M lithium chloride, 0·5 M sodium acetate, 0·004% gelatin in 50% aqueous alcohol)

No.	Concentration of γ-Benzene hexachloride–Millimolar	i_d, microamp.	i_d/c
1	0·202	1·73	8·55
2	0·404	3·46	8·57
3	0·606	5·26	8·68
4	0·808	6·87	8·50
5	1·212	10·35	8·54
6	1·515	12·76	8·43

When acetone was employed as the solvent, the sensitivity of the method was enhanced further as is indicated in Table VI. But, a detailed study of the polarograms obtained with varying concentrations of γ-benzene hexachloride and gelatin as the maximum suppressor, indicated that the method yielded satisfactory results if the concentration of gelatin was kept at about 0·012% instead of 0·001% as with the other solvent. Results of Table VI were obtained when a base solution containing 50% acetone, 0·5 M sodium acetate, 0·1 M lithium chloride and 0·012% gelatin, was employed.

TABLE VI

Effect of Concentration of γ-Benzene Hexachloride on the Diffusion Current in Acetone Solutions

(1·1M lithium chloride, 0·5 M sodium acetate, 0·012% gelatin in 50% aqueous acetone)

No.	Concentration of γ-Benzene hexachloride–Millimolar	i_d, microamp.	i_d/c
1	0·509	5·70	11·21
2	0·814	8·92	10·96
3	1·220	13·38	10·96
4	1·526	16·58	10·86

A comparison of Table VI with Table V shows that sensitivity is increased by 30%, when acetone is used as the solvent. As with alcohol, the concentration range with acetone is limited and the best polarograms were obtained for the concentration range given in Table VI. Table VII shows the change in the value of id/c with different concentrations of dioxane and alcohol.

TABLE VII

Effect of Different Concentrations of Solvent on the Value of i_d/c

Solvent	% by volume	i_d/c
Dioxane	50	3·95
,,	30	10·27
,,	30	12·64
Alcohol	50	8·55
,,	25	13·26
,,	15	15·05

Use of ammonium chloride as the supporting electrolyte

It has already been stated that Yasumori[12] could not obtain good polarograms by making use of 0·05 M ammonium chloride as the base electrolyte. When the concentration of ammonium chloride was increased to 0·5 M in 50% ethyl alcohol each of the polarograms had a hump and a crest. Using gelatin as maximum suppressor did not in any way improve the results. It can, therefore, be concluded that ammonium chloride even in high concentrations is not a suitable supporting electrolyte for the quantitative estimation of γ-benzene hexachloride.

Role of sodium acetate in the estimation of γ-benzene hexachloride

Polarograms were taken employing (i) 0·5 M ammonium acetate, (ii) 0·4 M sodium chloride and 0·1 M ammonium acetate, and (iii) 0·5 M sodium chloride and 0·001 M ammonium acetate, the concentration of γ-benzene hexachloride being 0·7 to 1·6 millimolar. All the three base solutions contained 50% alcohol, 0·1 M lithium chloride and 0·004 % gelatin. These test solutions corresponded to systems containing progressively decreasing concentrations of ammonium acetate and increasing concentrations of sodium ion. It was found that in the systems containing ammonium acetate, the horizontal plateau considerably diminished in length. In fact, increasing the concentration of sodium ion (NaCl) resulted in progressively well-defined waves. This clearly indicated that both the sodium and acetate ions were necessary for getting good polarograms. Hence, it would appear that the choice of sodium acetate as a supporting electrolyte was mainly responsible for the success of polarographic estimation of γ-benzene hexachloride in this investigation.

Estimation of γ-benzene hexachloride in commercial preparations

γ-Benzene hexachloride was estimated in commercial dust preparations (about 0·8% of the γ-isomer), using alcohol as the solvent. A weighed quantity of the preparation was extracted with alcohol in an all-glass soxhlet apparatus. The extract was made up to 100 c.c. To a known volume of the extract, a known weight of pure γ-isomer was added and the solution was polarographed after adding the base solution and making upto 10 c.c. A second polarogram was next obtained under the same experimental conditions but without the extract. In order to eliminate the interference of heptachlorocyclohexane on the value of the wave height the latter was measured from the base line at – 0·95 V as suggested by Dragt.[15] From the heights of the waves of the above polarograms the concentration of γ-benzene hexachloride in the commercial sample was calculated as follows:

(i) Weight of the commercial sample for analysis ..	4·2794 gm.
(ii) Volume of the alcoholic extract..	100 c.c.
(iii) Diffusion current (i_{d3}) with 2 c.c. of the extract + 2·478 mgm. of γ-benzene hexachloride + base solution	9·31 microamps.
(iv) Diffusion current (i_{d4}) with 2·478 mgm. of γ-benzene hexachloride + base solution	7·22 ,,
(v) Diffusion current for 2 c.c. of the extract only ($i_{d3}-i_{d4}$)	2·09 ,,
(vi) Diffusion current for 4 c.c. of extract + base solution	4·22 ,,

% of γ-benzene hexachloride in the sample

$$\frac{100 \times 0\cdot002478\times2\cdot09\times100}{4\cdot279\times7\cdot22\times2}=0\cdot84$$

Variation of half-wave potential with the nature of the medium

Kolthoff and Lingane[22] have pointed out the dependence of the half-wave potentials on the concentration, the pH and the composition of the medium. The polarograms obtained were, therefore, studied to elucidate the effect of the various concerned factors and these observations are presented below in Tables VIII, IX and X respectively. Table VIII shows the effect of the concentration of sodium acetate in the base solution. These results indicate that the concentration of sodium acetate has very little influence on the half-wave potentials. The results of Table IX indicate that with an increase in the concentration of γ-benzene hexachloride, the half-wave potential remains constant. The presence of organic solvent in the base solution alters the half-wave potentials to a marked degree as indicated in Table X. In general, the half-wave potential diminishes with a decrease in concentration of the organic liquid.

TABLE VIII

Effect of Concentration of Supporting Electrolyte

Concentration of sodium acetate	0·1 M	0·2 M	0·2 M	0·4 M	0·5 M	0·7 M	0·9 M
Half-wave potential* V	−1·33	−1·35	−1·34	−1·33	−1·34	−1·34	−1·33

* corrected for the iR drop

TABLE IX

Effect of Concentration of γ-Benzene Hexachloride

Concentration of γ-isomer $\times 10^{-3}$ M	0·4	0·8	1·0	1·5	2·0	4·0	6·0	8·0
Half-wave potential* V ..	−1·34	−1·34	−1·35	−1·35	−1·35	−1·37	−1·37	−1·38

* corrected for the iR drop

TABLE X

Effect of Concentration of the Solvent

Solvent	Dioxane			Alcohol		
Concentration by volume % ..	50	30	20	50	25	15
Half-wave potential* V ..	−1·35	−1·12	−0·96	−1·27	−0·96	−0·89

* corrected for the iR drop

DISCUSSION

Influence of solvent on the polarographic estimation of γ-benzene hexachloride

Reference to Tables II, IV and VII indicates that the diffusion current increases with the decrease in the concentration of dioxane. Similarly, it is noticed that there is a progressive increase in the sensitiveness when the concentration of alcohol in the base solution is diminished (Table VII). Kolthoff and Lingane[22] have stressed the importance of pH on the diffusion current particularly in the case of organic substance. In the present investigation, sodium acetate has been used throughout as the supporting electrolyte which happens to be a very good buffering salt. The measurement of pH of the different base solutions used in this work showed that there was very little change in the pH (8·3–8·6). Hence the change in the diffusion current cannot be attributed to a change in the pH of the base solution. Explanation for the variation of diffusion current with the change in the concentration of the organic solvent should therefore be sought from the Ilkovic[23] equation

$$i_d = 607\, n D^{\frac{1}{2}} c m^{\frac{2}{3}} t^{\frac{1}{6}}$$

where, i_d is the average diffusion current in microamperes, n, the number of electrons involved in the reduction process, D, the diffusion coefficient of the substance (cm.^{2} sec.$^{-1}$), c, the concentration of the reducible substance in millimoles per litre, m, the rate of flow of mercury from the dropping electrode in mg. sec.$^{-1}$, and t droptime in seconds. A change in any one of the factors on the right-hand side of the equation can bring about an alteration in the value of i_d.

Since m, t and c are constant and as it is unlikely that the number of Faradays of electricity involved per mole of the reducible substance would change, the variation of diffusion current can be assumed to be due to a change in the value of the diffusion coefficient. In this connection, it can be pointed out that in polarographic work the value used for the diffusion coefficient is calculated from the equivalent conductivity at infinite dilution. This value may not hold good because the diffusion coefficient under polarographic conditions will be different from the infinite dilution value. In the case of lead the value is 14%[24] smaller in 1 M potassium chloride than at infinite dilution. Experimental work in this laboratory has indicated that the diffusion coefficient of nitrobenzene in aqueous solutions is nearly halved when the base solution contains 50% alcohol. These results support the view that the change in i_d is mostly due to a change in the diffusion coefficient. Further work on the diffusion coefficients is in progress.

Effect of concentration of supporting electrolyte

Heyrovsky[25] and Ilkovic[23] state that the limiting current of an uncharged substance should be entirely diffusion controlled, since neutral molecules are not subject to electrical migration. They predict that the limiting current of an uncharged substance should be constant and independent of the presence of foreign salt. But, they could not verify their statement for lack of experimental data. The results obtained in the present investigation on γ-benzene hexachloride, which is an uncharged molecule, do not support the predictions of these authors. This is presumably due to the change in the diffusion coefficient of the substance.

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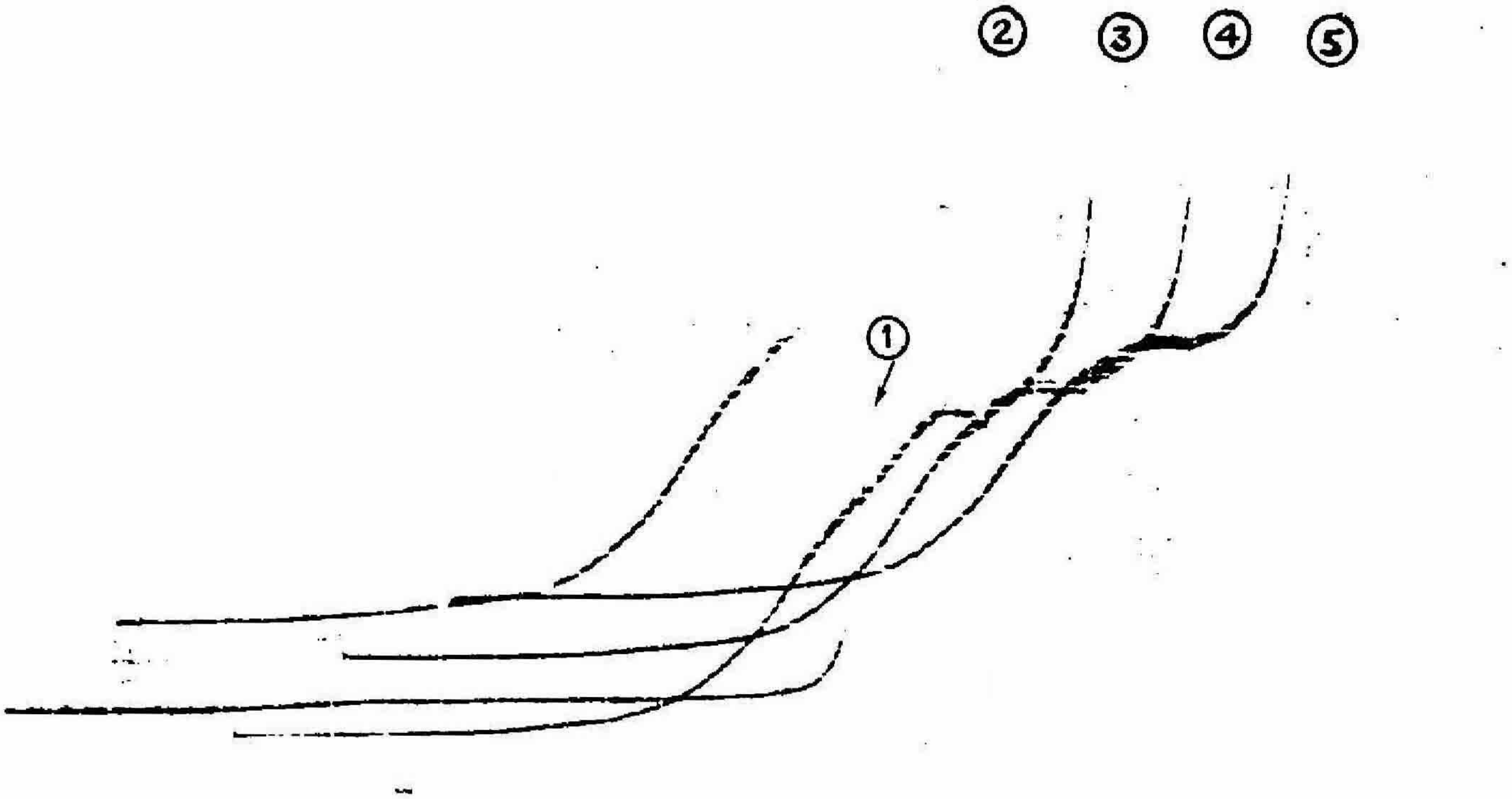

FIG. 1 (*a*). Polarograms of γ-benzene hexachloride (0·505 millimolar) in 50% aqueous dioxane solution containing 0·1 M lithium chloride and different concentrations of sodium acetate. (1) Blank; (2) 0·1 M sodium acetate; (3) 0·2 M sodium acetate; (4) 0·3 M sodium acetate; (5) 0·4 M sodium acetate. Sensitivity: *s*/30.

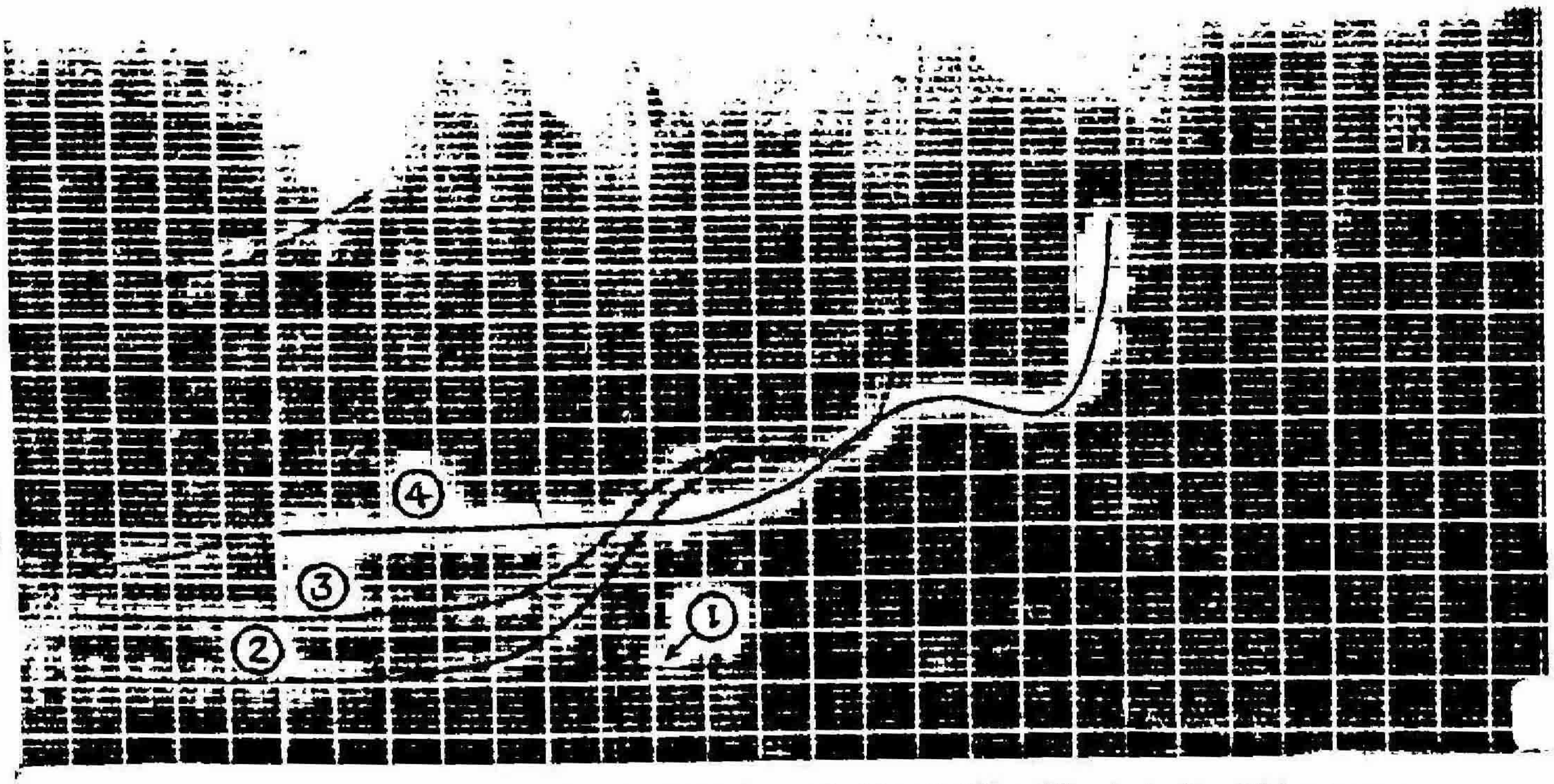

FIG. 1 (*b*). Polarograms of γ-benzene hexachloride (0·505 millimolar) in 50% aqueous dioxane solution containing 0·1 M lithium chloride and different concentrations of sodium acetate. (1) Blank; (2) 0·5 M sodium acetate; (3) 0·7 M sodium acetate; (4) 0·9 M sodium acetate. Sensitivity: *s*/30.

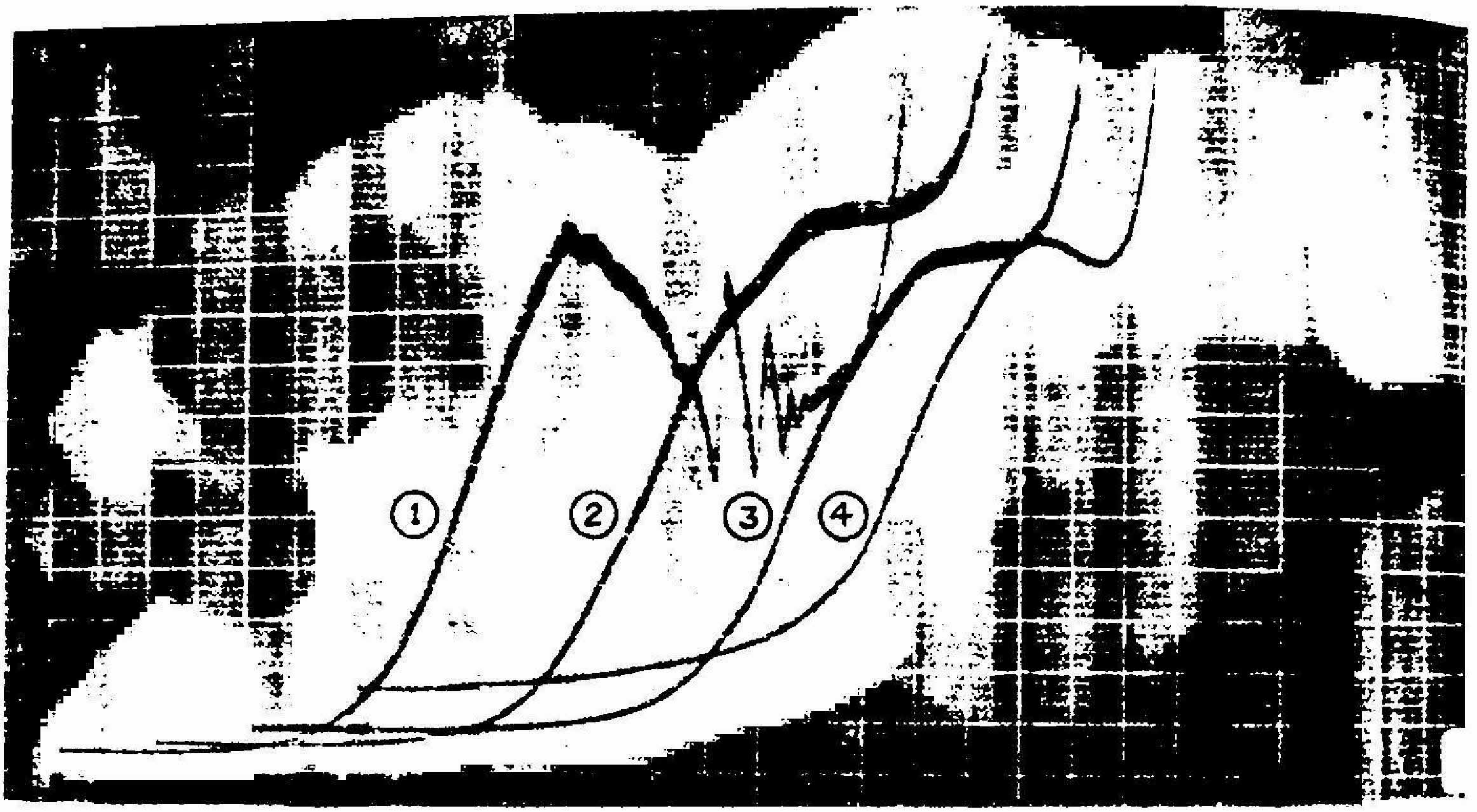

FIG. 2. Polarograms of γ-benzene hexachloride (1·0 millimolar) in (1) 30%; (2) 40%; (3) 50%; (4) 60% dioxane in aqueous solution containing 0·5 M sodium acetate and 0·1 M lithium chloride. Sensitivity: (1) *s*/70; (2) *s*/50; (3) *s*/30; (4) *s*/10.

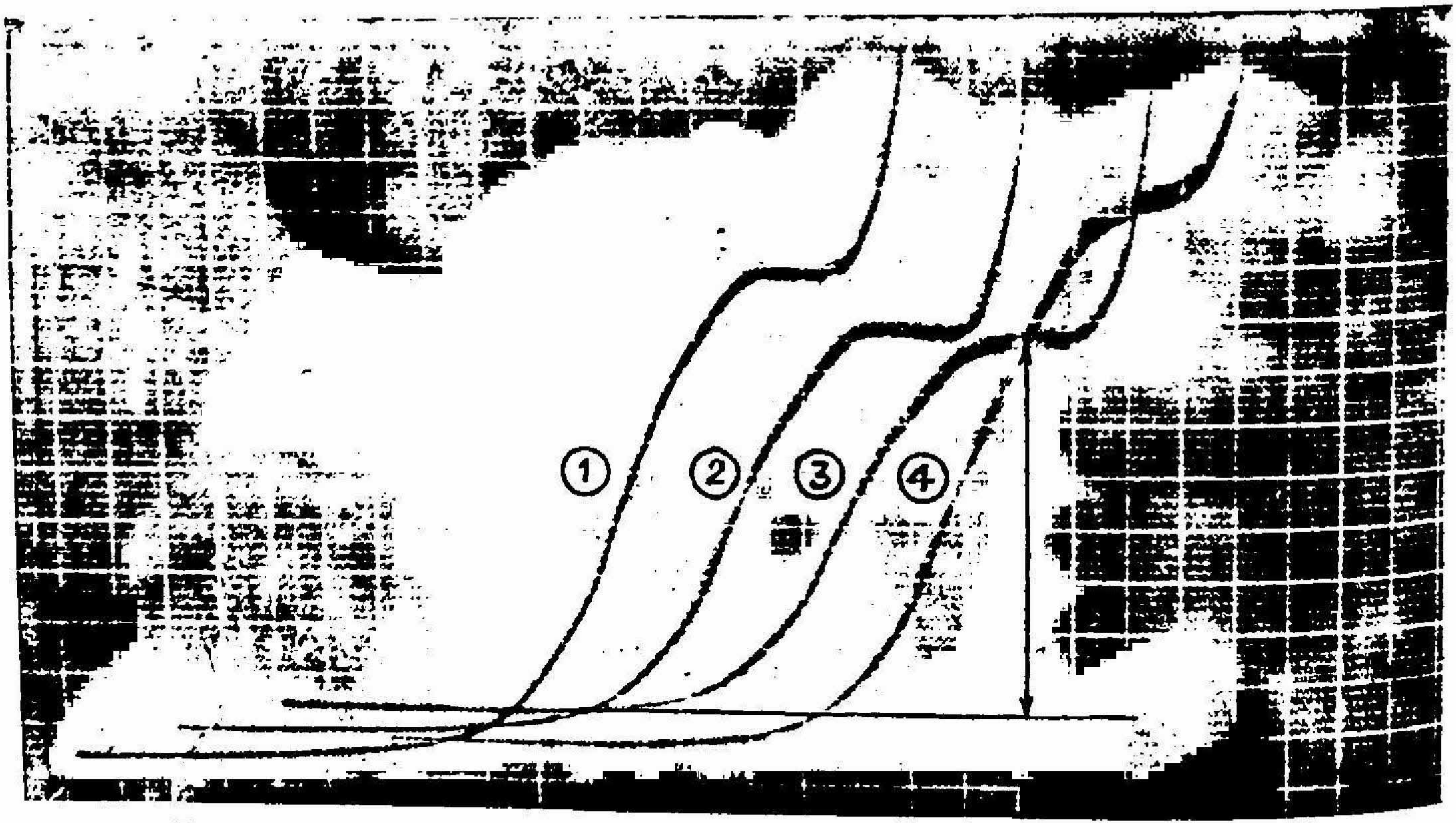

FIG. 3. Polarograms of (1) 0·80; (2) 1·00; (3) 1·50; (4) 2·00 millimolar γ-benzene hexachloride in 50% aqueous dioxane containing 0·5 M sodium acetate and 0·1 M lithium chloride. Sensitivity: (1) *s*/20; (2) *s*/30; (3) *s*/50; (4) *s*/50.

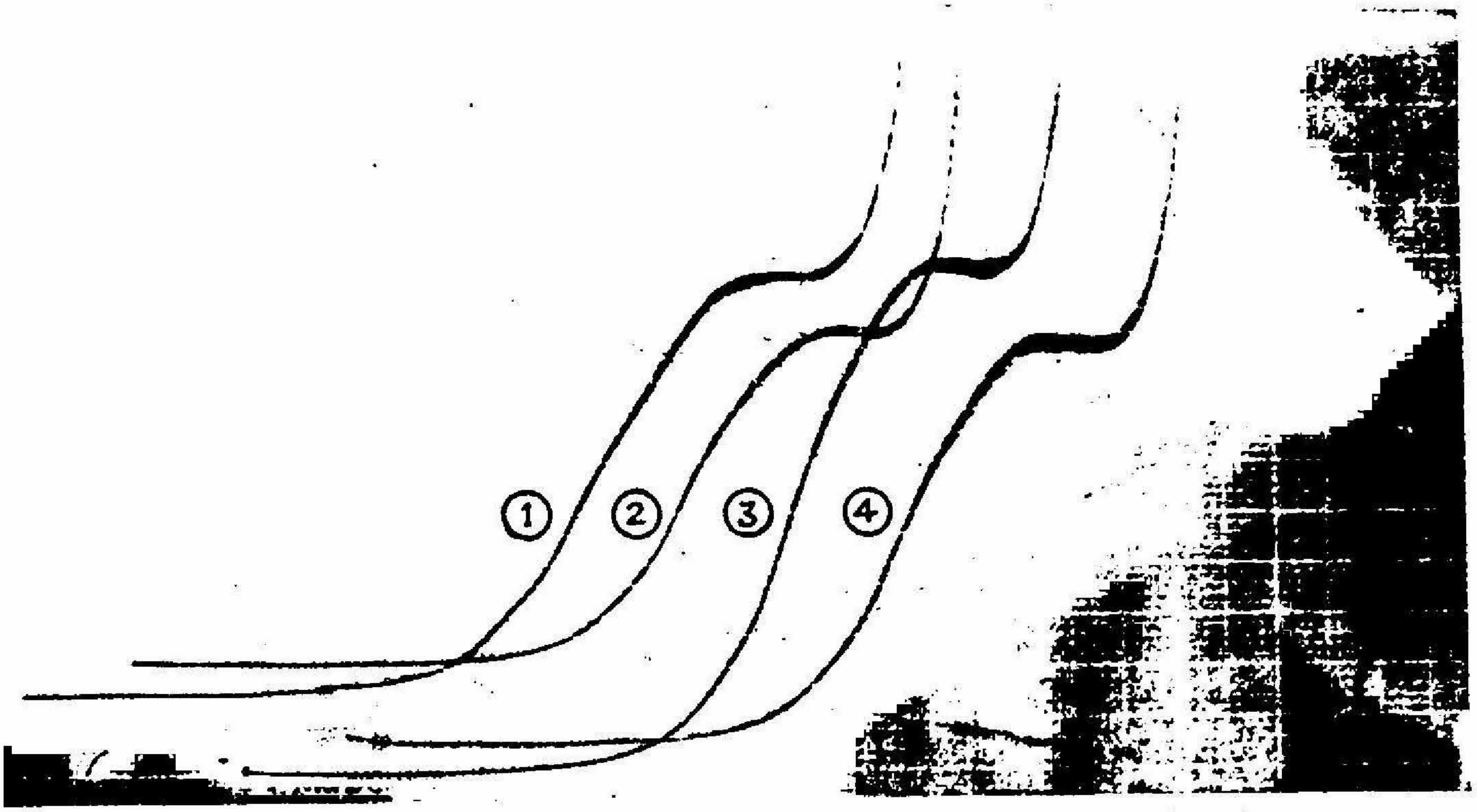

FIG. 4. Polarograms of (1) 0·8164; (2) 1·021; (3) 1·532; (4) 2·042 millimolar γ-benzene hexachloride in 50% aqueous dioxane containing 0·75 M sodium acetate, 0·1 M lithium chloride and 0·001% gelatin. Sensitivity: (1) *s*/20; (2) *s*/30; (3) *s*/30; (4) *s*/50.

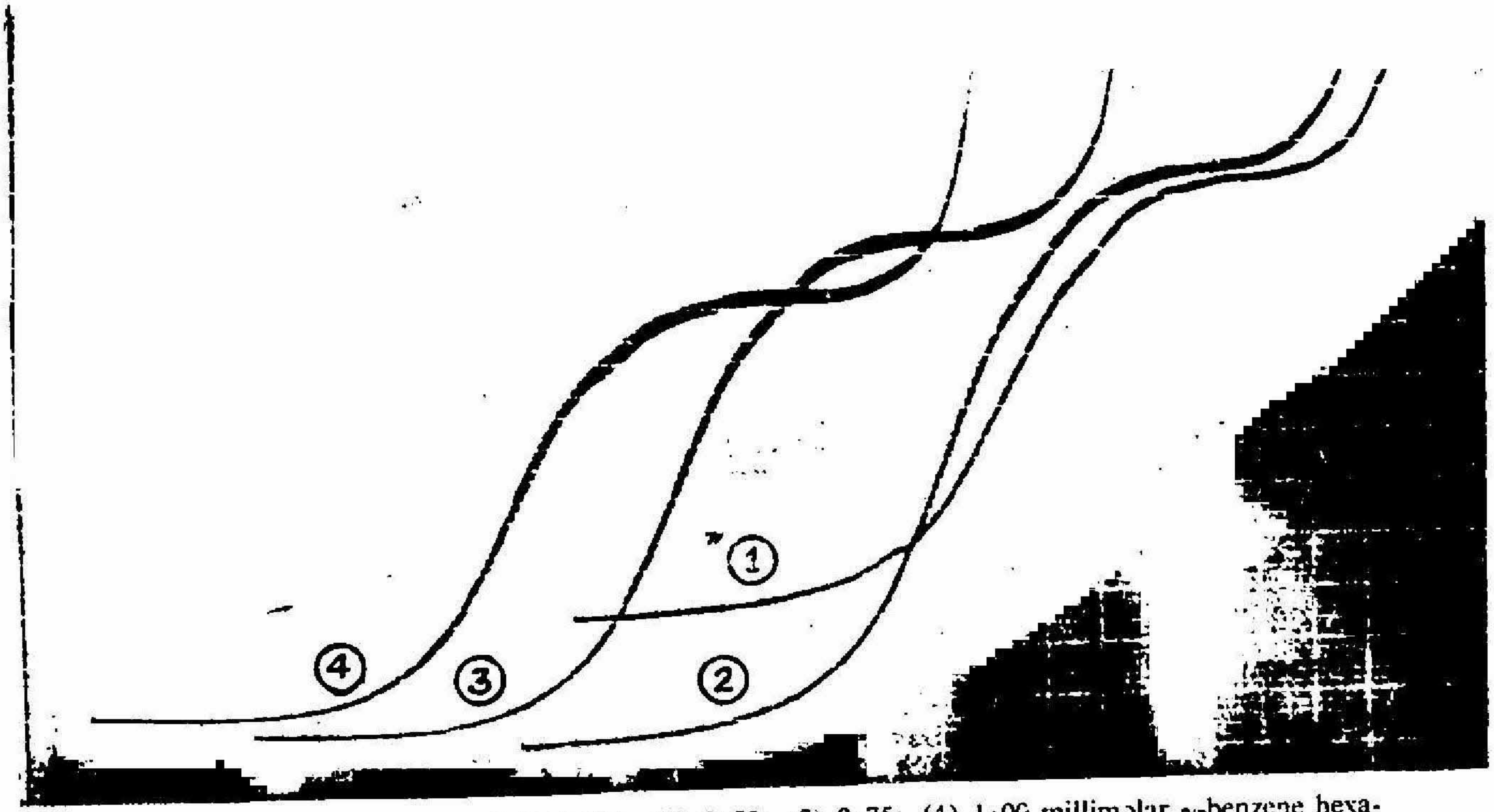

FIG. 5. Polarograms of (1) 0·25; (2) 0·50; (3) 0·75; (4) 1·00 millimolar γ-benzene hexachloride in aqueous solution containing 0·5 M sodium acetate, 0·1 M lithium chloride, 0·002% gelatin and 30% dioxane. Sensitivity: (1) *s*/20; (2) *s*/30; (3) *s*/50; (4) *s*/70.