1. N. N. Feodos'ev, Zhur. Fiz. Khim., 12, 291 (1938).
2. M. M. Popov and V. P. Kolesov, Zhur. Obshch. Khim., 26, 2385 (1956).
3. V. P. Kolesov, I. E. Paukov, and S. M. Skuratov, Zhur. Fiz. Khim., 36, No. 4 (1962) [Russ. J. Phys. Chem., in the press (1962)].
4. Proceedings of the Fourth Conference on Low-Temperature Calorimetry, Chem. Eng. News, 27, 2772 (1949).
5. A. A. Sklyankin and P. G. Strelkov, PMTF, 2, 100 (1960).
6. G. Furukawa, R. McCoskey, and G. King, J. Res. Nat. Bur. Stand., 47, 256 (1951).
7. A. Cole, J. Hutchens, R. Robie, and J. Stout, J. Amer. Chem. Soc., 82, 4807 (1960).
8. W. Osborne, E. Westrum, and H. Lohr, J. Amer. Chem. Soc., 71, 2737 (1955).
9. R. Busey, J. Amer. Chem. Soc., 78, 3263 (1956).
10. T. Davies and L. Staveley, Trans. Faraday Soc., 53, 19 (1957).

Lomonosov Moscow State University

Received 21st September 1961

A DEVICE FOR AUTOMATICALLY REPRODUCING AND REMOVING STATIONARY DROP ELECTRODES

A.Ya.Gokhshtein and Ya.P.Gokhshtein

Experimental conditions in polarography require the surface of a polarisable electrode to be periodically renewed. Nowadays the most widely used polarisable electrode is the dropping mercury electrode, which is renewed by means of a continuous natural mercury drop formation from a capillary. In this method the drops of mercury that serve as electrode increase in diameter continually, until they reach a certain size, when they break away spontaneously. But such an electrode is inconvenient for polarography using an oscilloscope: the potential–current curve is recorded for the lifetime of a single drop, and so during the time of recording (about one second) the electrode surface area varies continuously, the start of the curve corresponding to one area and the end to another, which makes the calculation extremely awkward. A further difficulty arises because the growing drop exists for such a short while that the electrode cannot be used for lengthy accumulation of substances in amalgam.

These circumstances have led to the use of stationary drop electrodes[1-4].

Together with methods of obtaining drop electrodes, others have been reported for the forced removal of the spent electrode. Various devices have been described[5-8] using a hammer, located outside the solution, that strikes the capillary through a tube, causing the drop to detach itself. These methods call for the capillary to have an elastic or free linkage to the mercury reservoir and to the container for the liquid under test. Another removal method, proposed by Stankoviansky, does not involve any impact on the capillary: an L-shaped blade on a long shaft is made to rotate in a bearing by a motor driving through a pulley transmission, so that it brushes against the drop and knocks it off[9].

This paper describes a device for automatically reproducing and removing stationary drop electrodes. A stationary mercury drop with a given fixed area is obtained by automatically raising a needle that closes the mouth of a capillary, for a closely controlled time interval measured in tenths of a second, using a solenoid for the purpose. The drop runs out of the capillary while the needle is raised, and remains hanging from the end after the needle has returned to its rest position. In practice it was found convenient to regulate the drop size both by the height to which the needle was raised, and also by the duration of the voltage pulse applied to the solenoid. For a capillary with an internal diameter of 0.2 mm and a suspended drop with a diameter of 0.3–1.5 mm, the needle lift required was a few tenths of a millimetre. For the drop size to be reproducible, one must prevent any chance of friction or of deviation by the needle from its correct path. Sliding guides would be unsuitable here, since while reducing friction by increase of clearance they also increase the possible side-play. Hence the apparatus (Fig. 1) uses elastic guides: a flange screwed to the blunt end of the needle is attached to the fixed structure by means of three radial springs at an angle of 120° to one another. The side of the needle's sharp end is in sliding contact with the roughly 90° conical mouth of the capillary, and experiments have shown that this sliding motion does not prevent the production of drops of reproducible size; so a single ring of three springs was found adequate to stabilise the needle in the vertical position. The distance between the mouth and the end of the capillary is 2 cm, and the glass tube connecting it to the mercury reservoir is 5 cm long including the ground section which fits into the top of the electrolyte vessel. The mercury above the capillary mouth is connected to that in the capillary by a platinum wire fused into the glass: if a needle without an insulating coating is used (*e.g.* one made of carbon steel), then it also serves to make the contact. The flange on the needle also serves as the armature of the solenoid. The apparatus contains two systems for producing two stationary drop electrodes of given areas, capable of working simultaneously.

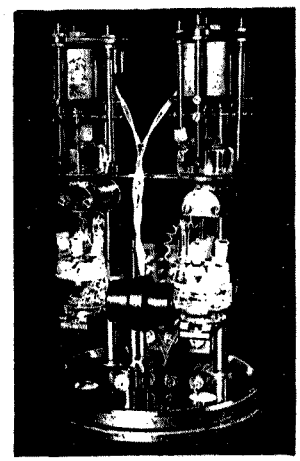


Fig. 1. Experimental model of the apparatus.

After the stationary electrode has been formed for a given length of time, it is used for the recording of the voltage–current characteristic of the solution under test. The spent drop electrode is then automatically removed by a magnetic rocker-arm actuated by the field of a solenoid and rotating in a vertical plane. The two rocker-arms work in parallel and are driven by a single solenoid located between the electrolyte vessels. The rocker-arm (Fig. 2) is a glass tube 18 mm long and 3.5 mm in external diameter, sealed at both ends and containing an iron core. Two glass axles are fused to the cylindrical section, and serve to support the arm on a pair of glass hooks fixed to the cover of the vessel. In operation the hooks and rocker-arm are immersed in the solution inside the vessel, and the drop is removed by the direct impact of one end of the arm.

The use of a rocker-arm to remove the drop electrode has several advantages. Firstly, quite a small magnetic field is enough to rotate the arm about its axle, since it is nearly balanced; what is more, the arm is not only attracted towards the solenoid but also orientates itself in the field like a compass needle. Secondly, the arm is made to return to its initial position, which is important if the removal of the electrode is to be reproducible, by the fact that one half of it is slightly longer than the other. When the solenoid current is interrupted, the arm returns spontaneously to the resting position, in which its outer end is in contact with a glass stop. The tip of the capillary serves as the other endstop, which the arm hits when it dislodges the drop.

In removing the spent drop electrode, the rocker-arm fulfils another useful function at the same time: it agitates the solution round the electrode before a new one is formed, and so eliminates the local exhaustion of the solution associated with electrolysis at the previous drop, which may otherwise impair the results considerably. When the apparatus is used for the accumulation of substances in an amalgam over a long period of time, the rocker-arm is set up so that it misses the electrode but stirs up the solution.

The dislodging of the spent drop by means of the rocker-arm, the lifting of the needle to produce a fresh drop electrode, and the supply of a pulse of polarising voltage to the electrode — these form the working cycle of the apparatus, which can be repeated many times. The required time intervals between operations in the cycle are maintained by means of a synchroniser unit (Fig. 3). A rectangular voltage pulse taken from the left-hand anode of V1 is differentiated and amplified by the right-hand half of V2, and the amplified pulse at its anode is used to trigger the flip-flop V3. The positive-going pulse at the right-hand anode of V3 is amplified by the left-hand half of V2, in whose anode circuit the rocker-arm solenoid RL2 is connected in parallel with the relay RL3 that triggers the flip-flop in the polarograph providing the delay for the pulse of polarising voltage. The trailing edge of the pulse at the left-hand anode of V3 is differentiated and then amplified by the right-hand half of V4, whose anode circuit contains the solenoid RL1 that lifts the needle. The duration of the working cycle is determined by the value of the resistance brought into circuit by the switch SW, and can be varied from a few seconds to tens of seconds. The interval between the operation of the rocker-arm and the lifting of the needle is 1.5 sec (this can be adjusted by varying the value of the capacitor shown as 0.01 μF in Fig. 3, up to 2 μF). If it is required to work for a long while with one stationary drop, then a single drop-production cycle is performed, after which the solenoids are open-circuited for the prescribed time. The mercury drop thus suspended can function for a long time, and can be replaced by closing the solenoid circuits again.

For the prolonged-accumulation mode of operation, the needle-lift solenoid is disconnected but the rocker-arm solenoid continues to work; the rocker-arm is then used to stir the solution round the suspended drop electrode regularly and reproducibly. The stirring period is from one to several seconds. To prevent the arm from hitting the drop in this mode of operation, the whole electrolyte vessel is displaced downwards in relation to the capillary by lowering its support through 1–2 mm. The guide bush of this support is fitted with a ratchet device that serves to hold the vessel in its working position, and this ratchet also regulates the vertical displacement of the vessel. If the accumulation experiment has to be carried out in an inert-gas atmosphere with all the ground-glass joints to the cover firmly made, then the arm is kept free of the drop not by displacing the vessel but by weakening the action of the solenoid on the arm. This is achieved either by shunting the solenoid or by altering its position vertically. It is also possible to introduce an extra endstop through one of the orifices in the cover to restrict the rotation of the arm.

Alternative designs can be suggested for parts of the instrument. For example, the needle flange with its

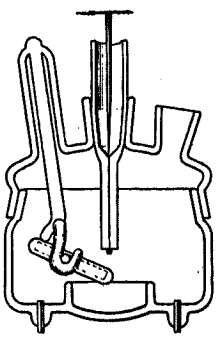


Fig. 2. Electrolyte vessel with rocker-arm resting on glass hooks; needle tip shown above.

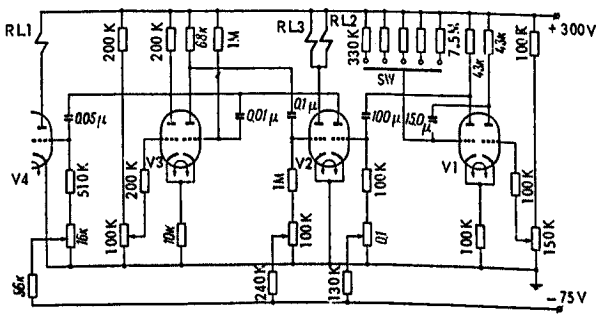


Fig. 3. Synchroniser unit circuit.

springs can be located inside the mercury reservoir, which is designed as a cylinder open at the top, the springs being fixed at their outer ends to an elastic tie-ring located from inside in an annular depression in the cylindrical section of the reservoir. This is tightly closed at its top end by a diamagnetic plate into which the solenoid armature is screwed. Through an orifice at the side, the reservoir can be periodically connected, *via* a ground joint, either to the atmosphere or to a space filled with an inert gas. If shaped plate springs are used, their ends can be clamped between the top edge of the reservoir and the cover plate.

The experimental model of the apparatus (Fig. 1) was made up according to the authors' drawings, and was 27 cm high with a base 18 cm in diameter. It was tested continuously for two and a half months, during which it went on reproducing stationary drop electrodes of constant surface area without a failure. Fig.4 shows two current–time oscillograms taken with two stationary drop electrodes produced one after the other but separated by several cycles of operation. The electrode potential was fixed at 0.8 V relative to the mercury in the base, and the solution was 10^{-5} M $CdCl_2$ + 1 M HCl. Each curve starts 0.05 sec after the removal of the previous drop by the rocker-arm, and the timebase duration is 10 sec. During the interval between rocker-arm operation and the lifting of the needle, the curve falls nearly to zero level; then an abrupt increase in the current corresponds to the rise of the needle and the sudden appearance of the drop, which ceases to grow after reaching its prescribed size. From that instant there is a smooth decay of the current, caused by the decrease of reagent concentration in the layer next to the electrode. The coincidence of the two oscillograms in form and amplitude demonstrates the accurate repetition of drop size achieved by the apparatus. In interpreting these curves one must remember that the diffusion governing the current is not plane but spherical; this point is particularly important after the first few seconds of the drop's existence. When considering prolonged electrolysis at a single drop, one must also take account of convection in the solution.

The apparatus has been used to obtain current–potential, current–time, and other polarograms in large numbers for various solutions. It has also been tested in the prolonged-accumulation operation with the rocker-arm acting as stirrer: the reproducibility of stirring and also of the polarograms obtained after accumulation was recorded on an OP1-61 oscilloscope-polarograph (made by the Central Design Office of the USSR Academy of Sciences Geochemical Institute), to which the synchroniser unit was connected.

The apparatus can be used not only for oscillographic polarography but also for other types of polarography. It can form the basis of a new variant of the normal polarograph, a single polarogram being recorded for a large number of consecutively-produced stationary drops, no current recording being made during the short intervals when the drops are growing and the double layer on their surface is acquiring its charge. The polarograms obtained by this means are free from charging-current effect. The apparatus can also be used to produce drop electrodes that grow in discrete steps, which is of value in the investigation of processes related to the charging of the double layer at the electrode–solution boundary. The experimental conditions are simplified by the lack of tangential motion on the drop surface after the mercury flow is interrupted. The apparatus can also be used in an automatic control system for industrial solutions.



Fig. 4. Current–time curves from successively produced electrodes.

The authors wish to thank N.V. Sergievskii, D.S. Skoropelov, and G.P. Sennikov for their valuable assistance in building the apparatus.

1. V. Kemulya, "Doklad na VIII Mendeleevskom S'ezde" (Communication to the Eighth Mendeleev Congress), Moscow, 1959.
2. G. Barker, Atomic Energy Research Estab., No. 1564, (1957).
3. G. Barker, Atomic Energy Research Estab., No. 1567, (1957).
4. R. Kalvoda, Zavod. Lab., 24, 1319 (1958).
5. G. Semerano and L. Riccoboni, Gazzetta, 72, 297 (1942).
6. P. N. Tereshchenko, Zavod. Lab., 14, 1319 (1948).
7. J. Airey and A. Smales, Analyst, 75, 287 (1950).
8. P. Favero and E. Vianello, Ricerca sci., 25, 1415 (1955).
9. S. Stankoviansky, Coll. Czech. Chem. Comm., 15, 734 (1950).

Institute of Electrochemistry, Academy of Sciences of the USSR, and Vernadskii Institute of Geochemistry and Analytical Chemistry

Received 1st September 1961

THE VISCOSITY OF LIQUID MIXTURES WITHOUT CHEMICAL INTERACTION

A. Ya. Deich

Discussion[1,2] on the relative advantages of the kinematic fluidity (reciprocal of the kinematic viscosity) and the logarithm of the viscosity as additive quantities has convinced me that the latter is superior. This view is based on the available experimental data. Thus in refs. 3–6 alone fourteen systems without chemical interaction are described, in which additivity of the logarithm of the viscosity has been established. If necessary many more similar systems may be quoted. Obviously, the above quantity must be used with caution since the variation of the viscosity of ideal systems is far from being completely understood.

The following considerations may be added to the objections already made[2] to the opposite view maintained by Zdanovskii[1].