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Effect of some dialkyl-, diaryl-, and diarylalkyl-disulphide derivatives on copper electrodeposition

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The effect of straight-chained di(ω-sulphoalkyl) disulphides and of diphenyl, dinaphthyl, dibenzyl, or dinaphthylmethyl disulphides with anionic (sulpho), cationic (dimethylamino), or nonionogenic (hydroxy) substituents on the overpotential of deposition of copper from sulphuric acid electrolytes and on the differential capacity of the electric double layer on polycrystalline copper surfaces have been studied. With few exceptions, the sulphoalkyl and sulphoaryl derivatives exhibit a depolarizing effect, the magnitude of which is related to the negative charge of the sulphide sulphur atoms. By contrast, the benzyl and naphthylmethyl derivatives produce strong polarization, more pronounced with dimethylamino compounds, as well as dimethylaminoaryl disulphides. The effect of the disulphides studied on the differential capacity is extremely varied. Four types of concentration dependencies are observed: monotonic increase or decrease, or the appearance of a minimum or maximum. No simple relationship between the structure of disulphide and the pattern of behaviour is apparent. Generally, the alkane derivatives increase the capacity with the exception of di-(3-sulphopropyl) disulphide, while all the aromatic ones, with the exception of di-(p-sulphobenzyl) disulphide decrease it.

1. Introduction

Some dialkyl-disulphide derivatives are widely used as components of brighteners in the electrodeposition of mirror-bright and highly levelled copper coatings in sulphuric acid electrolites [1–3]. Besides the already mentioned properties, dialkyl-disulphide derivatives have been patented [4–7] to give unstrained coatings of high ductility and strength and also to permit the preparation of brighteners without dye components. However, data on the effect of dialkyl disulphides on the electrode processes are rather scarce [8–11] while no data on the effect of diaryl disulphides could be found in the literature.

This paper reports a study on the effect on the cathode polarization and on the capacity of the electric double layer of a series of disulphides, R_2S_2, which can be subdivided into several classes either according to the hydrocarbon skeleton as n-alkane, benzene, or naphthalene derivatives, or according to the hydrophyllic substituent into anionic (sulphonic acids), neutral (hydroxy derivatives) and cationic (dialkylamino derivatives, positively charged in the acid electrolytes used). The compounds studied are listed in the Scheme shown in Fig. 1.

2. Experimental details

2.1. *Materials*

All inorganic reagents were of 'chemically pure' grade and were used without further purification. Commercial samples of compounds 2, 4, 6 and 12 were purified by recrystallization. Compounds 3 and 5 were prepared from the respective bromo sulphonic acids [12, 13] by treatment with sodium thiosulphate followed by oxidation with iodine. The sodium salts of 3 and 5 were recrystallized from 80% ethanol and their purity was determined as described [14]. The synthesis of compound 14 has been described previously [5]. The preparation and purity of the remaining compounds, some of them newly described, is reported in [14].

2.2. *Cathode polarization*

All measurements were carried out in an aqueous basic electrolyte (BE) containing $70\,\mathrm{g\,dm^{-3}}$ $CuSO_4 \cdot 5H_2O$, $170\,\mathrm{g\,dm^{-3}}$ sulphuric acid and $0.09\,\mathrm{g\,dm^{-3}}$ sodium chloride. Each of the studied organic additives was added separately to fresh portions of BE in concentrations $22\,\mathrm{mg\,dm^{-3}}$. Oxygen was purged by bub-

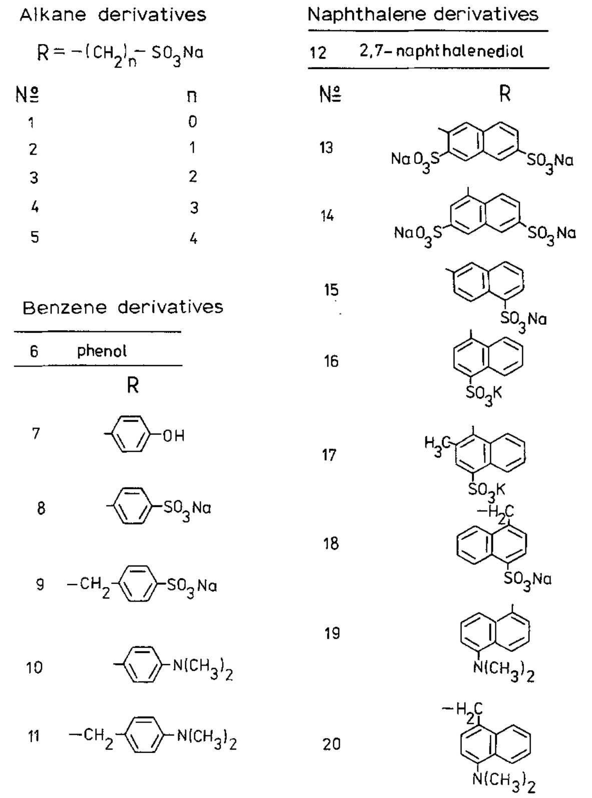

Fig. 1. Scheme for disulphides, R–S–S–R.

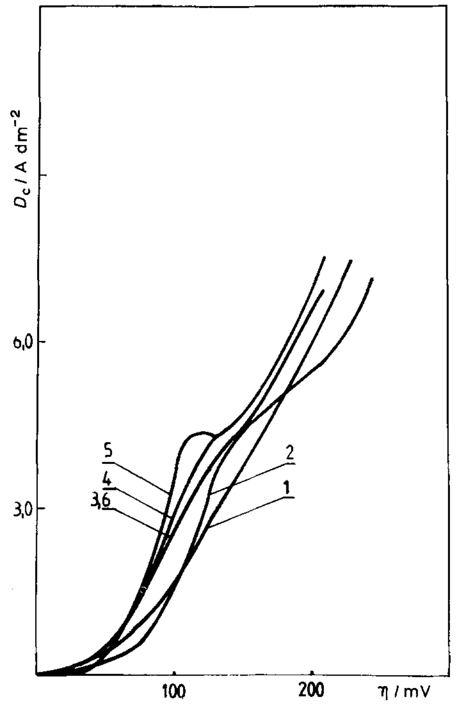

Fig. 2. Polarization curves for the electrodeposition of copper in the presence of alkane disulphide derivatives (22 mg dm^{-3}). Curve (1) BE. Curves and compounds, respectively: (2) 1, (3) 2, (4) 3, (5) 4, (6) 5.

bling pure argon; the bubbling was interrupted during the measurements. The overpotential of the copper deposition was measured in a thermostated glass cell at 25.0 ± 0.1° C with a water seal on a copper coated platinum electrode. The copper coating was formed for 10 min in the BE, before adding each of the studied organic additives, at a d.c. current density of 2 A dm^{-2}. The cathode was directly connected to the reference mercury(I) sulphate electrode through a Luggin capillary.

The polarization curves were recorded under potentiodynamic conditions by means of a potentiostat-galvanostat instrument (Type GWP 673, Germany), and an X–Y recorder (ENDIM 620.02, Germany). The potential was scanned at a rate of 20 mV s^{-1}. The potential range corresponded approximately to a current density range, in the electrolytes studied, of 0–6 A dm^{-2}. As the anode, copper of particularly high purity, OSCh 11-4 TzMTU-03-9-69 (USSR) was used.

2.3. *Electric double layer capacity*

The differential capacity of the electric double layer, C, was measured on a polycrystalline copper electrode as a function of the potential, ϕ, and the concentration, c, of the disulphides. The measurements were carried out by means of an a.c. bridge, Type H-568 [15], at a frequency of 210 Hz. The amplitude of the alternating voltage was 5 mV. Sulphuric acid, 0.5 M, was chosen as support electrolyte as this concentration of the acid is in the range used in industrial electrolytes. The electrochemical cell, the pretreatment of copper electrode and the measuring procedures have been described previously [16].

3. Results and discussion

It has been shown previously [6, 7] that inclusion of various dialkyl or diaryl disulphides in brightening agents for industrial application allows, under certain composition ratios and plating conditions, the deposition of copper coatings with desired properties, such as high ductility, high tensile strength, high microhardness, brightness, levelling, etc. It was also found that appropriate combinations of disulphides could provide coatings possessing a suitable set of these qualities.

The effect of organic additives on the properties of the coating is expected to be determined largely by their behaviour in the electric double layer and their adsorption on the cathode surface. Thus their effect on the capacity of the electric double layer, EDL, and the kinetics of the electrode process may provide insight into their action.

3.1. *Overpotentials*

The polarization curves for three types of disulphides, n-alkane, benzene, and naphthalene derivatives, are shown in Figs. 2–4. All the curves are for the same concentration of disulphide, close to the optimum used in brightening agents. Under similar conditions, a depolarization effect of the alkane sulphonic derivatives 3 [11] and 4 [9, 17] has been previously observed.

Figure 2 illustrates the effect of including methylene groups between the disulphide and sulpho groups in the simple inorganic compound sodium tetrathionate. In the interval 2–3 A dm^{-2}, depolarization increases with the number of methylene groups, $(S(CH_2)_nSO_3Na)_2$; the dependence, however, passes through a maximum

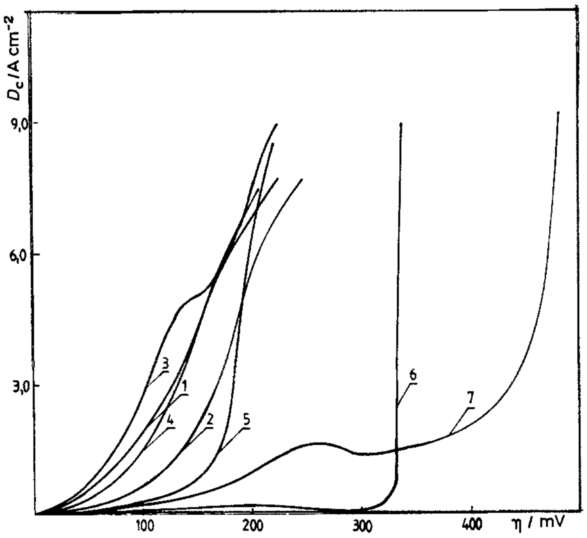

Fig. 3. Polarization curves for the electrodeposition of copper in the presence of benzene disulphide derivatives (22 mg dm^{-3}). Curve (1) BE. Curves and compounds, respectively: (2) 6, (3) 7, (4) 8, (5) 9, (6) 10, (7) 11.

at $n = 3$. At 3 A dm^{-2} the effect of tetrathionate, 1, is relatively small, -10 mV (Fig. 2, curve 2), each methylene group brings about a depolarization increase of about 10 mV (curves 3–5, compound 2–4), to decrease at $n = 4$ to a value of 25 mV (curve 6, compound 5).

It is noteworthy that the effect of compounds 1–5 on the kinetics of the electrode process depends on the potential or the current, respectively; up to a current density of 0.5 A dm^{-2} an increase of the overpotential is actually observed which changes to the above-described depolarization above this value.

The course of the polarization curves for the discharge of copper are significantly different when aromatic disulphides are added to the BE. Figure 3 depicts the curves obtained with benzene derivatives containing hydroxy, sulpho, or dimethylamino groups.

The effect of the benzene ring itself was modelled by the behaviour of phenol, 6, (curve 2) leading to a 36 mV increase in polarization. Attaching this molecule to a disulphide bridge in di-(4-hydroxyphenyl) disulphide, 7 results in a 25 mV depolarization effect (curve 3), apparently due to depolarization action of the disulphide moiety [9, 17]. The sulpho analogue, 8, hardly affects the rate of neutralization of Cu^{2+} at current densities greater than 3 A dm^{-2} and a weak polarizing effect (about 10 mV) for less than 3 A dm^{-2} (curve 4). A marked increase in the overpotential of over 50 mV is observed for the whole investigated interval of D_c. However, (curve 5) when a methylene group is included between the benzene ring and the disulphide group as with compound 9.

A drastic increase in the overpotential of copper deposition occurs on addition of the positively charged dimethylamino derivatives, compounds 10 and 11 (curves 6 and 7, respectively).

The polarization curves observed for the naphthalene derivatives are shown on Fig. 4. The effect of substituents on their behaviour is similar in its general trends to that described above for the benzene derivatives.

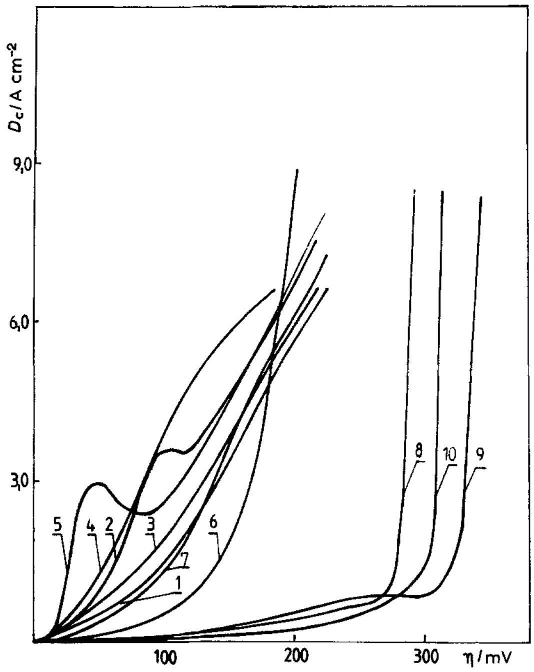

Fig. 4. Polarization curves for the electrodeposition of copper in the presence of naphthalene disulphide derivatives (22 mg dm^{-3}). Curve (1) BE. Curves and compounds, respectively: (2) 12, (3) 13, (4) 14, (5) 15, (6) 16, (7) 17, (8) 18, (9) 19, (10) 20.

The neutral molecule chosen as a model for the effect of the naphthalene ring, 2,7-dihydroxynaphthalene, 12, contrary to phenol, at 3 A dm^{-2} showed a depolarization of about 50 mV. At higher potentials (around 100 mV) however, a peak current for a pre-process is observed.

The naphthalenesulphonic acid derivatives, 13–17, show effects on the overpotential in the range -58 to $+27$ mV (curves 3–7). No relationship is apparent linking the effect to the number of sulphogroups or the position of the disulphide bridge with respect to the ring or the substituent(s). Compound 17 (curve 7) is a special case where the disulphide bridge is severely sterically hindered. Although an unambiguous interpretation is not possible, this disulphide exhibits practically no effect on the electrochemical process. It should be noted that in the case of compound 15 a strong peak current appeared at overpotentials of 50 mV, similar to that with 2,7-dihydroxynaphthalene.

The effect of introducing a methylene group between the aromatic sulphonic and the disulphide moieties, similarly to the benzene compounds, causes a polarization effect but of much greater magnitude (compound 18, curve 8) when compared to the similar structure 16.

Also in agreement with the observation with the benzene derivatives, the positively charged species 19 and 20 show very large polarization effects (curves 9 and 10).

The highly diverse behaviour of the disulphides studied (in order to make the example clear, Table 1 summarizes part of the data for the overpotential of copper deposition at 3 A dm^{-2} and of the capacity of the electric double layer for the corresponding potential) is difficult to explain. The most probable reason is the occurrence of an extra 'jump' in the potential in the dense part of the electric double layer as a result of

Table 1. Selected data for copper electrodeposition overpotential, EDL differential capacities and degrees of coverage in the presence of disulphides

Compound Ref. Scheme	$\Delta\phi$* (mV)	ΔC† (μF cm^{-2})	Θ (%)	*Compound Ref. Scheme*	$\Delta\phi$ (mV)	ΔC (μF cm^{-2})	Θ (%)
1	−10	−0.2	65	11	314	2.4	72
2	−23	−4	76	12	−54	6.5	81
3	−30	−9	82	13	−10	1.5	37
4	−40	10.6	85	14	−58	5.5	35
5	−25	−8.5	80	15	−28	10	80
6	36	4.5	39	16	27	10.5	45
7	−25	9.2	87	17	0	7	62
8	3	4.5	25	18	142	7.4	82
9	53	−12	89	19	190	13.2	92
10	204	8	74	20	167	5	75

* At DC = 3 A dm^{-2}. A minus sign indicates a depolarization effect.

† At the potential of neutral charge of copper. A minus sign indicates capacities greater than that in the supporting electrolyte.

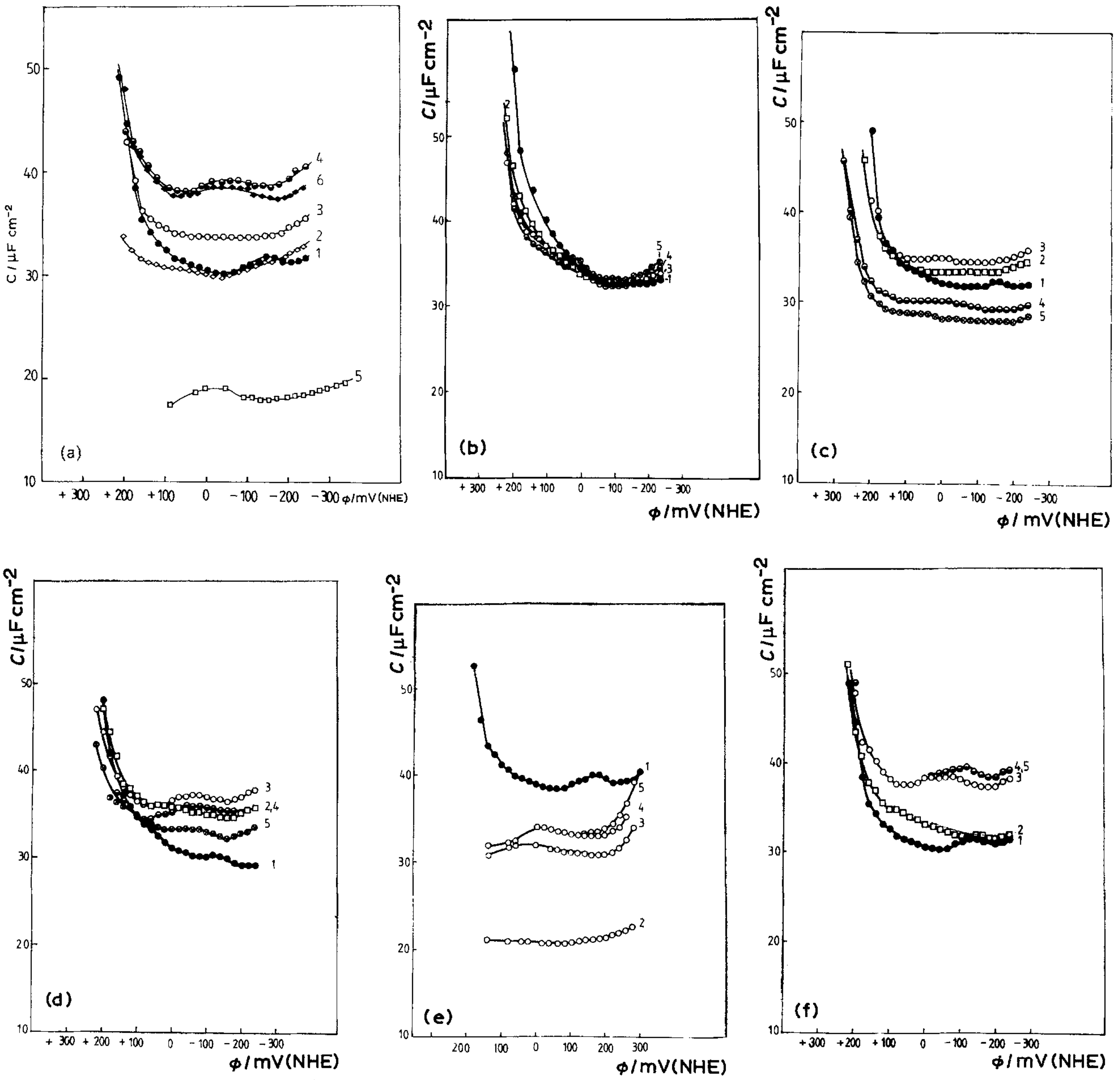

Fig. 5. (a) C–ϕ curves in the presence of alkane disulphide derivatives (22 mg dm^{-3}). Curve (1) SE (0.5 M sulphuric acid). Curves and compounds, respectively: (2) 1, (3) 2, (4) 3, (5) 4, (6) 5. (b) [NaO_3S–S–]$_2$, (c) [$NaSO_3$–CH_2–S–]$_2$, (d) [$NaO_3S(CH_2)_2$–S–]$_2$, (e) [NaO_3S–$(CH_2)_3$–S–]$_2$ and (f) [NaO_3S–$(CH_2)_4$–S–]$_2$. C–ϕ curves for compounds 1–5, respectively at various concentrations. Curves: (1) 0, (2) 5.5, (3) 11, (4) 22 and (5) 44 mg dm^{-3}.

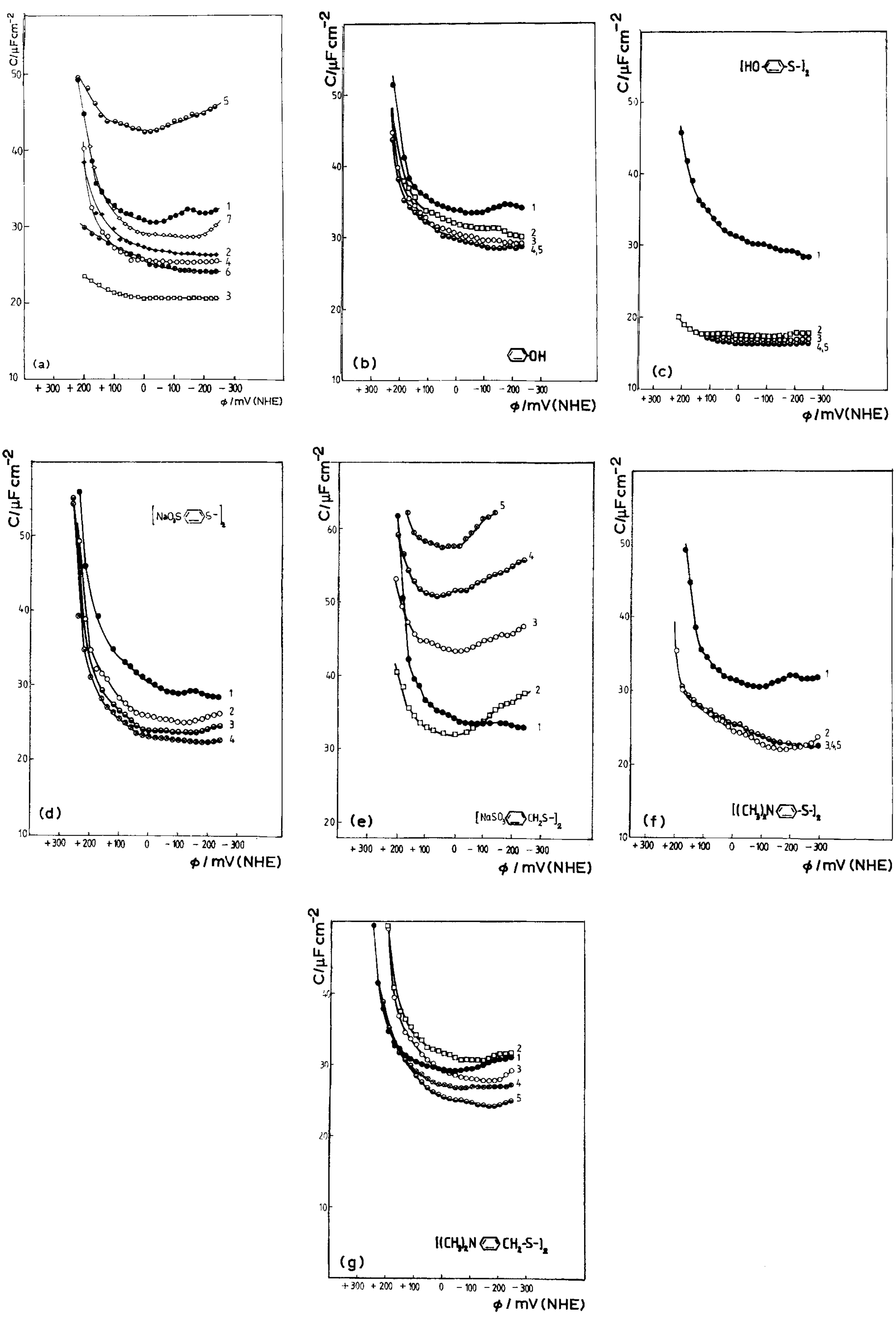

Fig. 6. (a) C–ϕ curves in the presence of benzene disulphide derivatives (22 mg dm^{-3}). Curve (1) SE (0.5 M sulphuric acid). Curves and compounds, respectively: (2) 6, (3) 7, (4) 8, (5) 9, (6) 10, (7) 11. (b), (c), (d), (e), (f) and (g) C–ϕ curves for compounds 6–11, respectively, at various concentrations. Curves: (1) 0, (2) 5.5, (3) 11, (4) 22 and (5) 44 mg dm^{-3}.

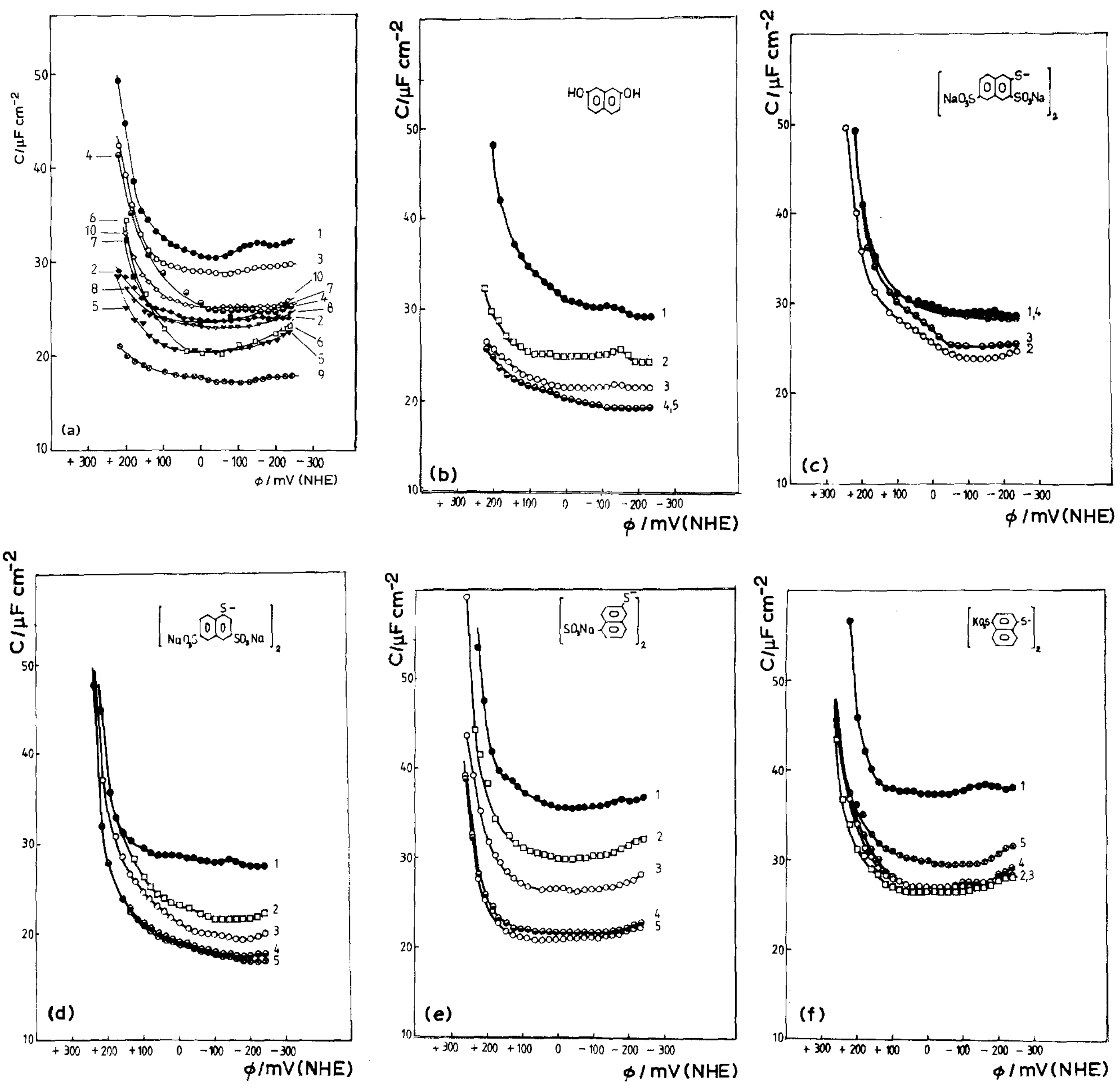

Fig. 7. (a) C–ϕ curves in the presence of naphthalene disulphide derivatives (22 mg dm^{-3}). Curve (1) SE (0.5 M sulphuric acid). Curves and compounds, respectively: (2) 12, (3) 13, (4) 14, (5) 15, (6) 16, (7) 17, (8) 18, (9) 19, (10) 20. (b), (c), (d), (e), (f), (g), (h), (i) and (j) C–ϕ curves for compounds 12–20, respectively, at various concentrations. Curves (1) 0, (2) 5.5, (3) 11, (4) 22 and (5) 44 mg dm^{-3}.

the orientated adsorption of the dipoles of the disulphides which are directed with their negative poles towards the cathode surface [18–20]. Also, the formation of complexes between the growing copper surface and the disulphides occurs. Thus, a decrease of the effective electron density (δ-) of sulphur atoms, makes the adsorption of sulphur containing organic molecules possible. This leads to an acceleration of electron transfer caused by the formation of complexes through bonding of sulphur atoms to the neutral copper atoms of the growing metal surface [21]. Other authors [22, 23] attribute the depolarization effect of sulphur-containing surfactants to their desulphurization on the active centres of growth leading to the formation of sulphides on the surface, which, as galvanic microelements, can act as additional nucleation centres. For disulphides in particular [10], the activation of the surface has been related to thiols formed during the electrodeposition process.

Our previous studies on the effect of the alkyl disulphide 4 on the EDL [16, 24] and the copper disulphides observed by means of Auger spectroscopy of a copper surface immersed in aqueous solution of the disulphides studied in [25] indicated that both adsorption and desulphurization are involved in determining the overpotentials of discharge.

The large set of data on the effect of disulphides on the overpotentials of Cu^{2+} discharge prompted an attempt to correlate the effect with their structures. At the outset in view of the many factors involved, such correlations are expected to hold within a given type of structure.

With a few exceptions, the overall quantitative effect is in accord with the well known observation [26] that negatively charged surfactants have a depolarizing effect on the discharge of cations, while neutral and positively charged ones have a polarizing effect.

An obvious parameter to gauge the adsorption

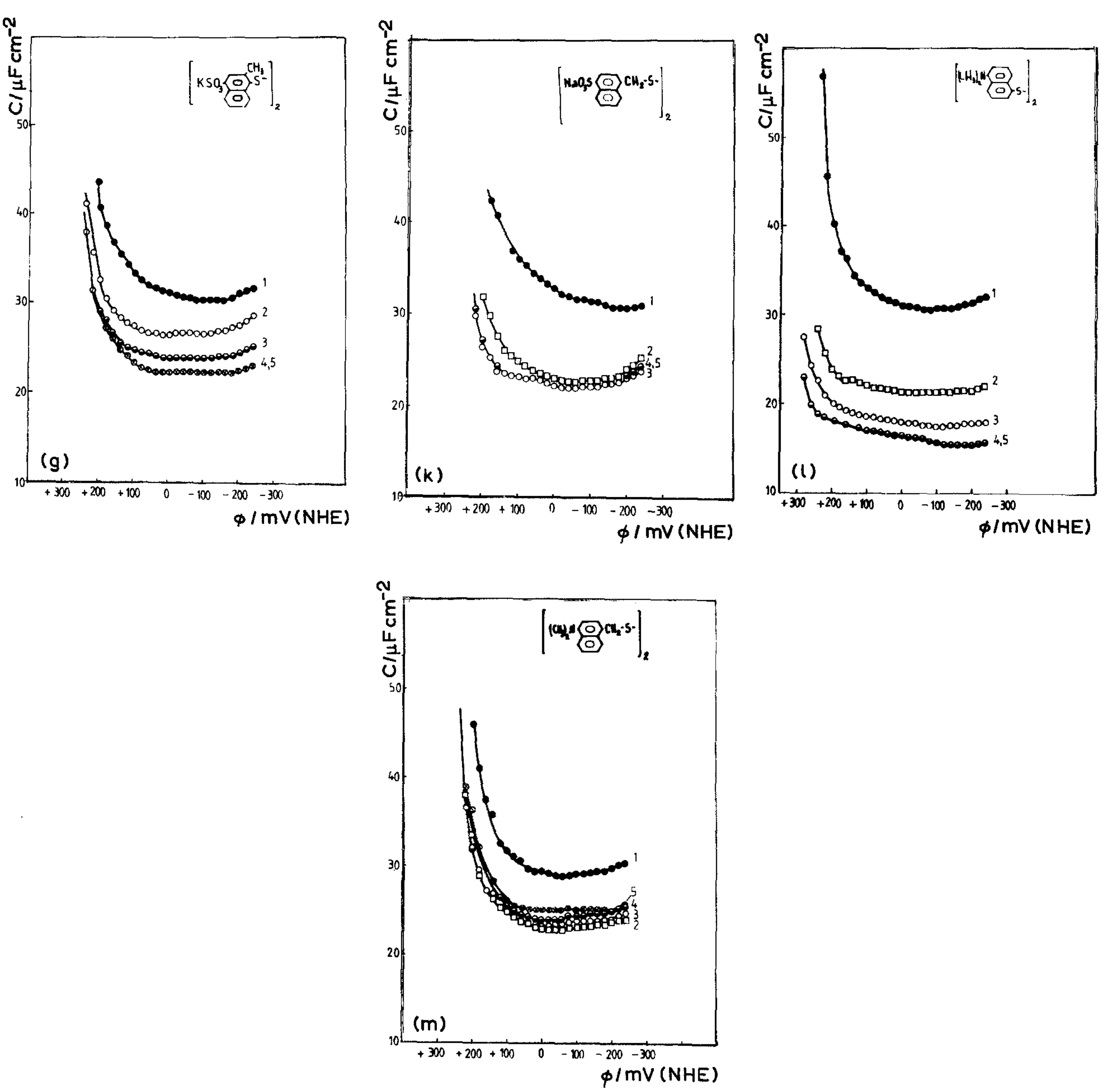

Fig. 7. Continued.

capability of the disulphide group, as well as its tendency to form complexes, is the negative charge of the sulphur atoms. The increase in overpotentials in the series of alkane sulphonic acids 2–4 accords with the strong increase in the basicity of the amino group in the analogous ω-aminoalkane sulphonic acids [27]. Interestingly, according to the theoretical considerations of Bell [27] this effect goes through a maximum, as observed with the overpotential in the presence of 5.

The electron density on sulphur also appears to confirm the observed behaviour of the naphthalene sulphonic acids 12–16. The charge on the sulphur should be smaller when its lone pairs can conjugate with the sulpho groups. In compounds 14 and 15 there is no conjugation between the lone pairs on sulphur and the sulpho group(s) and these compounds with expected large negative charge effect. On the basis of this dichotomy, conjugated *versus* nonconjugated, the comparison of compounds 13 and 17 and, respectively 14 and 15, indicates that introduction of a second negatively charged sulpho group contributes to a depolarization of some 30 mV at 3 A dm^{-2}.

The strong polarization effect of the sulphoarylmethyl disulphides 9 and 18, in contrast to aromatic ones, can be understood in terms of concurrent sulphide group and aromatic nucleus adsorption (the former depolarizing and the second polarizing) and the geometry of the two types of compounds. On a planar metal surface the aromatic ring prefers a position parallel to the surface. In the aromatic compounds the neighbouring sulphur atom is in the plane of the ring and is thus in direct contact with the metal and interaction can occur. In the case of arylmethyl disulphides such simultaneous contact can only be achieved at the expense of considerable strain so that aromatic nucleus adsorption takes place at the expense of the contacts of the disulphide group and its assumed depolarization effect, respectively. With dimethylamino derivatives, stronger polarization in the case of arylmethyl derivative is observed with the benzene pair 10 and 11, but not with the naphthalenes 19 and 20.

The electronic effect of the positively charged dimethylamino-group is similar to that of the sulpho group (as judged from the σ-values [28]), so that the large differences in the magnitudes of the polarization effects (sulpho from -54 to 142 mV and dimethylamino from 167 to 314 mV) of the two types of aromatic compounds cannot be related to the partial charge on the disulphide sulphur. Apparently this is a superposition of a strong electrostatic effect on the positively charged dimethylamino groups on the overpotential.

3.2. *Capacitance of the electric double layer*

In relation to the above results it was of interest to obtain quantitative results on the effect of the disulphides studied on the capacitance of the EDL and to determine the degree of coverage Θ, from the C–ϕ plots [29], or their adsorption capacity, respectively. Some of the results obtained, including concentration dependencies, are presented in Figs. 5–7.

Figures 4a, 5a and 6a show the effect of the alkane, benzene and naphthalene derivatives at the same concentration, 22 mg dm^{-3} (within the groups the changes in the molarities are small). All alkane derivatives with the exception of compound 4 increase the capacity, while aromatic disulphides again decrease it with one exception (compound 9).

However, inspection of the concentration dependencies of the capacity presented on the remaining part of the figures show these to be rather complex. Complex behaviour of some sulphur containing compounds has been observed before, e.g. xantogenate on mercury surfaces [30] and in the case of the propane derivative 4 has been previously reported [17]. The differential capacity of the latter compound is characterized by a sharp decrease at low concentrations followed by a rise in capacity to below that of the SE (Fig. 5e). The same pattern is followed in the concentration dependencies of the naphthalenedisulphonic acid 13, the naphthalene sulphonic acid 16, and by the dimethylaminonaphthylmethyl derivative 20 (Fig. 7c, f and j).

A second type of behaviour is observed with the disulphide derivatives of the short-chained alkanesulphonic acids 2 and 3, with which an initial increase of the capacity goes through a maximum (Fig. 5c and d). Two of the compounds studied exhibit a monotonic rise in the differential capacity with increasing concentration: di-(4-sulphobutyl), 5, and di-(4-sulphobenzyl) disulphide 9 (Figs. 5f and 6e). The rest of the compounds, for all concentrations studied, influence the capacity of the electric double layer as usual, i.e. increase in their concentration leads to a decrease in the electric double layer capacity.

Attempts to rationalize the relationship between the structure of the disulphide and its effect on the capacitance and its complex concentration dependencies proved unsuccessful in providing a comprehensive model for the disulphides studied. The preferred conformation of the disulphides is with two organic radicals at right angles to each other. Rotation around the S—S bond to bring the torsion angle to 180°, which would allow both radicals to come into contact with the surface, can take place at some expense of energy. A recent estimate of the barrier to this rotation, the maximum of which is at 180°, is 4 kcal mol^{-1} [31]. The complex pattern of the concentration dependencies suggests a restructuring of the adsorbed organic layer. One possibility is that, at low coverages, the organic molecules pivot with the disulphide bridge with the two radicals in contact with the surface, and at higher coverages, the interaction between the organic molecules freeing one of the radicals. This effectively increases the distance between the charged groups and the metal surface and is in quantitative agreement with the maximum in capacity observed with the methane and ethane derivatives 2 and 3. However, the behaviour of the next homologues of alkane sulphonic acids shows the role of other factors. The reason for the strong initial decrease in capacitance observed with the propane derivative 4, as well as with some of the naphthalene derivatives, is not clear. An interesting observation is that the two compounds for which a monotonic increase of the capacitance with concentration is observed, the butane derivative 5 and the toluene derivative 9, have practically the same distance between the end carbon atoms, *viz* 0.38 nm (extended conformation) and 0.42 nm, a distance usually considered to be the thickness of the Helmholz layer.

The neutral disulphide 7 (Fig. 6c) is characterized by a strong decrease in the capacity of the electric double layer over a wide range of potentials and is most probably indicative of the dominance of the effect of adsorption of the disulphide bridge. Similar curves are observed at high coverages with arylmonosulphonic acids showing a 'normal' concentration dependence (Figs. 6d and 7e, g, h) and, significantly, at some of the minima in capacity (Figs. 5e and 7e, f, j).

The suggestion that the high overpotentials caused by the benzyl derivatives may be due to concurrent adsorption of the aromatic rings is supported by the patterns depicted on Fig. 6e and g. The strong shifts of the minima in the C–ϕ curves to positive potentials for the sulpho acid and to negative ones for the dimethylamino compound shows the involvement of respective charges on the surface, and further, that the very high overpotentials observed with the amino disulphides 10 and 11 can be assigned to the superposition of an electrostatic effect.

In Table 1 the data for the calculated surface coverages [29] at a concentration of 11 mg dm^{-3} are compared with the values of the overpotentials at the practically important current density of 3 A dm^{-2}. There is no direct relationship between two sets of values. With most of the disulphides studied high degrees of surface coverage are observed. The latter with sulphonic acid derivatives, alkane and aromatic with the ring directly attached to the disulphide bridge, are associated with a depolarization effect. By contrast, high surface coverages with the dimethylamino and arylmethyl derivatives correspond to high overpotentials for the electrodeposition of copper.

It is of interest to note that, of the diaryl disulphides studied, bright copper deposits were obtained [32] on those showing $\Theta > 80\%$ and $\Delta\phi > 50\,\mathrm{mV}$ and that such values for these parameters were previously observed with brightening agents containing cationic dyes [24]. The reflectivity and levelling ability of the copper deposits is greatly enhanced in the case of disulphides with dimethylamino substituents.

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